

# Reference spectra of important adsorbed organic and inorganic phosphate binding forms for soil P speciation using synchrotron-based K-edge XANES spectroscopy

Jörg Prietzel,<sup>a\*</sup> Gertraud Harrington,<sup>a</sup> Werner Häusler,<sup>a</sup> Katja Heister,<sup>a‡</sup> Florian Werner<sup>a</sup> and Wantana Klysubun<sup>b</sup>

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‡ Current address: GeoLab, Faculty of Geosciences, Utrecht University, Princetonlaan 8, 3584 CB Utrecht, The Netherlands.

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<sup>a</sup>Technische Universität München, Lehrstuhl für Bodenkunde, Emil-Ramann-Strasse 2, D-85354 Freising, Germany, and

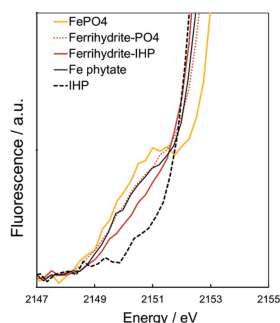
<sup>b</sup>Synchrotron Light Research Institute, 111 University Avenue, Muang District, Nakhon Ratchasima 30000, Thailand.

\*Correspondence e-mail: prietzel@wzw.tum.de

Direct speciation of soil phosphorus (P) by linear combination fitting (LCF) of P K-edge XANES spectra requires a standard set of spectra representing all major P species supposed to be present in the investigated soil. Here, available spectra of free- and cation-bound inositol hexakisphosphate (IHP), representing organic P, and of Fe, Al and Ca phosphate minerals are supplemented with spectra of adsorbed P binding forms. First, various soil constituents assumed to be potentially relevant for P sorption were compared with respect to their retention efficiency for orthophosphate and IHP at P levels typical for soils. Then, P K-edge XANES spectra for orthophosphate and IHP retained by the most relevant constituents were acquired. The spectra were compared with each other as well as with spectra of Ca, Al or Fe orthophosphate and IHP precipitates. Orthophosphate and IHP were retained particularly efficiently by ferrihydrite, boehmite, Al-saturated montmorillonite and Al-saturated soil organic matter (SOM), but far less efficiently by hematite, Ca-saturated montmorillonite and Ca-saturated SOM. P retention by dolomite was negligible. Calcite retained a large portion of the applied IHP, but no orthophosphate. The respective P K-edge XANES spectra of orthophosphate and IHP adsorbed to ferrihydrite, boehmite, Al-saturated montmorillonite and Al-saturated SOM differ from each other. They also are different from the spectra of amorphous FePO<sub>4</sub>, amorphous or crystalline AlPO<sub>4</sub>, Ca phosphates and free IHP. Inclusion of reference spectra of orthophosphate as well as IHP adsorbed to P-retaining soil minerals in addition to spectra of free or cation-bound IHP, AlPO<sub>4</sub>, FePO<sub>4</sub> and Ca phosphate minerals in linear combination fitting exercises results in improved fit quality and a more realistic soil P speciation. A standard set of P K-edge XANES spectra of the most relevant adsorbed P binding forms in soils is presented.

## 1. Introduction

Phosphorus (P) is a crucial element for life on Earth, and P bioavailability often limits ecosystem productivity, vegetation succession and food supply for humanity (Elser *et al.*, 2007; Gilbert, 2009). Soils store a large portion of the P in terrestrial ecosystems by accumulation of organic P from biomass residues (Walker & Syers, 1976; Harrison, 1987), P retention by Fe and Al oxyhydroxides (Parfitt, 1978, 1989; Sposito, 1984; Celi *et al.*, 1999) and precipitation of Ca, Fe or Al phosphates (Lindsay, 1999). The P nutritional status of terrestrial ecosystems is dependent on the availability of soil P, which in turn is regulated not only by the total soil P content but also by soil P speciation (Walker & Syers, 1976). However, at the moment, only few reliable data on soil P speciation are



**Table 1**  
Soil constituents used for the P retention experiment.

Compound	Formula	Specific surface area (BET-N <sub>2</sub> m <sup>2</sup> g <sup>-1</sup> )	Type	Reference
6-line ferrihydrite	Fe <sub>5</sub> O <sub>3</sub> (OH) <sub>9</sub>	247	Synthesized according to Schwertmann & Cornell (1991)	Pronk <i>et al.</i> (2012)
Goethite	α-FeOOH	25	Synthesized according to Schwertmann & Cornell (1991)	Prietzl <i>et al.</i> (2008)
Hematite	α-Fe <sub>2</sub> O <sub>3</sub>	3.5	Purchased from Merck (Product # 3924)	
Boehmite	γ-AlOOH	298	Capatal A Alumina, Sasol North America, Westlake, LA, USA	Pronk <i>et al.</i> (2012)
Montmorillonite	~(Al <sub>1.67</sub> Mg <sub>0.33</sub> )[(OH) <sub>2</sub> Si <sub>4</sub> O <sub>10</sub> ]·Na <sub>0.33</sub> (H <sub>2</sub> O) <sub>4</sub>	71	Ceratosil WG, Südchemie AG, Moosburg, Germany	Pronk <i>et al.</i> (2012)
	After Al-saturation	107		
	After Ca-saturation	102		
Calcite	CaCO <sub>3</sub>	2.1	Triassic 'Plattenkalk' rock outcrop, Linderhof, German Alps (fine-ground)	
Dolomite	CaMg(CO <sub>3</sub> ) <sub>2</sub>	1.5	Triassic 'Hauptdolomit' rock outcrop, Achenpass, German Alps (fine ground)	
Soil organic matter		2.8	Forest floor O layer Waldsassen, Germany (fine-ground)	Prietzl & Stetter (2010)

available, because commonly used wet-chemical procedures quantify operationally defined P fractions rather than P species.

Recently, synchrotron-based X-ray absorption near-edge structure (XANES) spectroscopy has emerged as a promising technique for direct P speciation in soils (Hesterberg *et al.*, 1999; Beauchemin *et al.*, 2003; Lombi *et al.*, 2006; Ajiboye *et al.*, 2007, 2008; Kruse & Leinweber, 2008; Kizewski *et al.*, 2011; Kar *et al.*, 2012; Khatiwada *et al.*, 2012; Prietzl *et al.*, 2013). The P speciation of a soil sample can be calculated by comparing its XANES spectrum with those of reference compounds using computer-based linear combination fitting (LCF) (Khare *et al.*, 2007; Werner & Prietzl, 2015) programs. Appropriate reference compounds are a prerequisite for accurate LCF results. However, at the moment only a limited set of reference spectra, including (i) free or cation-bound inositol hexakisphosphate (IHP) (He *et al.*, 2007), which is the dominant organic P form in soils (Stewart & Tiessen, 1987; Turner *et al.*, 2002), (ii) Ca, Al and Fe phosphate minerals (Hesterberg *et al.*, 1999; Khare *et al.*, 2004, 2005; Hesterberg, 2010; Prietzl *et al.*, 2013), as well as (iii) orthophosphate adsorbed to boehmite or ferrihydrite (Hesterberg *et al.*, 1999; Khare *et al.*, 2004, 2005; Hesterberg, 2010), are available. The importance of Fe and Al oxyhydroxides for the retention of orthophosphate in soils has been described repeatedly (*e.g.* Parfitt, 1989; Violante & Pigna, 2002), and some information is also available concerning the retention of IHP by these minerals (Anderson *et al.*, 1974; Ognalaga *et al.*, 1994; Celi *et al.*, 1999; Yan *et al.*, 2014). However, little is known about the efficiency of Al- or Ca-saturated clay minerals and Al- or Ca-saturated soil organic matter (SOM), calcite and dolomite with respect to the retention of orthophosphate or IHP in comparison with Fe and Al oxyhydroxides. Moreover, at the moment no published P *K*-edge XANES spectra are available for orthophosphate or IHP retained by other minerals than Al or Fe oxyhydroxides, which can be used as reference spectra in LCF exercises. With this paper we want to overcome this

deficit by presentation of P *K*-edge XANES spectra of orthophosphate and IHP retained by the most relevant soil constituents.

## 2. Material and methods

### 2.1. Investigated soil constituents supposed to be important for P sorption

The soil constituents suggested to be most relevant for P sorption in soils were identified by adding defined amounts of orthophosphate and IHP, respectively, to each constituent at P levels and pH values frequent in soils, and comparing their P retention efficiency after equilibration. The experiments were conducted with a large set of soil constituents which potentially are able to form associations with inorganic and organic P. The constituents included Fe (oxyhydr)oxides (6-line ferrihydrite, goethite, hematite), Al oxyhydroxide (boehmite), carbonates (calcite, dolomite), Ca- or Al-saturated montmorillonite and Ca- or Al-saturated SOM. Sources and important properties of the materials are described in Table 1. The purity of all minerals was confirmed by X-ray diffraction analysis. The montmorillonite had a cation exchange capacity (CEC) of 972 mmol<sub>c</sub> kg<sup>-1</sup> and a specific surface area of 71 m<sup>2</sup> g<sup>-1</sup>. The SOM was freeze-dried ground O layer material sampled from control plots in the Pfaffenwinkel Forest (Prietzl & Stetter, 2010). It was free of mineral components, had an organic carbon concentration of 441 g kg<sup>-1</sup> and a CEC (at pH<sub>CaCl2</sub> 2.7) of 285 mmol<sub>c</sub> kg<sup>-1</sup>. Saturation of montmorillonite and SOM with Al or Ca was conducted according to Bouazza *et al.* (2006). The calcite and dolomite samples were finely ground with a mill Fritsch Pulverisette 5.

### 2.2. Retention experiments

The P retention experiments were conducted by shaking 30 mg of the different soil constituents (forest floor material: 500 mg) for 18 h at 293 K in darkness with 100 ml 0.1 M NaCl

**Table 2**

P retention efficiency of different soil constituents as expressed as a percentage of P immobilized from the solution phase and (in parentheses) final P concentration of the sorbent as well as equilibrium pH (in italic style) after 18 h shaking 100 ml of  $3.23 \times 10^{-5} M$  (1 mg P L<sup>-1</sup>) NaH<sub>2</sub>PO<sub>4</sub> or inositol hexakisphosphate (IHP)/0.1 M NaCl solution with 0.03 g of constituent (soil organic matter: 0.5 g) at 293 K.

Initial pH values of solutions adjusted with HCl. ND: not determined.

Compound	Orthophosphate		IHP	
	Initial pH value		Initial pH value	
	4.0	6.0	4.0	6.0
Ferrihydrite	88% (2.92 mg P g <sup>-1</sup> ; 4.5)	87% (2.81 mg P g <sup>-1</sup> ; 6.3)	80% (2.68 mg P g <sup>-1</sup> ; 4.8)	68% (2.25 mg P g <sup>-1</sup> ; 6.1)
Goethite	30% (1.00 mg P g <sup>-1</sup> ; 4.1)	24% (0.81 mg P g <sup>-1</sup> ; 6.5)	64% (2.15 mg P g <sup>-1</sup> ; 4.2)	40% (1.34 mg P g <sup>-1</sup> ; 6.5)
Hematite	0% (0 mg P g <sup>-1</sup> ; 4.1)	0% (0 mg P g <sup>-1</sup> ; 6.6)	0% (0 mg P g <sup>-1</sup> ; 4.1)	0% (0 mg P g <sup>-1</sup> ; 5.7)
Boehmite	88% (2.92 mg P g <sup>-1</sup> ; ND)	81% (2.70 mg P g <sup>-1</sup> ; 6.8)	50% (1.67 mg P g <sup>-1</sup> ; ND)	32% (1.08 mg P g <sup>-1</sup> ; 6.7)
Al-saturated montmorillonite	77% (2.58 mg P g <sup>-1</sup> ; 4.6)	80% (2.67 mg P g <sup>-1</sup> ; 5.0)	87% (2.89 mg P g <sup>-1</sup> ; 4.7)	88% (2.94 mg P g <sup>-1</sup> ; 5.1)
Ca-saturated montmorillonite	0% (0 mg P g <sup>-1</sup> ; 5.3)	0% (0 mg P g <sup>-1</sup> ; 6.9)	7% (0.22 mg P g <sup>-1</sup> ; 5.1)	4% (0.13 mg P g <sup>-1</sup> ; 6.5)
Al-saturated soil organic matter	68% (0.14 mg P g <sup>-1</sup> ; 4.6)	83% (0.17 mg P g <sup>-1</sup> ; 4.9)	89% (0.18 mg P g <sup>-1</sup> ; 4.7)	90% (0.18 mg P g <sup>-1</sup> ; 5.0)
Ca-saturated soil organic matter	0% (0 mg P g <sup>-1</sup> ; 6.2)	0% (0 mg P g <sup>-1</sup> ; 6.9)	0% (0 mg P g <sup>-1</sup> ; 5.8)	0% (0 mg P g <sup>-1</sup> ; 7.3)
Calcite	ND	0% (0 mg P g <sup>-1</sup> ; 9.6)	ND	61% (2.03 mg P g <sup>-1</sup> ; 8.2)
Dolomite	ND	0% (0 mg P g <sup>-1</sup> ; 9.1)	ND	0% (0 mg P g <sup>-1</sup> ; 9.5)

**Table 3**

P retention efficiency of different soil constituents as expressed as percentage of P immobilized from the solution phase and (in parentheses) final P concentration of the sorbent after 18 h shaking 100 ml of  $3.23 \times 10^{-5} M$  (1 mg P L<sup>-1</sup>) NaH<sub>2</sub>PO<sub>4</sub> or inositol hexakisphosphate (IHP)/0.1 M Na acetate/ acetic acid buffer solution with 0.03 g of constituent (soil organic matter: 0.5 g) at 293 K.

Initial pH values of solutions adjusted with HCl. ND: not determined.

Compound	Orthophosphate		IHP	
	pH value		pH value	
	4.0	6.0	4.0	6.0
Ferrihydrite	89% (2.98 mg P g <sup>-1</sup> )	87% (2.91 mg P g <sup>-1</sup> )	84% (2.79 mg P g <sup>-1</sup> )	78% (2.62 mg P g <sup>-1</sup> )
Goethite	32% (1.07 mg P g <sup>-1</sup> )	31% (1.02 mg P g <sup>-1</sup> )	65% (2.16 mg P g <sup>-1</sup> )	76% (2.53 mg P g <sup>-1</sup> )
Hematite	0% (0 mg P g <sup>-1</sup> )	0% (0 mg P g <sup>-1</sup> )	10% (0.33 mg P g <sup>-1</sup> )	16% (0.52 mg P g <sup>-1</sup> )
Boehmite	ND	ND	ND	ND
Al-saturated montmorillonite	37% (1.22 mg P g <sup>-1</sup> )	76% (2.54 mg P g <sup>-1</sup> )	86% (2.86 mg P g <sup>-1</sup> )	85% (2.82 mg P g <sup>-1</sup> )
Ca-saturated montmorillonite	0% (0 mg P g <sup>-1</sup> )	0% (0 mg P g <sup>-1</sup> )	24% (0.79 mg P g <sup>-1</sup> )	1% (0.03 mg P g <sup>-1</sup> )
Al-saturated soil organic matter	96% (0.19 mg P g <sup>-1</sup> )	ND	99% (0.20 mg P g <sup>-1</sup> )	100% (0.20 mg P g <sup>-1</sup> )
Ca-saturated soil organic matter	14% (0.03 mg P g <sup>-1</sup> )	ND	78% (0.16 mg P g <sup>-1</sup> )	100% (0.20 mg P g <sup>-1</sup> )
Calcite	ND	0% (0 mg P g <sup>-1</sup> )	ND	76% (2.55 mg P g <sup>-1</sup> )
Dolomite	ND	0% (0 mg P g <sup>-1</sup> )	ND	0% (0 mg P g <sup>-1</sup> )

solution containing either orthophosphate or IHP with different P concentrations (1, 5, 10 mg L<sup>-1</sup>) as well as mixtures of orthophosphate and IHP at different initial pH values typical for soils (pH 4.0, 5.0 and 6.0 achieved by adding HCl). The solutions were produced by dissolving appropriate amounts of NaH<sub>2</sub>PO<sub>4</sub> and/or IHP (phytic acid Na salt; C<sub>6</sub>H<sub>18</sub>O<sub>24</sub>P<sub>6</sub>Na); both purchased in reagent grade from Aldrich. To check for pH change effects during P sorption on sorption efficiency, additional sorption experiments were conducted with 0.1 M acetic acid/Na acetate buffer solution for which the pH had been set by HCl addition to 4.0 and 6.0, respectively, and remained at these values throughout the entire sorption experiment. At the end of the experiments, the suspensions were filtered through 0.45 µm cellulose acetate filters (Millipore). The total P concentration of the filtrates was analyzed by ICP-OES (Varian Vista Pro). For the orthophosphate–IHP mixtures, additionally the orthophosphate concentration was analyzed colorimetrically using a modified version (John, 1970) of the ascorbic acid method (Murphy & Riley, 1962), and IHP concentrations were calculated by subtracting orthophosphate P from total P. The air-dried

residues were scraped from the filters with a spatula and homogenized for acquisition of XANES spectra.

### 2.3. Phosphorus K-edge XANES spectroscopy

All samples obtained after P retention by different soil constituents in phosphate–NaCl solution, whose P concentrations in most cases ranged between 0.2 and 3 g kg<sup>-1</sup> (Tables 2 and 3) were analyzed by XANES spectroscopy at the P K-edge. Additional P K-edge XANES spectra were acquired for samples of (see Fig. S1 of the supporting information) non-crystalline AlPO<sub>4</sub>, crystalline AlPO<sub>4</sub> (berlinite), non-crystalline FePO<sub>4</sub>·2H<sub>2</sub>O, Ca<sub>5</sub>(OH)(PO<sub>4</sub>)<sub>3</sub> (hydroxy apatite), CaHPO<sub>4</sub>·2H<sub>2</sub>O, Ca(H<sub>2</sub>PO<sub>4</sub>)<sub>2</sub>·H<sub>2</sub>O, free IHP, as well as for X-ray amorphous (Fig. S1) Ca, Al and Fe(III) phytate precipitates. Crystalline AlPO<sub>4</sub>, non-crystalline FePO<sub>4</sub>·2H<sub>2</sub>O, Ca<sub>5</sub>(OH)(PO<sub>4</sub>)<sub>3</sub> and CaHPO<sub>4</sub>·2H<sub>2</sub>O, Ca(H<sub>2</sub>PO<sub>4</sub>)<sub>2</sub>·H<sub>2</sub>O were purchased in reagent grade from Sigma-Aldrich. The amorphous AlPO<sub>4</sub> was produced following the procedure of Hsu & Sikora (1993), and the phytate compounds were produced following the procedure of He *et al.* (2006). To minimize

confounding self-adsorption during XANES spectra acquisition, all purchased and synthesized P compounds were finely ground and diluted with fine-ground quartz to a final concentration of 2 g P kg<sup>-1</sup> (Prietz et al., 2013). All spectra were acquired at beamline 8 of the electron storage ring (1.2 GeV; bending magnet; beam current 80–150 mA; 1.1 to 1.7 × 10<sup>11</sup> photons s<sup>-1</sup>) at the Synchrotron Light Research Institute (SLRI) in Nakhon Ratchasima, Thailand (Klysubun et al., 2012). Finely ground homogenized powder of each sample was spread as a thin film (area 2 cm × 0.5 cm) and carefully distributed with a spatula to yield a homogeneous particle distribution on Kapton<sup>®</sup> tape (Lanmar Inc., Northbrook, IL, USA) and then mounted on a sample holder. After energy calibration using elemental P powder ( $E = 2145.5$  eV; precision ±0.11 eV), spectra were acquired in the energy range 2110–2350 eV in 5.0 eV (2105 to 2135 eV; 2205 to 2350 eV) and 0.25 eV increments (2135 to 2205 eV). We used an InSb(111) double-crystal monochromator with an energy resolution ( $\Delta E/E$ ) of 3 × 10<sup>-4</sup>; i.e. 0.5 eV at the P *K*-edge. Spectrum acquisition time varied between 1 and 3 s, depending on the P content of the sample. Incident X-ray intensity was measured using a N<sub>2</sub> gas-filled ion chamber, while the fluorescence emitted from the sample (irradiated sample area 1.8 cm × 0.12 cm) was recorded with a 13-channel Ge detector. To minimize X-ray absorption by air, the sample compartment was filled with He gas. For each sample, depending on the P content, between two and four spectra were acquired and merged. All spectra were baseline-corrected (energy region: 2115–2145 eV) and edge-normalized (energy region: 2190–2215 eV) using the software package *ATHENA* (Ravel & Newville, 2005). LCF performed on the P *K*-edge XANES spectra of the IHP–orthophosphate mixture retained by ferrihydrite and of the soil samples presented in the *Discussion* in the energy range 2140–2200 eV was also performed with *ATHENA*. Because the three samples were taken from different soils, each probably characterized by a different P speciation, we refrained from conducting a principal component analysis prior to the LCF.

### 3. Results

#### 3.1. P retention efficiency of different soil constituents

The P retention efficiency of the different soil constituents with respect to orthophosphate at an initial P concentration of 1 mg L<sup>-1</sup> and an initial pH of 4.0 in unbuffered 0.1 M NaCl solution, defined as a percentage of retained to initially applied P, decreases in the order (Table 2): ferrihydrite = boehmite (88%) > Al-saturated montmorillonite (77%) > Al-saturated SOM (68%) >> goethite (30%) >> Ca-saturated montmorillonite, hematite, calcite, dolomite (0%). At an initial pH of 6.0, the sequence is: ferrihydrite (87%) > Al-saturated SOM (83%) ≥ boehmite (81%) ≥ Al-saturated montmorillonite (80%) >> goethite (24%) >> hematite, Ca-saturated montmorillonite, Ca-saturated SOM, calcite, dolomite (0%). During orthophosphate retention at an initial pH of 4.0, solution pH increases in the following sequence (Table 2):

hematite = goethite (pH 4.1) < ferrihydrite (4.5) ≤ Al-saturated montmorillonite = Al-saturated SOM (4.6) < Ca-saturated montmorillonite (5.3) < Ca-saturated SOM (6.2). In contrast, at an initial pH of 6.0, the pH decreases during orthophosphate retention by Al-saturated montmorillonite (5.0) and Al-saturated SOM (4.9). For the other soil constituents, the pH increases in the sequence: ferrihydrite (6.3) < goethite (6.5) < hematite (6.6) < boehmite (6.8) < Ca-saturated montmorillonite = Ca-saturated SOM (6.9) << dolomite (9.1) < calcite (9.6).

Like orthophosphate, IHP is not or only negligibly retained by hematite, Ca-saturated SOM and Ca-saturated montmorillonite (Table 2). In contrast, IHP retention efficiency was particularly large for Al-saturated montmorillonite (87% and 88% at pH 4 and 6, respectively) and Al-saturated SOM (89% at pH 4 and 90% at pH 6), and considerably exceeds orthophosphate retention efficiency. Also ferrihydrite has a large IHP retention efficiency (80% and 68% at pH 4 and 6, respectively); yet, it is smaller than that of orthophosphate. With an IHP retention efficiency of 40% at pH 6 and 64% at pH 4, goethite has a much more pronounced IHP than orthophosphate retention efficiency. The opposite is the case for boehmite, whose retention efficiency is smaller for IHP (50% and 32% at pH 4 and 6, respectively) compared with orthophosphate. In contrast to orthophosphate, IHP is strongly retained by calcite at pH 6 (P retention efficiency: 61%), but no IHP retention is observed for dolomite. During IHP retention at an initial pH of 4.0, solution pH increases in the following sequence (Table 2): hematite (pH 4.1) < goethite (pH) < Al-saturated montmorillonite = Al-saturated SOM (4.7) < ferrihydrite (4.8) < Ca-saturated montmorillonite (5.1) < Ca-saturated SOM (5.8). In contrast, at an initial pH of 6.0, the pH decreases during IHP retention by hematite (5.7), Al-saturated montmorillonite (5.1) and Al-saturated SOM (5.0). For the other soil constituents the pH increased in the sequence: ferrihydrite (6.1) < Ca-saturated montmorillonite = goethite (6.5) < boehmite (6.7) < Ca-saturated SOM (7.3) < dolomite (8.2) < calcite (9.5).

When equal amounts of orthophosphate P and IHP-P are applied simultaneously at a total P concentration of 1 mg L<sup>-1</sup>, P retention efficiency of ferrihydrite, boehmite and Al-montmorillonite is about midway between their respective P retention efficiencies for pure orthophosphate and pure IHP solutions (Fig. S2 of the supporting information). For increased P concentrations (5 and 10 mg L<sup>-1</sup>) P retention efficiencies of ferrihydrite and boehmite are larger for IHP/orthophosphate mixtures than their respective retention efficiencies after application of pure orthophosphate or IHP with the same total P concentration. This feature is absent for Al-saturated montmorillonite. With increasing P concentration, orthophosphate is preferred over IHP by ferrihydrite, whereas Al-saturated montmorillonite preferentially retains IHP. For the orthophosphate sorption experiments performed in buffered acetic acid/Na acetate solution (Table 3), P retention efficiencies of the different soil constituents generally are similar or identical to the respective efficiencies obtained in unbuffered NaCl solution, except for Al-saturated montmor-

Table 4

Important features of P K-edge XANES spectra acquired for orthophosphate (o-PO<sub>4</sub> applied as NaH<sub>2</sub>PO<sub>4</sub>) or inositol hexakisphosphate (IHP) after retention by different soil constituents and for Al, Fe Ca orthophosphate and phytate precipitates.

ND: not determined. PE: post-edge peak.

	White line WL				Post-edge feature				Signal intensity ratio WL/PE	
	Energy (eV)		Intensity†		Energy (eV)		Intensity†			
	o-PO <sub>4</sub>	IHP	o-PO <sub>4</sub>	IHP	o-PO <sub>4</sub>	IHP	o-PO <sub>4</sub>	IHP	o-PO <sub>4</sub>	IHP
P retained by boehmite	2154.8	2154.7	7.7	7.5	2172	2170	1.9	2.0	4.1	3.8
P retained by Al-saturated SOM	2155.0	2154.8	8.0	7.0	(1) 2162 (2) 2172	2163 2171	1.6 2.0	1.5 1.9	4.0	3.7
P retained by Al-saturated montmorillonite	2155.0	2155.0	10.0	8.3	(1) 2162 (2) 2172	2162 2172	1.7 2.1	1.7 2.1	4.8	4.0
Non-crystalline Al precipitate (AlPO <sub>4</sub> , Al phytate)	2154.7	2154.7	8.1	6.4	2172	2170	2.0	1.9	4.1	3.4
Crystalline AlPO <sub>4</sub>	2155.3	–	6.0	–	(1) 2164 (2) 2173	– –	1.7 2.0	– –	3.0	–
P retained by ferrihydrite	2154.8	2154.7	7.3	6.4	2172	2172	1.9	1.9	3.8	3.4
Non-crystalline Fe precipitate (FePO <sub>4</sub> , Fe phytate)	2154.8	2155.0	7.3	6.2	2172	2170	1.9	1.9	3.8	3.3
P retained by calcite	ND	2154.3	ND	5.9	ND	2157 2170	Tailing PE	2.3 1.9	ND	3.1
Non-crystalline Ca phytate	ND	2154.2	ND	6.0	ND	2157 2170	Tailing PE	2.3 1.9	ND	3.2
Ca(H <sub>2</sub> PO <sub>4</sub> ) <sub>2</sub> ·H <sub>2</sub> O	2154.7	–	5.6	–	(1) 2157.2 (2) 2164.3 (3) 2172	– – –	Tailing PE 1 PE 2	2.2 1.7 1.9	2.9	–
CaHPO <sub>4</sub> ·2H <sub>2</sub> O	2154.5	–	5.4	–	(1) 2158 (2) 2164 (3) 2170	– – –	Tailing PE 1 PE 2	1.5 1.5 1.7	3.2	–
Ca <sub>5</sub> (OH)(PO <sub>4</sub> ) <sub>3</sub>	2154.2	–	5.9	–	(1) 2158 (2) 2164 (3) 2170	– – –	Tailing PE 1 PE 2	1.5 1.5 1.7	3.5	–

† Signal intensity relative to edge step.

illonite at pH 4 (37% orthophosphate retention efficiency compared with 77% at an equilibrium pH of 4.6 in unbuffered 0.1 M NaCl solution) and Al-saturated SOM at pH 4 (96% orthophosphate retention efficiency compared with 68% at an equilibrium pH of 4.6 in unbuffered 0.1 M NaCl solution). For IHP sorption experiments in buffered acetic acid/Na acetate solution, P retention efficiencies of the different soil constituents generally are similar or identical to the respective efficiencies obtained in NaCl solution for Al-saturated montmorillonite, for goethite and ferrihydrite at pH 4, and increase for Al- or Ca-saturated SOM as well as for ferrihydrite and goethite at pH 6.

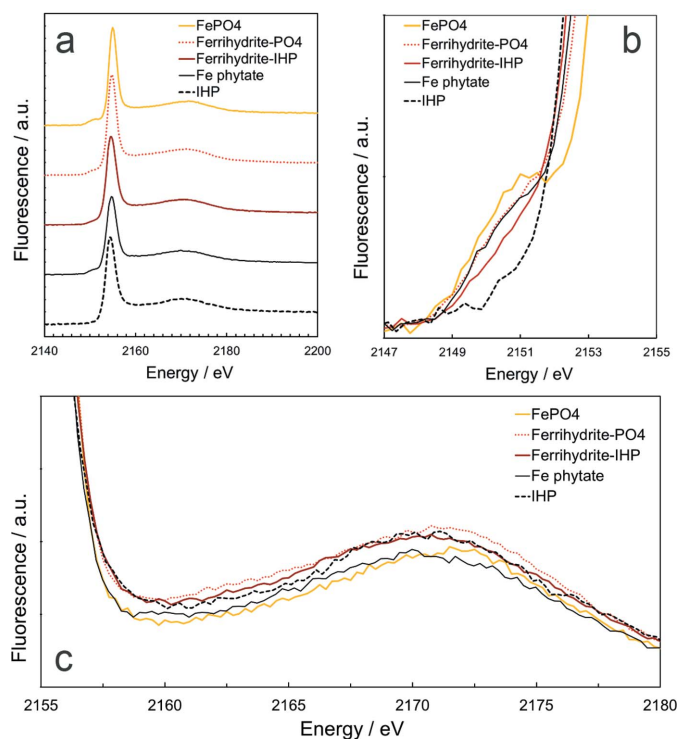
In summary, besides ferrihydrite and boehmite, Al-saturated expandable 2:1 clays as represented by Al-saturated montmorillonite in our study as well as Al-saturated SOM also seem to be particularly important for the retention of inorganic P (orthophosphate) and organic P (IHP) in moderately acidic soils, whereas goethite, Ca-saturated montmorillonite, Ca-saturated SOM and dolomite are far less relevant. Calcite seems to be irrelevant for the retention of inorganic P, but relevant for the retention of IHP.

### 3.2. P K-edge XANES spectra

In contrast to the XANES spectrum of free IHP (white-line energy: 2154.3 eV), the spectra of non-crystalline

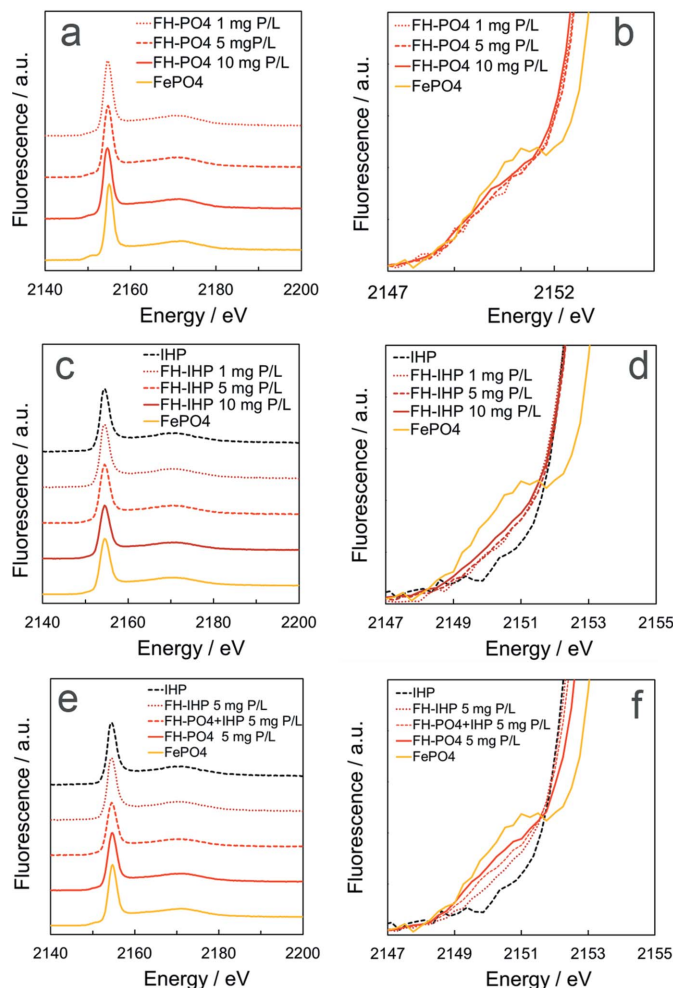
FePO<sub>4</sub>·2H<sub>2</sub>O, Fe(III) phytate and those of orthophosphate or IHP retained by ferrihydrite have higher white-line (WL) energies (Fig. 1a; Table 4). The spectra of Fe(III)-bound orthophosphate always have larger WL intensities and white-line signal intensity/post-edge peak signal intensity (WL/PE) ratios than the respective Fe(III)-bound IHP phases (Table 4). Additionally, all Fe(III)-bound P compounds are characterized by a distinct pre-edge signal in the energy range 2148.5–2151.5 eV (Fig. 1b), which has been reported earlier (Hesterberg *et al.*, 1999; Khare *et al.*, 2004, 2005, 2007). The pre-edge signal of non-crystalline FePO<sub>4</sub>·2H<sub>2</sub>O differs from those of orthophosphate retained by ferrihydrite [already reported earlier by Khare *et al.* (2005, 2007)] and IHP retained by ferrihydrite (not reported before) by being a true pre-edge peak, whereas the pre-edge signals of the sesquioxide-bound-P spectra are merely shoulders, with the shoulder being considerably smaller for IHP retained by ferrihydrite compared with orthophosphate retained by ferrihydrite (Fig. 1b). The pre-edge peak of Fe(III) phytate is larger than the pre-edge peak of IHP retained by ferrihydrite, and its shape is almost identical to that of orthophosphate retained by ferrihydrite. The WL peaks of orthophosphate or IHP retained by ferrihydrite are slightly larger for the variants with an initial solution concentration of 1 mg P L<sup>-1</sup>, resulting in a final P concentration of the P-loaded ferrihydrite after retention of about 3 g kg<sup>-1</sup>, compared with the variants with





**Figure 1**  
 (a) Phosphorus *K*-edge XANES spectra of non-crystalline  $\text{FePO}_4 \cdot 2\text{H}_2\text{O}$ , free inositol hexakisphosphate (IHP), Fe phytate, orthophosphate retained by ferrihydrite, and IHP retained by ferrihydrite (initial solution concentration  $1 \text{ mg P L}^{-1}$ ; background  $0.1 \text{ M NaCl}$ ; initial pH 5.0). (b) Close-up view of pre-edge region. (c) Close-up view of post-edge region.

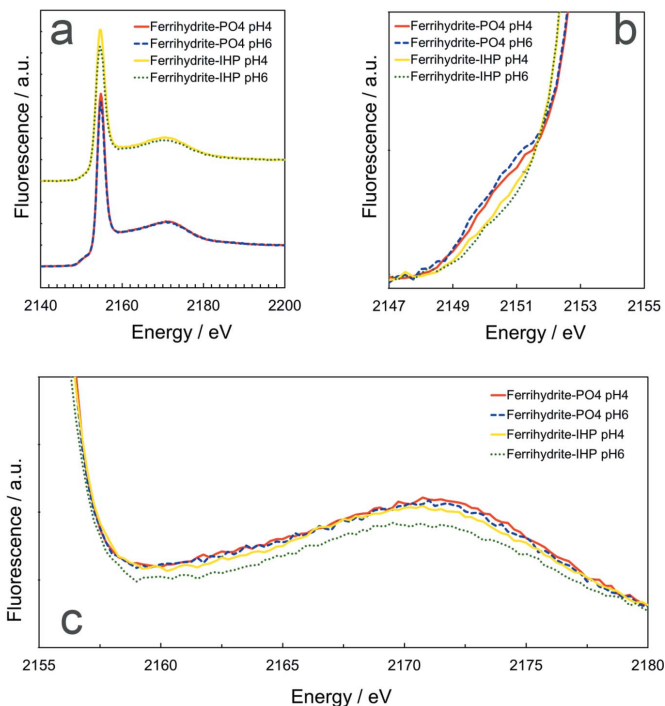
initial solution concentrations of 5 or  $10 \text{ mg P L}^{-1}$  (final P content of ferrihydrite after retention:  $8\text{--}15 \text{ g kg}^{-1}$ ) (Figs. 2a and 2c). Pre-edge signals of orthophosphate or IHP retained by ferrihydrite are more pronounced for the largest initial concentrations of aqueous P ( $10 \text{ mg L}^{-1}$ ; amount of retained P:  $25 \text{ g kg}^{-1}$ ) compared with the 1 and  $5 \text{ mg P L}^{-1}$  variants, but always differ markedly from the pre-edge signals of non-crystalline  $\text{FePO}_4 \cdot 2\text{H}_2\text{O}$  (Figs. 2b and 2d). The pre-edge feature of the P *K*-edge XANES spectrum of a 1:1-molar (regarding the number of P atoms) orthophosphate/IHP mixture retained by ferrihydrite is an intermediate between the features of orthophosphate retained by ferrihydrite and IHP retained by ferrihydrite (Fig. 2f). Analysis of orthophosphate and total P in the aqueous phase after retention equilibrium indicated a ratio of retained orthophosphate-P:IHP-P of 59%:41% for this mixture. LCF was performed on its P *K*-edge XANES spectrum including either the entire spectrum (energy range: 2140–2200 eV) or the pre-edge region (2148.5–2151.4 eV) only. It yielded an orthophosphate-P:IHP-P partitioning of 51%:49% for analysis of the entire spectrum and an orthophosphate-P:IHP-P partitioning of 52%:48% when only the pre-edge region was analyzed. The spectrum of orthophosphate retained by ferrihydrite at an initial pH of 4.0 (equilibrium pH: 4.5) is identical to that of orthophosphate retained by ferrihydrite at an initial pH of 6.0 (equilibrium pH: 6.3). In contrast, the spectrum acquired for IHP retained by ferrihydrite at an initial pH value of 4.0



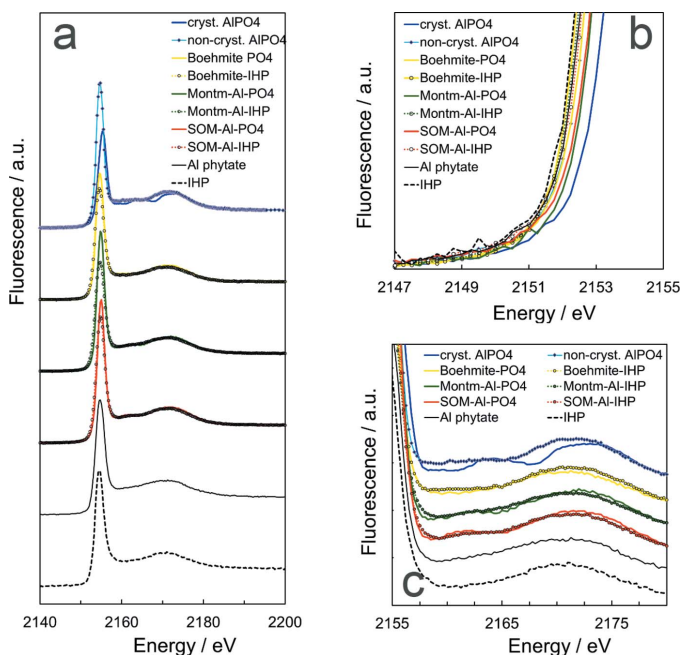
**Figure 2**  
 Comparison of the P *K*-edge XANES spectra of non-crystalline  $\text{FePO}_4 \cdot 2\text{H}_2\text{O}$ , free inositol hexakisphosphate (IHP) (a, b) orthophosphate retained by ferrihydrite, (c, d) IHP retained by ferrihydrite for initial solution concentrations 1, 5 and  $10 \text{ mg P L}^{-1}$ , and (e, f) a 1:1 molar (with respect to the number of P atoms) mixture of orthophosphate and IHP retained by ferrihydrite (initial solution concentration  $5 \text{ mg P L}^{-1}$ ).

(equilibrium pH: 4.8) has larger WL, pre-edge and post-edge signals than the spectrum of IHP retained by ferrihydrite at an initial pH value of 6.0 (equilibrium pH: 6.1) (Fig. 3); yet the WL/PE ratios are identical.

Edge-normalized P *K*-edge XANES spectra of orthophosphate or IHP (initial solution concentration:  $1 \text{ mg P L}^{-1}$ ) retained by Al-saturated montmorillonite, Al-saturated SOM or boehmite as well as those of non-crystalline  $\text{AlPO}_4$  and Al phytate show almost identical WL energies (2154.7–2155.0 eV) and shapes (Fig. 4a). However, as for the Fe(III)-bound phases, WL intensities as well as the WL/PE ratios are markedly larger for orthophosphate-Al phases compared with the respective IHP-Al phases (Table 4). All *K*-edge XANES spectra of Al-bound P lack a pre-edge signal (Fig. 4b). The P *K*-edge XANES spectra of the non-crystalline Al-phosphate phases are characterized by one (boehmite, non-crystalline  $\text{AlPO}_4$ ) or two (P retained by Al-saturated montmorillonite or Al-saturated SOM) distinct specific post-edge signals at



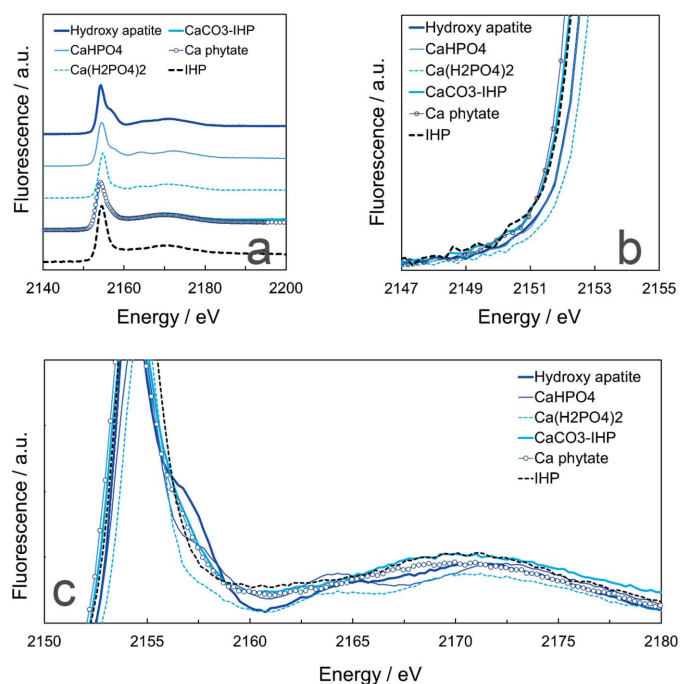
**Figure 3**  
 (a) Phosphorus *K*-edge XANES spectra of orthophosphate and inositol hexakisphosphate (IHP) retained by ferrihydrite at initial pH values of 4.0 and 6.0, respectively. (b) Close-up view of pre-edge energy region. (c) Close-up view of post-edge region.



**Figure 4**  
 (a) Phosphorus *K*-edge XANES spectra of crystalline  $\text{AlPO}_4$ , non-crystalline  $\text{AlPO}_4$ , free inositol hexakisphosphate (IHP), Al phytate, as well as of orthophosphate or IHP retained by boehmite, Al-saturated montmorillonite and Al-saturated soil organic matter (SOM from the O layer of forest soil Waldsassen, Germany); initial pH 4.0. (b) Close-up view of pre-edge energy region. (c) Close-up view of post-edge region.

energies of  $2162 \pm 1$  and  $2172 \pm 1$  eV (Table 4; Fig. 4c). For the post-edge features of orthophosphate and IHP retained by Al-saturated montmorillonite, differences can be noted in the energy regions 2160 eV, 2165 eV and 2173 eV. Most important, the post-edge signal of crystalline  $\text{AlPO}_4$  differs markedly from those of any other Al-bound P phase by a larger WL energy and a smaller WL/PE ratio (Table 4). Moreover, it shows a pronounced first post-edge peak at 2164 eV and a distinct minimum at 2168 eV (Fig. 4c). Similar to orthophosphate or IHP retained by ferrihydrite, for none of the Al-bearing minerals and Al-saturated SOM, the *K*-edge XANES spectra of orthophosphate or IHP retained at initial pH values of 4.0 and 6.0, respectively, differ from each other (Figs. S3 and S4).

The P *K*-edge XANES spectra of all Ca-bound P phases differ markedly from those of the Al- or Fe(III)-bound P phases: they all lack a pre-edge feature (Fig. 5b), but have distinct WL tailings with characteristic shapes for different Ca-bound P phases (Figs. 5a and 5c). The spectra of amorphous Ca phytate and of IHP retained by calcite are almost identical (Fig. 5; Table 4). They differ from the spectra of the investigated Ca phosphate minerals in the shape of the WL tailing and by lacking a post-edge signal at 2164 eV (Table 4). Compared with free IHP (WL intensity: 6.4; WL/PE ratio: 3.6), the spectrum of Ca-bound IHP has a smaller WL intensity and WL/PE ratio as well as a more pronounced WL tailing.



**Figure 5**  
 (a) Phosphorus *K*-edge XANES spectra of hydroxy apatite  $[\text{Ca}(\text{OH})(\text{PO}_4)_3]$ ,  $\text{CaHPO}_4$ ,  $\text{Ca}(\text{H}_2\text{PO}_4)_2$ ,  $\text{CaCO}_3$ -IHP, inositol hexakisphosphate (IHP) retained by calcite ( $\text{CaCO}_3$ ), and free IHP at an initial pH value of 6.0. (b) Close-up view of pre-edge energy region. (c) Close-up view of post-edge region.

## 4. Discussion

### 4.1. Efficient P retention by Al-saturated montmorillonite and Al-saturated SOM, but not by Ca-saturated montmorillonite, Ca-saturated SOM, calcite and dolomite

The strong affinity of ferrihydrite and boehmite to orthophosphate and IHP as reported in our study is well known (Anderson & Arlidge, 1962; Parfitt, 1978, 1989; Ognalaga *et al.*, 1994; Celi *et al.*, 2003; Khare *et al.*, 2005; Hesterberg, 2010). The marked orthophosphate retention efficiency of Al-saturated montmorillonite and Al-saturated SOM shown in our study also has been reported before (Bloom, 1981; Haynes & Swift, 1989; Kasama *et al.*, 2004); yet, no direct comparison of these soil constituents with Fe or Al oxyhydroxides has been published up to now. Our observation, that Al-saturated montmorillonite at moderately acidic pH retains IHP more efficiently than ferrihydrite and boehmite, is novel. In contrast to Al-saturated montmorillonite, ferrihydrite and boehmite, only negligible amounts of orthophosphate are retained by hematite, calcite, dolomite, Ca-saturated montmorillonite or Ca-saturated SOM. The poor P retention efficiency of hematite has been reported before (Elzinga & Sparks, 2007). Coleman *et al.* (1960) reported a large P retention on Al-saturated montmorillonite, whereas P sorption to K-, Na- or Ca-saturated montmorillonite was negligible. In line with our results, Haynes & Swift (1989) reported considerably larger P retention by Al-saturated compared with Ca-saturated peat. One reason for the enormous differences between the P retention efficiencies of Al-saturated montmorillonite and Ca-saturated montmorillonite or between those of Al-saturated SOM and Ca-saturated SOM may be the circumstance that exchangeable Ca provides a much smaller formation energy and stability of the Ca-PO<sub>4</sub> ion-pair bond compared with the Al-PO<sub>4</sub> ion-pair bond established with exchangeable Al (Jenkins *et al.*, 1971; Gerke & Hermann, 1992; Gerke, 1993). Moreover, hydrolysis of Al bound to clay minerals at pH values >4 (Coleman & Thomas, 1964) and of Al bound to SOM at pH values >3 (White & Thomas, 1981) results in strongly increased P retention (Coleman *et al.*, 1960; White & Thomas, 1981). Our results highlight the importance of Al-saturated 'high-activity' 2:1 clay minerals and Al-saturated SOM for the P retention capacity of soils at least in the pH range between 4 and 6, where, according to Vreysen & Maes (2006), Kasama *et al.* (2004) and Zhao *et al.* (2012), the Al is either mostly or exclusively present as Al<sub>13</sub> hydroxy polymer cations ('Keggin ions') (pH 4–5), 'Keggin ion' pillars (Kasama *et al.*, 2004) and/or surface-precipitated Al(OH)<sub>3</sub> (pH 5–6). Because P sorption to different high-activity 2:1 clay minerals in the investigated pH range is mostly related to the OH functional groups of the Al 'Keggin ion' pillars, but little to the reactive sites on the edge surface of the different clay minerals (Kasama *et al.*, 2004), the montmorillonite in our study very likely well represents the P sorption properties of most, if not all, high-activity 2:1 clay minerals. Therefore, the results of our study show that, in moderately acid soils which are rich in high-activity clay minerals and/or SOM, Al bound to these clay minerals or SOM can contribute significantly to soil P

retention and speciation. This is particularly true and ecologically relevant for soils poor in Fe oxyhydroxides due to low parent material Fe contents or anoxic conditions resulting in Fe oxyhydroxide dissolution. Yet, we suggest to extend comparing P retention efficiency studies and acquisition of P K-edge XANES spectra to the pH range 2–4, where the Al on clay mineral surfaces is monomeric Al (Vreysen & Maes, 2006; Zhao *et al.*, 2012).

The absence of orthophosphate retention by fine-ground lithogenic calcite or dolomite in our experiment contrasts with results of earlier studies (Cole *et al.*, 1953; Griffin & Jurinak, 1973; Amer *et al.*, 1985). The lack of orthophosphate retention by calcite and dolomite in our study is probably due to their small specific surface areas (SSA; 2.1 and 1.5 m<sup>2</sup> g<sup>-1</sup>, respectively; Table 1). In line with our results, Celi *et al.* (2000) also reported only little P retention [0.18 g P (kg calcite)<sup>-1</sup>] after shaking dilute (equilibrium concentration: 0.1–10 mg P L<sup>-1</sup>) solutions of K orthophosphate for 24 h with calcite with an SSA of 2.8 m<sup>2</sup> g<sup>-1</sup> derived from fine-ground limestone at pH 8.3. In that study, a strong increase in P retention to >4 g P (kg calcite)<sup>-1</sup>, which was attributed to the formation of Ca phosphate precipitates, was not recorded before the orthophosphate concentration of the solution was increased to 45 mg P L<sup>-1</sup>, which is far larger than the initial P solution concentration in our study (1 mg L<sup>-1</sup>). Cole *et al.* (1953) reported even smaller retention of orthophosphate by calcite [ $<0.1$  g P (kg calcite)<sup>-1</sup>] at low solution P concentration (<3 mg L<sup>-1</sup>). However, weathering strongly increases the SSA of CaCO<sub>3</sub> (Holford & Mattingly, 1975), which is strongly correlated to its orthophosphate retention efficiency (Amer *et al.*, 1985). Orthophosphate retention by calcite or dolomite in real soils (Borrero *et al.*, 1988), particularly by secondary carbonate formed during pedogenesis, which has a large SSA, thus may be considerable. In contrast to orthophosphate, IHP was retained strongly by calcite. This will be discussed in more detail in §4.2.

### 4.2. Many soil constituents retain IHP more efficiently than orthophosphate

In our experiment, IHP was retained (in terms of P atoms) more efficiently than orthophosphate by all soil constituents except boehmite and ferrihydrite. This is in line with results from earlier studies (Anderson *et al.*, 1974; Stewart & Tiessen, 1987; Celi *et al.*, 1999; Martin *et al.*, 2004; Shang *et al.*, 2013). In soils with noticeable contents of Al-saturated montmorillonite or Al-saturated SOM, IHP, which is the dominating form of organic P in soils (Stewart & Tiessen, 1987; Turner *et al.*, 2002; Martin *et al.*, 2004), therefore may be more efficiently retained than orthophosphate. The pronounced IHP retention by most soil constituents in our study is probably caused by formation of a stable multi-dentate surface complex as a result of multiple P group bonding (Ognalaga *et al.*, 1994; Celi *et al.*, 1999; Martin *et al.*, 2004) and restricted remobilization of retained IHP by desorption and/or enzymatic breakdown (Celi *et al.*, 2003; Martin *et al.*, 2004; Yan *et al.*, 2014). The high IHP retention efficiency probably contributes to the accu-



mulation of IHP (also compared with other organic phosphates; Yan *et al.*, 2014) in soils during pedogenesis and suggests a major contribution of IHP to the large pool of unavailable P (Walker & Syers, 1976) in soils of mature ecosystems.

Even though neither fine-ground bedrock calcite nor fine-ground bedrock dolomite retained measurable amounts of orthophosphate in our study, the same calcite (but not the dolomite) showed considerable IHP retention efficiency. Similar results were reported earlier in the study conducted with fine-ground calcite mentioned above by Celi *et al.* (2000): at solution P equilibrium concentrations between 1 and 15 mg L<sup>-1</sup>, IHP retention by calcite was between two and six times larger than orthophosphate retention. This is probably due to precipitation of Ca<sub>3</sub>-IHP solids which form in the presence of calcite at any pH and even at very low IHP concentrations (Celi *et al.*, 2000). Thus, in calcite-containing environments, in addition to IHP sorption to calcite, simultaneous precipitation of Ca<sub>3</sub>-IHP is an important P retention mechanism even at low IHP concentrations. Three facts suggest that the calcite-retained IHP in our study is merely to a minor extent IHP adsorbed to calcite, but mostly surface-precipitated Ca phytate, probably Ca<sub>3</sub>-IHP: first, the P *K*-edge XANES spectrum of IHP retained by calcite in our study was almost identical to the spectrum of Ca phytate, whereas this was not the case for comparisons between IHP retained by ferrihydrite and Fe(III) phytate or between IHP retained by different Al phases and Al phytate. Moreover, no IHP retention was observed by dolomite, which is far more resistant against dissolution; furthermore, in contrast to Ca phytate, Mg phytate is soluble in the pH range between 6 and 9.7 (Jackman & Black, 1951). Finally, the WL intensity and the WL/PE ratio of IHP retained by calcite is much smaller than that of free IHP (6.4; WL/PE 3.6) indicating precipitation (Khare *et al.*, 2005) and even slightly smaller than that of the synthesized Ca phytate. However, at larger P concentrations (>30 mg P L<sup>-1</sup>), formation of Ca phosphate precipitates is more efficient than formation of Ca<sub>3</sub>-IHP precipitates, and orthophosphate retention by calcite is more pronounced than IHP retention (Celi *et al.*, 2003). However, such large aqueous P concentrations are unlikely to occur in most soils.

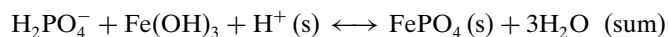
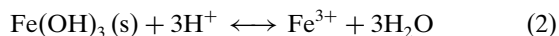
#### 4.3. Major processes of P retention by different soil minerals

Different mechanisms have been suggested for the retention of orthophosphate by Fe and Al (oxyhydr)oxides: (i) chemisorption by ligand exchange and inner-sphere surface complexation (Parfitt & Atkinson, 1976; Parfitt, 1978; Sposito, 1984; Elzinga & Sparks, 2007) and (ii) surface precipitation (van Riemsdijk & Lyklema, 1980; Laiti *et al.*, 1998; Ler & Stanforth, 2003; Yan *et al.*, 2014). The relevance of the latter compared with the former process has been suggested to increase with increasing phosphate concentration (van Riemsdijk & Lyklema, 1980; Laiti *et al.*, 1998; Ler & Stanforth, 2003). Moreover, chemisorbed phosphate has been reported to change into a surface precipitate with increasing contact time between the retained phosphate and the (oxy)hydroxide

surface (Laiti *et al.*, 1998; Yan *et al.*, 2014). Concerning the retention of IHP by Fe and Al (oxyhydr)oxides, both inner-sphere [goethite, amorphous Al(OH)<sub>3</sub>; Ognalaga *et al.*, 1994; Celi *et al.*, 2001; Guan *et al.*, 2006; Johnson *et al.*, 2012] and outer-sphere complexation (goethite; Johnson *et al.*, 2012) have been reported to occur. Moreover, surface precipitation of IHP was reported (Ler & Stanforth, 2003; Yan *et al.*, 2014) to occur on ferrihydrite, goethite and amorphous Al(OH)<sub>3</sub>, but not on boehmite. Orthophosphate retained by surface precipitation in soils is commonly assumed to be non-crystalline AlPO<sub>4</sub>. Yet, studies by Goldshmid & Rubin (1988) and Duffy & van Loon (1995) indicate that in soils with a pH > 4 non-crystalline Al hydroxy phosphates may be important (surface) precipitates.

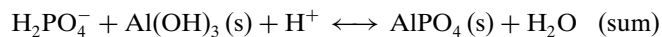
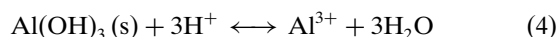
Our study was not aimed at elucidating the mechanisms of phosphate and IHP retention by important soil constituents, and has not been designed for that purpose. Nevertheless, evaluation of the P *K*-edge XANES spectra in our study provides some information concerning this issue. Thus, the presence of a pre-edge signal at 2151 eV for the P *K*-edge XANES spectra of orthophosphate and IHP retained by ferrihydrite indicates a transition of P 1s electrons into Fe (4p)–O (2p) antibonding molecular orbitals (Khare *et al.*, 2007). The circumstance that in our study the pre-edge features of orthophosphate retained by ferrihydrite were less pronounced than those of amorphous FePO<sub>4</sub>·2H<sub>2</sub>O or Fe(III) phytate and also than the pre-edge features of various Fe(III) phosphate minerals in earlier studies (strengite, phosphosiderite, heterosite, vivianite; Hesterberg *et al.*, 1999; Lombi *et al.*, 2006; Ajiboye *et al.*, 2007; Kruse & Leinweber, 2008) suggests that P retention by ferrihydrite occurs partly *via* surface precipitation, but also *via* chemisorption through ligand exchange and inner-sphere complexation (Khare *et al.*, 2005). However, according to Hesterberg *et al.* (1999) and Khare *et al.* (2005), adsorbed phosphate can also be distinguished from precipitated phosphate by a larger and narrower WL and a larger WL/PE ratio of their respective edge-normalized P *K*-edge XANES spectra. In our study, the WL intensity as well as the WL/PE ratio of the P *K*-edge XANES spectrum of orthophosphate retained by ferrihydrite (P concentration 3 g kg<sup>-1</sup>) are identical to the WL intensity and the WL/PE ratio of the spectrum of non-crystalline FePO<sub>4</sub>·2H<sub>2</sub>O diluted with quartz to a P concentration of 2 g kg<sup>-1</sup>. In summary, evaluation of the pre-edge feature on one hand and of the WL intensity or the WL/PE ratio of the P *K*-edge XANES spectrum of orthophosphate retained by ferrihydrite on the other yield different results: whereas the WL intensity indicates a dominance of surface precipitation, the less pronounced pre-edge compared with that of non-crystalline FePO<sub>4</sub>·2H<sub>2</sub>O indicates a considerable contribution of chemisorption by inner-sphere complexation, with the relevance of surface precipitation increasing with larger amounts of retained P. The pH increase associated with the retention of orthophosphate by ferrihydrite, goethite and hematite in unbuffered solution (Table 2) does neither support nor question the concept of a dominance of P chemisorption by inner-sphere complexation over surface precipitation in our

retention experiments, because not only chemisorption by inner-sphere complexation but also precipitation of  $\text{FePO}_4$  is associated with a net consumption of  $\text{H}^+$  ions:



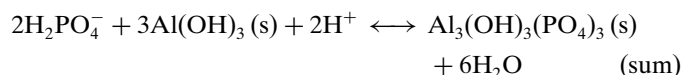
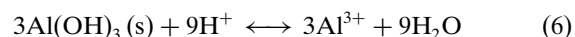
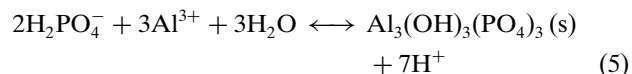
In contrast to free IHP, the P *K*-edge XANES spectrum of IHP retained by ferrihydrite has a pre-edge feature, indicating ligand exchange between the IHP and the ferrihydrite. However, this feature is less prominent than the pre-edge features of Fe(III) phytate or of orthophosphate retained by ferrihydrite. Moreover, the spectrum of IHP retained by ferrihydrite has a more pronounced WL and a larger WL/PE ratio than the spectrum of Fe(III) phytate. These findings suggest that, compared with orthophosphate, the retention of IHP by ferrihydrite at the studied P concentration levels is characterized by a larger contribution of chemisorption and a smaller contribution of surface precipitation.

The WL/PE ratios of P *K*-edge XANES spectra of orthophosphate retained by boehmite or Al-saturated SOM in the pH range 4.5–6.8 are not larger than that of the P *K*-edge XANES spectrum of non-crystalline  $\text{AlPO}_4$ . According to the concept of Hesterberg *et al.* (1999) and Khare *et al.* (2005), this finding suggests that at the studied P concentration levels the P is exclusively or predominantly retained by surface precipitation rather than adsorption. Moreover, the spectra of orthophosphate retained by boehmite or Al-saturated SOM generally are very similar to that of non-crystalline  $\text{AlPO}_4$ . By contrast, they are markedly different from the spectrum of crystalline  $\text{AlPO}_4$ , suggesting that surface precipitates formed during retention of orthophosphate by boehmite or Al-saturated SOM are non-crystalline. In contrast to orthophosphate retained by boehmite or Al-saturated SOM, the larger WL/PE ratio of the P *K*-edge XANES spectrum of orthophosphate retained by Al-saturated montmorillonite at an equilibrium pH range of 4.6–5.0 indicates a significant contribution of chemisorption to the P retention process. Similar to Fe, also the pH increase during retention of orthophosphate by boehmite does neither support nor question the concept of a dominance of P chemisorption by inner-sphere complexation over surface precipitation in our retention experiments, because not only chemisorption by inner-sphere complexation, but also precipitation of  $\text{AlPO}_4$  in systems containing superficial  $\text{Al}_{13}$  Keggin ion and/or Al (oxy)hydroxide phases, is associated with a net consumption of  $\text{H}^+$  ions:



At low solution P concentrations ( $<1 \text{ mg L}^{-1}$ ) in the pH range 4–6, precipitation of non-crystalline Al hydroxy phosphate compounds, including  $\text{Al}_3(\text{OH})_3(\text{PO}_4)_3$  (Goldshmid &

Rubin, 1988) and other amorphous precipitates with varying stoichiometry (Klein *et al.*, 2000), is favored over the precipitation of  $\text{AlPO}_4$  (Goldshmid & Rubin, 1988). Also the precipitation of amorphous Al hydroxy phosphate is associated with  $\text{H}^+$  consumption:



The pH decrease during orthophosphate retention by Al-saturated montmorillonite and Al-saturated SOM is probably caused by desorption and subsequent hydrolysis of Al cations due to exchange with  $\text{Na}^+$  ions supplied in excess by the 0.1 M NaCl solution.

Compared with the P *K*-edge XANES spectrum of Al phytate, the P *K*-edge XANES spectra of IHP retained by boehmite, Al-saturated montmorillonite or Al-saturated SOM have considerably larger WL/PE ratios, indicating a significant contribution of chemisorption to the IHP retention process under our experimental conditions. As for orthophosphate, the WL/PE ratio and thus the contribution of chemisorption to IHP retention are larger for Al-saturated montmorillonite than for boehmite and Al-saturated SOM. In contrast, the spectrum of IHP retained by calcite is almost identical to that of Ca phytate. This indicates that under the conditions of our experiment addressing IHP retention by calcite, Ca phytate precipitation is strongly dominating over IHP chemisorption on calcite surfaces.

#### 4.4. Implications for soil P speciation by *K*-edge XANES spectroscopy

Our study shows that the P *K*-edge XANES spectra of (i) orthophosphate retained by ferrihydrite, (ii) IHP retained by ferrihydrite, (iii) non-crystalline  $\text{FePO}_4 \cdot 2\text{H}_2\text{O}$  and (iv) Fe(III) phytate differ from each other in the shape of their pre-edge signals and/or their WL intensity and WL/PE ratio. These findings underline the necessity to include reference spectra of all these different Fe-bearing compounds [except Fe(III) phytate; see below] as reference compounds, when the P speciation in soils containing Fe-bearing phases is assessed by LCF on their P *K*-edge XANES spectra in order to yield most accurate fitting results. Fe(III) phytates may precipitate at high ( $>50 \text{ mg L}^{-1}$ ) P concentrations (Jackman & Black, 1951). However, Nolan *et al.* (1987) showed that Fe(III) phytate does not precipitate at any pH, when IHP concentrations are  $<3.6 \text{ mg P L}^{-1}$  and Fe concentrations are  $<5.6 \text{ mg L}^{-1}$ . Thus, the existence of free precipitated Fe(III) phytate in soils seems unlikely, and Fe(III) phytate has not to be included as a reference compound in LCF fits. On the other hand, the different spectral properties of inorganic and organic P bound to or in the investigated Fe-bearing phases in theory provide the opportunity for a detailed quantification of different Fe-

**Table 5**

Important chemical properties of the Bad Brückenau Cambisol BC horizon, the Stalldorf Luvisol E horizon, and the Gotzentalm Cambisol Bw horizon.

Soils formed from basalt (Bad Brückenau), loess (Stalldorf) and limestone (Gotzentalm).  $CEC_{eff}$ : effective cation exchange capacity as determined by extraction with 0.5 M  $NH_4Cl$ . BS: base saturation. SOC: soil organic carbon. Fe oxal, Al oxal, Fe dith, Al dith: Fe and Al extractable with acidic  $NH_4$  oxalate (pH 3.2) and dithionite-citrate-bicarbonate, respectively.

	pH ( $CaCl_2$ )	$CEC_{eff}$ ( $mmol_e\ kg^{-1}$ )	BS (%)	SOC ( $g\ kg^{-1}$ )	Total P ( $g\ kg^{-1}$ )	Fe oxal ( $g\ kg^{-1}$ )	Fe dith ( $g\ kg^{-1}$ )	Al oxal ( $g\ kg^{-1}$ )	Al dith ( $g\ kg^{-1}$ )
Bad Brückenau BC	4.5	81	73	12	2.82	17.7	49.7	8.1	10.7
Stalldorf E	3.6	57	12	12	0.51	3.7	7.6	1.5	1.6
Gotzentalm Bw	7.2	ND	100	15	0.57	3.6	23.0	3.9	3.6

bound P species in soils. The accuracy and precision of such quantification are to be tested in follow-up studies with different defined mixtures similar to those of Ajiboye *et al.* (2007) and Werner & Priezel (2015). The results of LCF conducted on the equimolar binary mixture of orthophosphate and IHP retained by ferrihydrite in our study suggest that the relative shares of P retained by association with Fe (oxyhydr)oxides either as orthophosphate or as IHP can be fairly well estimated by LCF in the energy range of the pre-edge feature, similar to the approach used by Khare *et al.* (2005) for the quantification of phosphate adsorbed to (oxyhydr)oxides of Al and Fe, respectively, in binary mixtures. However, in real soils such an estimation may be confounded by interference of the pre-edge signals of other Fe(III)-bound P species such as orthophosphate adsorbed to mixed non-crystalline Al-Fe-hydroxide phases (Liu & Hesterberg, 2011) which, depending on the Al:Fe ratio, can be similar to the pre-edge feature of orthophosphate-IHP mixtures adsorbed to ferrihydrite in our study. Thus, for the investigation of real soils rather than binary mixtures, LCF conducted on the entire spectrum instead of the pre-edge region probably is the better option. Our study showed that not only Al (oxy)hydroxides like boehmite, gibbsite or non-crystalline  $Al(OH)_3$  but also Al-saturated high-activity clay minerals and Al-saturated SOM can be important for the retention of inorganic and organic P. Furthermore, it showed that the K-edge XANES spectra of orthophosphate or IHP retained by these compounds differ from that of crystalline  $AlPO_4$ . For orthophosphate retained by boehmite, amorphous  $Al(OH)_3$  and gibbsite, this has already been reported by Khare *et al.* (2004). Additionally, we showed that IHP can be retained as strongly as orthophosphate by Al-saturated SOM or more strongly than orthophosphate by Al-saturated montmorillonite. Because the P K-edge XANES spectra of orthophosphate or IHP retained by boehmite, non-crystalline  $AlPO_4$ , crystalline  $AlPO_4$ , Al-saturated montmorillonite and Al-saturated SOM differ from each other in the shapes of their respective post-edge signals and/or their WL intensities and WL/PE ratios, they should be included as reference spectra, when the P speciation in soils containing Al-bearing phases is assessed by LCF on their P K-edge XANES spectra in order to yield most accurate fitting results.

However, the fact that the differences among the spectral features of orthophosphate retained by boehmite, Al-saturated SOM and non-crystalline  $AlPO_4$  are only subtle, renders

a reliable differentiation and specific quantification of these P species difficult. Therefore we suggest pooling the relative shares assigned of any of these P species by LCF. The same applies for the spectra of IHP retained by boehmite, Al-saturated SOM and Al-saturated montmorillonite. In contrast, orthophosphate assigned to the respective pooled P species on one hand and IHP assigned to the respective pooled P species on the other can be quantified separately, because the respective spectra differ markedly from each other, *e.g.* in their WL/PE ratios. Also the spectra of crystalline  $AlPO_4$  and Al phytate are sufficiently unique to allow quantification of these P species by LCF. The fact that the P K-edge XANES spectra of Ca phytate and of IHP retained by calcite are nearly identical (as pointed out in §4.3, IHP retained by calcite is probably mainly Ca phytate), but are different from those of other Ca phosphates, allows to quantify soil P bound as Ca phytate. Therefore we suggest to include the spectrum of Ca phytate in LCF exercises conducted on calcareous or Ca-bearing soils with  $pH > 5$ .

In summary, we recommend (i) the inclusion of P K-edge XANES spectra of Al phytate as well as of orthophosphate and IHP retained by ferrihydrite, boehmite, Al-saturated montmorillonite, Al-saturated SOM (and for soils with  $pH > 5$  also of Ca phytate) as reference spectra in addition to traditionally used spectra of  $FePO_4$ ,  $AlPO_4$ , Ca phosphates and free IHP in LCF exercises performed on P K-edge XANES spectra for the P speciation in soils to avoid erroneous results.

The advantage of such inclusion is demonstrated in the following for three German forest soils developed from different parent materials and characterized by different chemical properties (Table 5). For these soils we compared the results of LCF analyses (Table 6) with and without inclusion of orthophosphate and IHP retained by various pedogenic minerals (ferrihydrite, boehmite, Al-montmorillonite) or Al-saturated SOM as well as Ca phytate as predictor compounds in addition to free IHP,  $AlPO_4$ ,  $FePO_4$  and various Ca phosphates. For all three soils, inclusion of these P species resulted in considerable improvement of fit quality, as indicated by smaller R-factors and  $\chi^2$  values (Table 6). Moreover, the calculated contribution of different P species to total P changed markedly from an unrealistic P speciation (*e.g.* large contribution of free IHP up to 100% of total P in a B horizon) to a more realistic P speciation (*e.g.* significant contribution of adsorbed IHP in E and B horizons, of apatite in a soil formed from basalt, and of Ca-bound IHP in a soil formed from

Table 6

Results of linear combination fitting conducted on P *K*-edge XANES spectra of samples from three Bavarian forest soils formed from basalt (Cambisol Bad Brückenau), loess (Luvisol Stalldorf) and limestone (Cambisol Gotzentalm) without (W/O) and with inclusion of reference spectra of orthophosphate P and inositol hexakisphosphate (IHP) retained by ferrihydrite (FH), boehmite (Boe), Al-saturated montmorillonite (Mont-Al) and Al-saturated soil organic matter (SOM-Al).

	<i>R</i> -factor	$\chi^2$	Free IHP	AlPO <sub>4</sub>	FePO <sub>4</sub>	Ca-bound PO <sub>4</sub>	Ca-bound IHP	FH + PO <sub>4</sub>	FH + IHP	Boe + PO <sub>4</sub>	Boe + IHP	Mont-Al + PO <sub>4</sub>	Mont-Al + IHP	SOM-Al + PO <sub>4</sub>
Bad Brückenau BC														
W/O adsorbed P	0.0027	0.0075	36 ± 2	0	43 ± 1	20 ± 3	–	–	–	–	–	–	–	–
With adsorbed P	0.0006	0.0007	0	0	18 ± 2	49 ± 6	0	0	0	0	0	0	33 ± 3	0
Stalldorf E														
W/O adsorbed P	0.0152	0.0244	43 ± 2	0	57 ± 8	0	–	–	–	–	–	–	–	–
With adsorbed P	0.0018	0.0029	0	19 ± 2	3 ± 7	0	0	0	30 ± 1	0	0	0	48 ± 1	0
Gotzentalm Bw														
W/O adsorbed P	0.0416	0.0737	100 ± 8	0	0 ± 0	0 ± 8	–	–	–	–	–	–	–	–
With adsorbed P	0.0225	0.0398	40 ± 14	0	0	0	60 ± 6	0	0	0	0	0	0	0

limestone). Furthermore, we recommend (ii) pooling the calculated shares of orthophosphate retained by boehmite, Al-saturated SOM and non-crystalline AlPO<sub>4</sub>, as well as (iii) pooling the calculated shares of IHP retained by boehmite, Al-saturated montmorillonite or Al-saturated SOM.

## 5. Conclusions

Inclusion of P *K*-edge XANES spectra of orthophosphate and IHP retained by various pedogenic minerals (ferrihydrite, boehmite, Al-montmorillonite) or Al-saturated SOM as well as Ca phytate as predictor compounds in addition to traditionally used spectra of free IHP, AlPO<sub>4</sub>, FePO<sub>4</sub> and various Ca phosphates as reference compounds for LCF exercises in many cases results in considerable improvement of fit quality and significantly improved accuracy of soil P speciation results. Nevertheless, it is not a panacea warranting an accurate P speciation. We strongly advise (i) to include additional standards as predictor compounds, when XANES spectra obtained from samples of recently fertilized soils are deconvoluted by LCF (*e.g.* depending on the type of fertilizer: mono- or di-ammonium phosphate, potassium dihydrogen phosphate, struvite; Ajiboye *et al.*, 2008; Lombi *et al.*, 2006; Kar *et al.*, 2012; Khatiwada *et al.*, 2006). Additionally, (ii) the set of currently available P *K*-edge XANES spectra of reference compounds for soil P speciation by LCF analysis should be further extended by, for example, spectra of P retained by allophane, imogolite, mixed amorphous and crystalline Al/Fe (oxy)hydroxides as well as by spectra of Al hydroxy phosphates. Moreover, (iii) principal component analysis and/or utilization of information derived from thermodynamic stability calculations can help to select the most probable P phases to be used in LCF from a large number of available reference compounds. Finally, it is advised (iv) to combine synchrotron-based XANES spectroscopy with other techniques of soil P speciation (Kruse *et al.*, 2015). Spectra data files for all P-bearing compounds presented in this paper are provided in Tables S3–S10 of the supporting information. They can additionally be requested by email from the first

author or downloaded from the internet (URL: <http://www.soil-science.com/download>).

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