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Speciation and distribution of P associated with Fe and Al oxides in aggregate-sized fraction of an arable soil

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Abstract

To maximize crop productivity fertilizer P is generally applied to arable soils, a significant proportion of which becomes stabilized by mineral components and in part subsequently becomes unavailable to plants. However, little is known about the relative contributions of the different organic and inorganic P bound to Fe/Al oxides in the smaller soil particles. The alkaline (NaOH-Na_2EDTA) extraction with solution ^{31}P-nuclear magnetic resonance (^{31}P-NMR) spectroscopy is considered as a reliable method for extracting and quantifying organic P and (some) inorganic P. However, any so-called residual P after the alkaline extraction has remained unidentified. Therefore, in the present study, the amorphous (a) and crystalline (c) Fe/Al oxide minerals and related P in soil aggregate-sized fractions (>20, 2–20, 0.45–2 and <0.45 µm) were specifically extracted by oxalate (a-Fe/Al oxides) and dithionite (DCB, both a- and c-Fe/Al oxides). These soil aggregate-sized fractions with and without the oxalate and DCB pre-treatments were then sequentially extracted by alkaline extraction prior to solution ^{31}P-NMR spectroscopy. This was done to quantify the various chemical P forms which were associated with a- and c-Fe/Al oxides both in alkaline extraction and in the residual P of different soil aggregate-sized fractions.

The results showed that overall P contents increased with decreasing size of the soil aggregate-sized fractions. However, the relative distribution and speciation of varying P forms were found to be independent of soil aggregate-size. The majority of alkaline extractable P was in the a-Fe/Al oxide fraction (42–47 % of total P), most of which was orthophosphate (36–41 % of total P). Furthermore, still significant amounts of particularly monoester P were bound to the oxides. Intriguingly, however, Fe/Al oxides were not the main bonding sites for pyrophosphate. Residual P contained similar amounts of total P associated with both a- (10–13 % of total P) and c-Fe oxides (10–12 % of total P) in various aggregate-sized fractions, suggesting that it was likely occluded within the a- and c-Fe oxides in soil. This implies that with the dissolution of Fe oxides, these P may be released and thus available for plants and microbial communities.

1 Introduction

Phosphorus is after nitrogen the most limiting soil nutrient for agricultural crops and plays an important role in the overall functioning of the agro-ecosystems (Bowman and Moir, 1993; Wei et al., 2014). To increase or maintain crop productivity, P in the form of synthetic and animal based fertilizer is applied to arable soils. However, the long term (over-)application of P in excess of plant crop requirements has increased P in surface and subsurface soils, generally over time transforming it into various unavailable forms (Arai et al., 2005; He, 2009; Sims et al., 2000).

Soil organic and inorganic P are in the majority of cases stabilized by association with mineral components. Negatively charged phosphorus compounds attach themselves to mineral components such as aluminosilicates minerals and hydrous Fe or Al oxides (Solomon and Lehmann, 2000; Turner et al., 2005). The P reactivity in Fe/Al oxyhydroxides turns large proportions of soil P into unavailable forms (Arai and Livi, 2013; Solomon and Lehmann, 2000; Solomon et al., 2002). Different Fe/Al oxides however have varying P adsorption capacities and some studies showed amorphous Fe/Al oxides carried the majority of P in soils, despite higher abundance of crystalline Fe oxides (Arai and Livi, 2013; Arai et al., 2005; Rick and Arai, 2011). Few studies have distinguished organic and inorganic P associated with different Fe/Al oxides (i.e. amorphous and crystalline Fe/Al oxides) (Mahieu et al., 2000), despite the fact that P speciation will ultimately determine the different P bioavailability, mobility and mineralization in soil (Dick and Tabatabai, 1978; Liu et al., 2014). The study by Mahieu et al. (2000) found that amorphous Fe oxides had strong correlations with some organic P forms in the humic acid and calcium humate extracts of lowland rice soils. However, little is known about speciation and distribution of P associated with varying Fe/Al oxides. Additionally, finer-sized soil fractions were found to be enriched in highly active and easily mineralized organic P than larger particles (Rubæk et al., 1999). Similarly, organic P forms in general increased with decreasing particle size in forest and cropland soils (Cade-Menun, 2005). It seems that smaller soil particles are more reactive and have higher

P retaining capacity due to increased surface area than larger soil particles. In this context, it is important that different soil aggregate-sized fractions are also considered when studying P associated with Fe/Al oxides in soil.

Alkaline extraction and solution ^{31}P-NMR spectroscopy are widely thought as reliable methods for quantifying organic phosphorus (Turner, 2008). Inorganic phosphate (Pi) in alkaline soil extracts is assumed to originate from complexes with both Fe and Al (Turner, 2008). However, the distribution of organic P (Po) related to Fe/Al oxides in the alkaline extracts is still unclear. Our study aims to provide a novel method to understand the distribution of Pi and Po on Fe/Al oxides in the alkaline extract of soil. Furthermore, the residual P after alkaline extraction still accounts for significant proportion of P for some soils, most apparent in high-pH soil or for unamended soils with low P concentration (Cade-Menun and Liu, 2014; Cheesman et al., 2012; McDowell et al., 2007; Turner et al., 2007, 2003). It is by definition unidentified and is simply presumed to be recalcitrant in the environment (Cheesman et al., 2010). Therefore, an improved understanding of the residual P distribution, its bonding and "true" recalcitrance in soil is important for developing strategies to exploit this P as an "in part-additional" source for plant uptake or microbial usage. This is probably feasible in line with the observation by He et al. (2008), which suggested that most of this residual P could be orthophosphate.

Our current study did aim (i) to provide a comprehensive insight on the distribution of P bound to amorphous and crystalline Fe and Al (hydr)oxides in different soil aggregate-sized fractions, (ii) to identify the speciation and distribution of Pi and Po associated with amorphous and crystalline Fe/Al (hydr)oxides in NaOH-Na$_2$EDTA soil extracts and (iii) to provide detailed information on residual P distribution after alkaline extraction. It is in order to provide further information on the partition and quantification of these (unavailable) P forms in the arable soil, which is critical to better understand P dynamics in soils. In this study, we extracted amorphous and crystalline Fe/Al oxides from a bulk soil and different soil aggregate-sized fractions of an arable field. Additionally, the isolated amorphous Fe oxides-free and all Fe oxides-free aggregate-sized fractions were then treated by alkaline extraction. Simultaneously, the original bulk soil and various aggregate-sized fractions were also treated with alkaline extraction and studied by solution ^{31}P-NMR spectroscopy.

2 Materials and methods

2.1 Site description and soil fractionation

Composite topsoil sample (0–15 cm, pH: 7.64) was collected from a cultivated field in the German Tereno experimental platform site Selhausen (50°52′08″ N; 6°26′59″E; arable soil, luvisol) in March 2013. The field was cultivated with winter wheat in October 2011–2012 and winter barley in September 2013. No P fertilization was applied in years 2011–2013. More details about soil physicochemical characteristics and N fertilization of the test field were provided in Supplement Table S1 and Kupisch et al. (2015). The soil sample was fractionated using the soil particle-size fractionation method (Séquaris and Lewandowski, 2003) which explicitly avoids the destruction of small aggregates in soil (Berns et al., 2008). Concisely, 100 g soil sample was suspended in 200 mL ultrapure water (Milli-Q) and horizontally shaken at 150 rpm for 6 h. After that, 600 mL ultrapure water was added and mixed allowed to settle. Soil phases containing varying soil-aggregated sizes were collected by the pipette method based on Stoke's law. The soil fraction >20 µm (sand-sized aggregates, with mass ratio of 82.3 % of total soil) was obtained by removing supernatant after settling 6 min. The supernatant was sequently settled for 12 h and then remove the new supernatant to obtain soil fraction from 2 to 20 µm (silt-sized aggregates, with mass ratio of 12.9 % of total soil). The obtained new supernatant was subsequently separated into particle size of 0.45–2 µm (with mass ratio of 4.0 % of total soil) by spinning the samples at 2525 $\times g$ for 4 min (Biofuge, Heraeus), according to Stoke's law calculations with an assumed particle density of 2.65 g cm^{-3}. Lastly, <0.45 µm fraction (with mass ratio of 0.57 % of total soil) was obtained by spinning the supernatant at 2525 $\times g$ for 68 min

(Biofuge, Heraeus). The final supernatant only contained the electrolyte phase as well as a small amount of nanoparticles which has been investigated in our other concurrent work (Jiang et al., 2015). The soil aggregate-sized fractions were then freeze-dried for the elements analysis (i.e. Fe, Al, P and Ca) by inductively coupled plasma mass spectrometer (ICP-MS).

2.2 Oxalate and dithionite-citrate-bicarbonate (DCB) treatments

Acid ammonium oxalate was used to dissolve amorphous, poorly crystalline and organo Fe and Al (hydr)oxides (Kleber et al., 2005; Masiello et al., 2004; Neubauer et al., 2013). The bulk soil and different aggregate-sized fractions were treated with acid ammonium oxalate according to the extraction method of Kiem and Kögel-Knabner (2002) and Schwertmann (1964). Briefly, 200 mg soil sample was dispersed in 40 mL of 0.2 M acidic oxalate solution (0.113 M ammonium oxalate and 0.087 M oxalic acid) and shaken for 2 hours in the dark, followed by centrifugation. The supernatants were subsequently analyzed for Fe (Fe_{ox}), Al (Al_{ox}), P (P_{ox}) and Ca (Ca_{ox}) by ICP-MS.

The DCB mainly extracts organically-bound, amorphous and crystalline Fe oxides and only parts of dissolve oxides for Al and Si. For DCB extraction the protocol of Kiem and Kögel-Knabner (2002) was used. Briefly, 200 mg sample was extracted using 30 mL 0.3 M sodium citrate solution, 10 mL 1 M sodium hydrogen carbonate solution and 1 g sodium dithionite. After shaking for 16 h at room temperature, the soil suspension was centrifuged. The residue was then dispersed in 32 mL magnesium sulfate (0.05 M) to exchange the adsorbed Fe with magnesium, and centrifuged a second time. The two supernatant phases were combined and ICP-MS was used to measure Fe (Fe_{DCB}), Al (Al_{DCB}), P (P_{DCB}) and Ca (Ca_{DCB}).

2.3 Solution ^{31}P-NMR spectroscopy

To highlight the chemical composition of inorganic and organic P species in the bulk soil and different aggregate-sized fractions (> 20, 2–20, 0.45–2 and < 0.45 µm), these aggregate-sized fractions without and with oxalate and DCB pre-treatments were shaken 16 h with a mixture of 0.25 M NaOH and 50 mM Na_2EDTA (soil and solution mass ratio is 1 : 20–25, pH ≥ 13) (Cade-Menun and Preston, 1996) and centrifuged at 2525 ×g for 68 min (Biofuge, Heraeus). The P ($P\text{-}_{NaOH}$), Fe ($Fe\text{-}_{NaOH}$), Al ($Al\text{-}_{NaOH}$) and Ca ($Ca\text{-}_{NaOH}$) were analyzed by ICP-MS for the supernatants. These supernatants were then frozen and subsequently lyophilized. Na_2S dissolved in D_2O was added to the lyophilized materials to maintain reducing conditions for the removal of paramagnetic ions (i.e. Fe and Mn) during precipitation (Vestergren et al., 2012). The solution was centrifuged at 13 400 ×g for 20 min (Centrifuge 5415R, Eppendorf). Solution ^{31}P-NMR spectra were obtained using a Bruker Avance 600 MHz spectrometer equipped with a prodigy-probe, operating at 242.95 MHz for ^{31}P (Izarova et al., 2014). Extracts were measured with a D_2O-field lock at room temperature. Chemical shifts were referenced to 85 % orthophosphoric acid (0 ppm). The NMR parameters generally used were: 32 K data points, 0.5 s repetition delay (We tested the bulk soil with 0.5 s and 2 s repetition delay and no differences for the solution 31P-NMR spectra were observed.), 30° pulse width, 24000 scans and 0.7 s acquisition time for the Bruker 600 Avance spectrometers.

2.4 Calculations

The schematic diagram of whole soil sample preparation is shown in Fig. 1. The P contents in the various extracted fractions were calculated as follows:

$$(P_{\text{a-Fe}})_N = P_N - P_{\text{N-I}} \tag{1}$$

$$(P_{\text{c-Fe}})_N = P_{\text{N-I}} - P_{\text{N-II}} \tag{2}$$

$$(P_{\text{other}})_N = P_{\text{N-II}} \tag{3}$$

where, $(P_{\text{a-Fe}})_N$ = NaOH-Na_2EDTA extractable P associated with amorphous Fe/Al oxides;

$(P_{\text{c-Fe}})_N$ = NaOH-Na_2EDTA extractable P associated with crystalline Fe oxides;

$(P_{\text{other}})_N$ = NaOH-Na_2EDTA extractable P associated with other matters;
P_N = NaOH-Na_2EDTA extractable P in soil samples;
$P_{\text{N-I}}$ = NaOH-Na_2EDTA extractable P in “amorphous FeO-free” soil samples;
$P_{\text{N-II}}$ = NaOH-Na_2EDTA extractable P in “FeO-free” soil samples.

Relative distribution of Pi and Po in NaOH-Na_2EDTA extracts of soil samples, a-Fe/Al oxides-free and Fe/Al oxides-free soil samples were characterized by solution ^{31}P-NMR spectroscopy (Fig. 2 and Supplement Fig. S1). Here only orthophosphate, phosphate monoesters and pyrophosphate were scaled to 100 %. Therefore, the distribution of Pi and Po associated with a- and c-Fe/Al oxides in NaOH-Na_2EDTA extracts (Table 1) was calculated with the combination of NaOH-Na_2EDTA extraction (Table S2) and corresponding solution ^{31}P-NMR spectras (Fig. 2 and Fig. S1).

The residual P after alkaline extraction was separated into P bound to a-Fe oxides, c-Fe oxides and other matters as follows:

$$(P_{\text{a-Fe}})_{\text{resi}} = P_{\text{a-Fe}} - (P_{\text{a-Fe}})_N \tag{4}$$

$$(P_{\text{c-Fe}})_{\text{resi}} = \text{“}P_{\text{c-Fe}}\text{''} - (P_{\text{c-Fe}})_N = (P_{\text{Fe}} - P_{\text{a-Fe}}) - (P_{\text{c-Fe}})_N \tag{5}$$

$$(P_{\text{other}})_{\text{resi}} = P_T - P_{\text{Fe}} - P_{\text{N-II}} \tag{6}$$

where, $(P_{\text{a-Fe}})_{\text{resi}}$ = residual P associated with amorphous Fe oxides;
$(P_{\text{c-Fe}})_{\text{resi}}$ = residual P associated with crystalline Fe oxides;
$(P_{\text{other}})_{\text{resi}}$ = residual P associated with other matters;
$P_{\text{a-Fe}}$ = P associated with amorphous Fe/Al oxides (i.e. oxalate extractable P);
P_{Fe} = P associated with amorphous and crystalline Fe/Al oxides (i.e. DCB extractable P);
$P_{\text{c-Fe}}$ = P associated with crystalline Fe/Al oxides;
P_T = total P.

3 Results and discussion

3.1 Total, oxalate and DCB extractable P, Fe, Al and Ca in soil aggregate-sized fractions

Table 2 represents ICP-MS results of elemental contents (i.e. P, Fe, Al and Ca) in the bulk soil and different aggregate-sized fractions, and their oxalate and DCB extracts. Total P was 0.73 g kg^{-1} in bulk soil with a significant increase from large particles to small particles (range between 0.54 and 2.47 g kg^{-1}). Total Fe and Al in different soil aggregate-sized fractions showed the same gradient with total P. Total P had a strong positive relationship with total Fe and Al ($R^2 > 0.99$; $P < 0.006$) in these aggregate-sized fractions, which indicated that P was, to a large extent, associated with Fe and Al in all aggregate-sized fractions. The high correlation also indicated the cause why smaller particles contained more P. There was more Fe and Al in the smaller size fractions, and the minerals containing these elements (i.e. Fe and Al) acted as important P carriers.

Oxalate extractable P, Fe and Al (P_{ox}, Fe_{ox} and Al_{ox}) also had an increasing trend with smaller particle sizes. Oxalate extractable P corresponded to 53–62 % of the total P in varying soil aggregate-sized fractions, although the amounts of amorphous Fe and Al oxides fractions were low with respect to total Fe (15–17 %) and total Al (2–4 %) (Table 2). DCB extractable P (P_{DCB}) was 70–75 % of the total P in these aggregate-sized fractions, which implied that Fe/Al oxides were the major carriers of P in the soil (Table 2). The differences between DCB extractable Fe and Al oxides and oxalate extractable Fe and Al oxides represent the amounts of extracted crystalline Fe (c-Fe) and Al (c-Al) oxides. There was a large amount of c-Fe (6.31–28.4 g kg^{-1}, 31–37 % of total Fe). In contrast, c-Al content was low (only 0–0.34 g kg^{-1}, 0–0.6 % of total Al) in the various aggregate-sized fractions (Table 2). Similarly, high amount of c-Fe and low amount of c-Al were also found in sandy soils (Borggaard et al., 1990). This is probably because organic matter in soil inhibits Al oxides crystallization (Borggaard et al., 1990). Currently there is some ongoing discussion in the literatures (Acebal et al., 2000; Borggaard et al., 1990; Ryan and Gschwend, 1991) with respect to the extent in which c-Al is extracted by DCB and what reasons for such an incomplete extraction of this Al are. Only 12–20 % of total P (c-P, the difference between P_{DCB} and P_{ox}, Table 2) was released with crystalline Fe and Al oxides (Table 2). It shows that amorphous Fe/Al oxides are more important for P bonding compared to crystalline Fe/Al oxides. Several researchers did already report that P was dominantly associated with amorphous Fe and Al oxides fractions in various soil types in USA (Arai et al., 2005; Rick and Arai, 2011). It was presumed that specific anion adsorption (e.g. P) suppressed the transformation from amorphous to crystalline Fe oxides (Arai et al., 2005; Biber et al., 1994), which could explain the low amount of P associated with crystalline Fe oxides.

Oxalate extracted P also had a strong positive linear correlation with oxalate extracted Fe ($R^2 = 0.997$) and Al ($R^2 = 0.976$). The similar high correlation between oxalate extractable P and Fe oxides has already been shown in acidic and neutral soils (Forsmann and Kjaergaard, 2014). Nevertheless, c-Fe and c-Al contents were not strongly correlated with c-P. Although there was a smaller amount of Ca in different aggregate-sized fractions compared to Fe and Al (Table 2), DCB also dissolved between 48 and 100 % of total Ca in varying aggregate-sized fractions (Supplement Table S3). Therefore, it could be assumed that a small amount of the measured c-P (Table 2) was related to Ca minerals (Ca-P precipitates) in the soil.

Although there were higher amounts of total Fe, Al and P in smaller particles compared with larger particles, there were no clear discernible proportional differences in oxalate and DCB extractable Fe, Al and P fractions with respect to total Fe, Al and P between various aggregate-sized fractions. Therefore, there was a clear indication that the relative proportional distributions of amorphous, crystalline Fe/Al oxides and related P in this soil were independent on the aggregate-size of soil particles a result not found previously. Kiem and Kögel-Knabner (2002) did suggest that there was a similar Fe_{ox}/Fe_{DCB} ratio across three size separates of arable soil fractions < 6 µm. Fe/Al (hydr)oxides and organic matter bind clay particles together into soil aggregates (Tisdall and Oades, 1982). Therefore, these Fe/Al oxides as inorganic binding agents and associated P were distributed on soil aggregates with all varying sizes proportionally.

3.2 Speciation and distribution of P forms in soil aggregate-sized fractions

There was 58–65 % of total P extracted by NaOH-Na_2EDTA in different soil size fractions (Table S2). A similar extraction efficiency (average of 63 % of total P) was found in a recent study of dried wetland soil samples (Cheesman et al., 2012). Inorganic and organic P contents in NaOH-Na_2EDTA extracts were characterized by solution ^{31}P-NMR spectroscopy. Inorganic (orthophosphate and pyrophosphate) and organic (phosphate monoesters, phosphate diesters and phosphonates) P forms were present in our soil aggregate-sized fractions.

The orthophosphate and phosphate monoesters were major detected inorganic and organic P forms in all soil aggregate-sized fractions (Fig. 3). NaOH-Na_2EDTA extractable orthophosphate (^{31}P-NMR chemical shift of 5–7 ppm) (Cade-Menun, 2005) ranged from 0.25 to 1.27 g kg^{-1}, accounting for the majority of P (47–51 % of total P) in all the aggregate-sized fractions (Fig. 3). Phosphate monoesters (3-6 ppm) (Bol et al., 2006; Cade-Menun, 2005; Fuentes et al., 2012) were always the dominant organic P with the contents of 53–332 mg kg^{-1} (10–14 % of total P) (Fig. 3). Phosphate monoesters are generally the dominant group of organic phosphorus compounds in most soils: they occur mainly as inositol phosphates, a family of phosphoric esters of hexahydroxy cyclohexane (inositol) (Turner et al., 2005). The content of pyrophosphate (−4 to −5 ppm) (Cade-Menun, 2005) was only up to 15 mg kg^{-1} (less than 1 % of total P). Phosphonates (12 ppm) and phosphate diesters (2.5 to −1 ppm) (Cade-Menun, 2005) did only contribute 0.6–1.0 % of total P (Fig. 3). We found that there were only little if any P-diesters in fine particles (Fig. 3). Many microbial products such as teichoic acid P or DNA-P would exhibit these structures (Makarov et al., 2002).

All the identified P forms had a larger content in < 2 µm soil fraction when compared to larger sized particles. However, the distributions of different P forms in our study did seem to be independent of soil aggregate-size (Fig. 3). In contrast, some studies have found that soil size fractions drive the differential P distributions in forest and arable soils (Liu et al., 2014; Solomon et al., 2002). Our novel finding about the similar P distribution in various aggregate-sized fractions of this soil was probably due to the comparable Fe and Al oxides distribution in aggregate-sized fractions when considering that Fe and Al oxides were domain P carriers in the soil.

3.3 NaOH-Na$_2$EDTA extractable P associated with Fe and Al oxides in soil aggregate-sized fractions

The bulk soil and aggregate-sized fractions after oxalate and DCB pre-treatments were also extracted by NaOH-Na$_2$EDTA for ^{31}P-NMR analysis. We found that the bulk soil (Fig. 2) and other soil aggregate-sized fractions (Fig. S1) after oxalate pre-treatment revealed a higher phosphate monoesters/orthophosphate ratio in NaOH-Na$_2$EDTA extracts compared to that without oxalate treatment. The bulk soil (Fig. 2) and other soil aggregate-sized fractions (Fig. S1) after DCB pre-treatment had the highest phosphate monoesters/orthophosphate ratio among the three types of samples. This finding implied that relatively high amounts of orthophosphate were removed by oxalate and particularly DCB, i.e., it was mainly orthophosphate that was bound to a- and c-Fe oxides in aggregate-sized fractions rather than organic P. Besides, most pyrophosphate still remained in Fe/Al oxides-free aggregate-sized fractions (Fig. 2 and Fig. S1). Pyrophosphate is perceived to be contained within live fungal tissue (Koukol et al., 2008) or sorbed to the mineral soil matrix (Gunary, 1966). However, the present study suggested that Fe/Al oxides (part of mineral matrix) were not the main sites for pyrophosphate adsorption.

Because orthophosphate and phosphate monoesters were the dominant P forms, only they were discussed below (Table 1). The amount of P bound to Fe/Al oxides in NaOH-Na$_2$EDTA extracts accounted for 49–54 % of total P in various aggregate-sized fractions, including orthophosphate (41–47 % of total P) and phosphate monoesters (7–9 % of total P) (Table 1). The amorphous oxides carried more orthophosphate and phosphate monoesters (36–41 and 6–8 % of total P, respectively) than did the crystalline oxides (3–6 and 1–2 % of total P, respectively) in the NaOH-Na_2EDTA extracts (Table 1). The P adsorption experiment from Borggaard (1983) showed that a-Fe oxides absorbed more phosphate than c-Fe oxides in soils. Generally, phosphate monoesters are commonly assumed to be stabilized in soils by association with amorphous metal oxides, which have greater sorption affinity compared to crystalline metal oxides (Celi and Barberis, 2007; Turner and Engelbrecht, 2011).

Noteworthy, only rare amounts of Fe (0–1 % of total Fe) from "untreated" soil aggregate-sized fractions were dissolved by NaOH-Na_2EDTA (Table S3). Although the presence of Na_2EDTA caused some dissolved Fe ions precipitating in humic-iron compounds, the precipitation was negligible at hydroxide ion concentrations ≥ 100 mM ($\geq$ pH 13) (Turner, 2008). Therefore, it indicated that a- and c-Fe oxides associated P present in NaOH-Na_2EDTA extracts was probably attached on the surface of Fe oxides. Alkaline extraction could remove P held to Fe and Al components of soil surface by chemisorption (Hedley et al., 1982; McLaughlin et al., 1977; Ryden et al., 1977).

High contents of dissolved Al were still found in NaOH-Na_2EDTA extracts, and which were similar with those in oxalate and DCB extracts of soil aggregate-sized fractions (Tables 2 and S3). Similarly, high Al and low Fe contents were found in NaOH-Na_2EDTA extracts from a tropical forest soil (Turner, 2008). Considering that little Si was dissolved in NaOH-Na_2EDTA in all aggregate-sized fractions (data not shown), it indicated that NaOH-Na_2EDTA extracted Al mainly stemmed from amorphous Al oxides (rare c-Al oxides in the soil, Table 2) rather than aluminosilicate minerals in the soil. Therefore, the Al-P in NaOH-Na_2EDTA extracts contained P probably both on surface of Al oxides and occluded in Al oxides.

There was still 8–11 % of total P (including 4–6 % orthophosphate and 4–5 % phosphate monoesters) in NaOH-Na_2EDTA extracts which were not associated with Fe/Al oxides of different aggregate-sized fractions (Table 1). The NaOH-Na_2EDTA extraction included P contained within microbial cells (Turner and Blackwell, 2013). Besides, inositol phosphate is stabilized mainly through a strong adsorption on the surface of amorphous metal oxides and clay minerals (Celi and Barberis, 2007), so we assumed that a part of these P compounds were adsorbed on the surfaces of clay minerals. Additionally, it was also believed that there was P associated with Ca minerals in this NaOH-Na_2EDTA extracts considering that 43–98 % of total Ca was dissolved in NaOH-Na_2EDTA extracts of different aggregate-sized fractions (Table S3).

3.4 Residual P in soil aggregate-sized fractions

Using our specific separation method, the residual P was separated into P bound to a-Fe oxides, c-Fe oxides and other matters (Eqs. 4–6 and Table 1). The P in residual fractions accounted to 35–42 % of total P in aggregate-sized fractions. We found that 10–13 % of total P in different aggregate-size fractions was bound to a-Fe oxides and 10–12 % of total P was associated with c-Fe oxides (Table 1). The 20–24 % of total P associated with Fe oxides (Table 1) was equivalent to 53–66 % of the P present in the residual fraction. Therefore, the majority of P in residual fraction was associated with Fe oxides (Table 1). The remaining 12–18 % of total P (i.e. 34–47 % of the P present in residual fractions) was bound to other minerals or organic matter which was dissolved or released neither in DCB nor in NaOH-Na_2EDTA of different aggregate-sized fractions (Table 1).

We believe our novel results suggested that the a- and c-Fe oxides associated P in the residual P fraction were most likely occluded inside of a- and c-Fe oxides. This was in contrast to the a- and c-Fe oxides associated P present in NaOH-Na_2EDTA extracts which were absorbed on the surface of Fe oxides. The P associated with Fe oxides in residual fractions probably was held at the internal surfaces of Fe oxides by chemisorption at protonated surface sites or by the replacement of surface hydroxyls in soil aggregates (Hedley et al., 1982; Ryden et al., 1977), or diffused into the bulk of Fe oxides or into pores and defects (McLaughlin et al., 1977). It means that with the changes in soil conditions (e.g. soil anoxic condition, acidic condition, high concentrations of organic acid or siderophore) (Forsmann and Kjaergaard, 2014; Kraemer, 2004) when Fe oxides become dissolved, then P associated with the Fe oxides may become available to plants or the microbial population. The a-Fe/Al oxides did adsorb more orthophosphate and monoesters than c-Fe/Al oxides (Table 1: NaOH-Na_2EDTA extractable P). However, there were similar amounts of occluded P inside of both a- and c- Fe oxides (Table 1: Residual P).

The Ca-P complexes present in residual fractions of soil aggregate-sized fractions should contribute to a proportion of the remaining residual P, ca. 12–18 % of total P. Cheesman et al. (2010) suggested that there were inorganic Ca-phosphates in the residual P from detritus and surface soils. In the present study, 12 % of total P was not associated with Fe oxides in residual P of $< 0.45\,\mu$m soil fractions (Table 1), despite that almost all the Ca was already extracted by NaOH-Na_2EDTA and DCB (Table S3). It seemed therefore that the majority of the 12–18 % of total P was bound to other materials. In our other concurrent work (Jiang et al., 2015), we found that some P in the soil nanoparticles after DCB treatment was still bound to Fe bearing phyllosilicate minerals (i.e. Fe structurally embedded into the crystalline structure of phyllosilicate minerals via isomorphic substitution) (Regelink et al., 2014). It is possible that these Fe bearing phyllosilicate minerals may also be responsible for the bonding of the remaining P in the NaOH-Na_2EDTA non-extracts. Noteworthy, soil aggregate-sizes do not have a significant effect on the relative distribution of P forms bond to a- and c-Fe/Al oxides for NaOH-Na_2EDTA extracts and residual soil P (Table 1).

4 Conclusions

We concluded for this arable German soil that: (1) with decreasing aggregate-sized fractions soil P content increased, however the distribution and speciation of varying P forms were independent of aggregate-size. (2) Most of the NaOH-Na_2EDTA extractable P (Pi and Po) was attached on the surface of amorphous Fe oxides and Al oxides, or alternatively inside of the Al oxides. (3) The majority of P in the residual fraction was occluded within Fe oxides, which implies that this P may be released and become available for plants and microbial communities following the dissolution of Fe oxides in soil.

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Table 1. NaOH-Na_2EDTA extractable P and residual P distribution (%, with respect to total P of each soil aggregate-sized fraction) associated with amorphous and crystalline oxides, and other matters.

	NaOH-Na_2EDTA extractable P						Residual P		
	$(P_{a\text{-}Fe})_N$		$(P_{c\text{-}Fe})_N$		$(P_{other})_N$		$(P_{a\text{-}Fe})_{resi}$	$(P_{c\text{-}Fe})_{resi}$	$(P_{other})_{resi}$
	Ortho.	Mono.	Ortho.	Mono.	Ortho.	Mono.			
Bulk soil	39	6	5	2	5	4	10	11	18
Sand-sized > 20 µm	36	6	6	1	4	4	12	12	18
Silt-sized 2–20 µm	39	7	3	1	6	5	10	10	18
Clay 0.45–2 µm	37	8	4	1	6	5	13	10	16
Clay < 0.45 µm	41	6	6	1	6	5	11	12	12

Ortho. = orthophosphate; Mono. = P-monoesters. $(P_{a\text{-}Fe})_N$ = NaOH-Na_2EDTA extractable P associated with amorphous Fe/Al oxides. $(P_{c\text{-}Fe})_N$ = NaOH-Na_2EDTA extractable P associated with crystalline Fe oxides. $(P_{other})_N$ = NaOH-Na_2EDTA extractable P associated with other matters. $(P_{a\text{-}Fe})_{resi}$ = Residual P associated with amorphous Fe oxides. $(P_{c\text{-}Fe})_{resi}$ = Residual P associated with crystalline Fe oxides. $(P_{other})_{resi}$ = Residual P associated with other matters.

Table 2. The amounts of P, Fe, Al and Ca in bulk soil and soil aggregate-sized fractions, and extracted by oxalate and dithionite (DCB) ($\mathrm{g\,kg^{-1}}$). Fraction in bracket (%) with respect to total P, Fe, and Al values of each aggregate-sized fraction shown in Table 2 are given in parentheses. Data are the mean values of three replicates with standard deviations.

Aggregate -sized fractions	P_T^c	Fe_T^c	Al_T^c	Ca_T^c	P_{ox}^d	Fe_{ox}^d	Al_{ox}^d	P_{DCB}^e	Fe_{DCB}^e	Al_{DCB}^e	c-P[f]	c-Fe[f]	c-Al[f]
Bulk soil[a,b]	0.73 ± 0.03	24.0 ± 0.7	44.6 ± 2.1	4.03 ± 0.12	0.41 ± 0.01 (56)	3.75 ± 0.10 (16)	0.88 ± 0.03 (2)	0.53 ± 0.02 (72)	11.6 ± 0.5 (48)	1.03 ± 0.08 (2)	0.12 (16)	7.80 (33)	0.15 (0.3)
Sand-sized > 20 µm[a,b]	0.54 ± 0.05	19.5 ± 2.9	37.4 ± 2.3	3.63 ± 0.32	0.29 ± 0.01 (53)	2.92 ± 0.24 (15)	0.59 ± 0.04 (2)	0.40 ± 0.04 (73)	9.24 ± 0.53 (47)	0.81 ± 0.07 (2)	0.11 (20)	6.31 (32)	0.22 (0.6)
Silt-sized 2–20 µm[a,b]	1.40 ± 1.00	44.7 ± 3.9	73.8 ± 0.9	5.63 ± 0.40	0.82 ± 0.04 (58)	7.00 ± 0.23 (16)	1.83 ± 0.07 (2)	0.98 ± 0.04 (70)	20.7 ± 0.5 (46)	1.93 ± 0.04 (3)	0.17 (12)	13.7 (31)	0.10 (0.1)
Clay 0.45–2 µm[a,b]	2.37 ± 0.06	69.3 ± 3.5	108 ± 2	7.10 ± 0.30	1.38 ± 0.01 (58)	11.6 ± 0.1 (17)	3.28 ± 0.05 (3)	1.72 ± 0.06 (73)	36.8 ± 0.7 (53)	3.62 ± 0.31 (3)	0.33 (14)	25.2 (36)	0.34 (0.3)
Clay < 0.45 µm[a,b]	2.47 ± 0.06	76.4 ± 3.3	114 ± 2	8.23 ± 0.35	1.54 ± 0.07 (62)	12.4 ± 0.5 (16)	4.36 ± 0.28 (4)	1.85 ± 0.09 (75)	40.8 ± 1.1 (53)	4.11 ± 0.35 (4)	0.31 (13)	28.4 (37)	ND

[a] Amounts increase with decreasing particle size. [b] Relative proportions of isolated fractions are independent of decreasing particle size. [c] Total P, Fe, Al and Ca. [d] Oxalate extractable P, Fe and Al. [e] DCB extractable P, Fe and Al. [f] The c-(P, Fe, Al) means the difference between $(\mathrm{P, Fe, Al})_{DCB}$ and $(\mathrm{P, Fe, Al})_{ox}$. ND: not detected.

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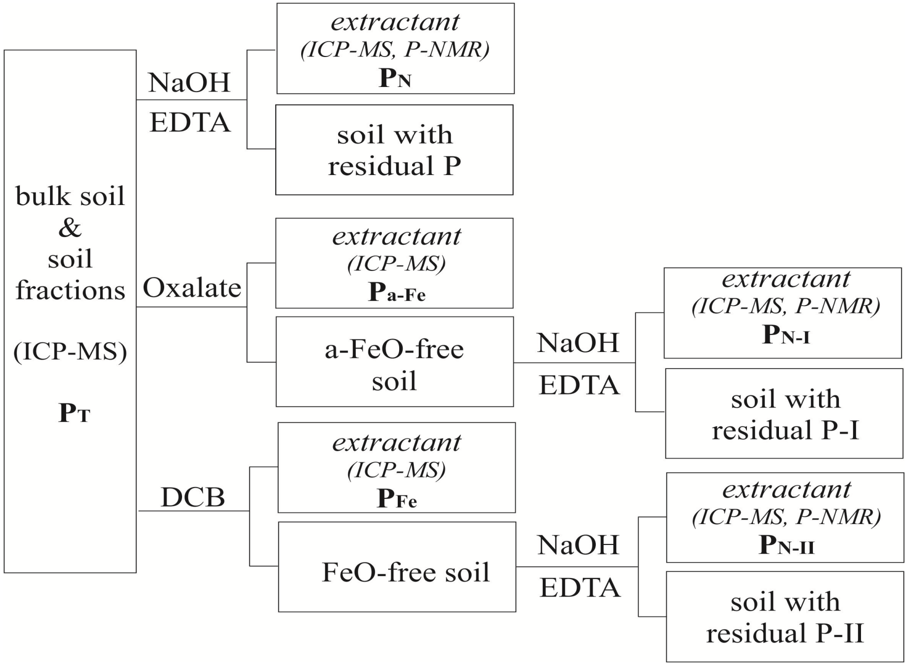
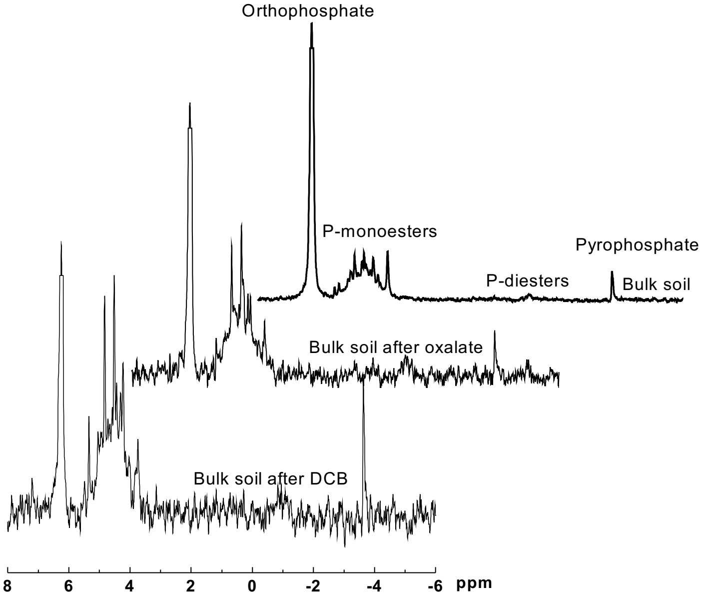


Figure 1. A schematic diagram of the soil sample treatments.



	Orthophosphate (%)	P-monoesters (%)	Pyrophosphate* (%)
Bulk soil	79.4	19.1	1.4
Bulk soil after oxalate	60.8	35.0	4.2
Bulk soil after DCB	51.5	43.0	5.5

*All other P forms are not included.

Figure 2. Solution phosphorus-31 nuclear magnetic resonance spectra of NaOH-Na_2EDTA extracts of bulk soil without and with oxalate and dithionite (DCB) pre-treatments (all subfigures have been reduced by the same factors). The associated table only shows the relative mass distribution (%) of orthophosphate, P-monoesters and pyrophosphate in NaOH-Na_2EDTA extracts of bulk soil without and with oxalate and DCB pre-treatments.

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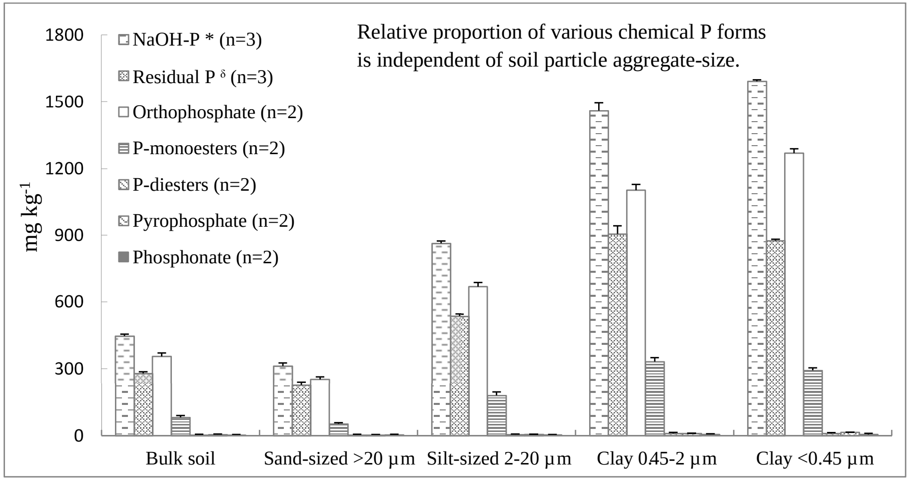

Relative proportion of various chemical P forms is independent of soil particle aggregate-size.

* NaOH-Na_2EDTA extractable P. $^{\delta}$ NaOH-Na_2EDTA non-extractable P.

Figure 3. Phosphorus forms and contents (mg kg^{-1}) identified by solution phosphorus-31 nuclear magnetic resonance spectroscopy in the NaOH-Na_2EDTA extracts of bulk soil and different aggregate-sized fractions. The varying chemical P contents were determined by multiplying the proportion of spectral area by NaOH-Na_2EDTA extractable P.