

## Biogeosciences

We thank the referee for the comments to help to improve the manuscript. We adhered to the suggestions made during revision of the manuscript.

**Comment:** The authors used an indirect method (Fig. 1) to "infer", not measure directly, the P fractions bound to Fe oxides. This might be problematic because the pretreatment of soil with oxalate and DCB could have changed the extraction efficiency of NaOH-EDTA. For example, direct extraction with NaOH-EDTA (alkaline) might target for different soil components to that after pretreatment with oxalate (acidic). This can be partly seen from Table S3, where Ca<sub>N</sub> (in the extract of NaOH-EDTA) differed greatly from Ca<sub>ox</sub>. Was it possible that oxalate and DCB attacked different fractions of P to NaOH-EDTA? To partly examine this, I suggest the authors directly extract Fe (with oxalate or DCB) from the residual soil, after first extraction with NaOH-EDTA, and then compare the extracted P from residual soil with their present results calculated by Equ (4)-(6).

**Answer:** We actually think, based on references' by Forsmann and Kjaergaard (2014) and Rick and Arai (2011), that oxalate and DCB do attack different fractions of P when compared to extractions by NaOH-Na<sub>2</sub>EDTA. Oxalate extracted P is considered as P derived from the surface and inside of amorphous Fe (a-Fe) oxides. Whereas, DCB extractable P is thought to be P derived from the surface and inside of amorphous and crystalline Fe (c-Fe) oxides. Finally, NaOH-Na<sub>2</sub>EDTA extractable P (P<sub>N</sub>) will extract P (also chemisorbed) present on the surface of amorphous and crystalline Fe oxides (Hedley et al., 1982) and a minor part of P associated to Ca minerals and clay minerals as we discussed in the text (P9891 Lines 11-14, P9891 Line 26 to P9892 Line 4). That is one of the main reasons why the NaOH-Na<sub>2</sub>EDTA extractable Ca (Ca<sub>N</sub>) also differed greatly from oxalate extractable Ca (Ca<sub>ox</sub>). Therefore after the oxalate pre-treatment, NaOH-Na<sub>2</sub>EDTA extractable P in the oxalate-treated soil samples (P<sub>N-I</sub>) would contain mainly P from the surface of crystalline Fe oxides and a part of P associated to Ca minerals and clay minerals. However, after DCB pre-treatment, the NaOH-Na<sub>2</sub>EDTA extractable P in the DCB-treated soil samples (P<sub>N-II</sub>) most likely contained only P bound to Ca minerals and clay minerals.

As suggested by the referee, we directly extracted Fe and related P with oxalate treatment from the residual soil after first extraction with NaOH-Na<sub>2</sub>EDTA in the bulk soil. We also rechecked our calculation and found some minor mistake in residual P distribution between (P<sub>a-Fe</sub>)<sub>resi</sub> and (P<sub>c-Fe</sub>)<sub>resi</sub> in Table 1. The calculated new values of (P<sub>a-Fe</sub>)<sub>resi</sub> and (P<sub>c-Fe</sub>)<sub>resi</sub> increases and decreases on average by 2% (0-4%) respectively, which has no effect on the results and discussion in our manuscript. The comparison of the indirect (12±3% of total P, Table 1) and direct (15±1% of total P) methods for oxalate based extract of residual P ((P<sub>a-Fe</sub>)<sub>resi</sub>) in bulk soil suggested a very little difference. However, further studies

including direct DCB extraction after first NaOH-Na<sub>2</sub>EDTA treatment are needed and will be taken in account in subsequent work.

Table 1 NaOH-Na<sub>2</sub>EDTA 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 as shown in Eqs.1-6.

	NaOH-Na <sub>2</sub> EDTA extractable P						Residual P		
	$(P_{a-Fe})_N$		$(P_{c-Fe})_N$		$(P_{other})_N$		$(P_{a-Fe})_{resi}$	$(P_{c-Fe})_{resi}$	$(P_{other})_{resi}$
	Ortho.	Mono.	Ortho.	Mono.	Ortho.	Mono.			
Bulk soil	39	6	5	2	5	4	12	9	18
Sand-sized >20 μm	36	6	6	1	4	4	11	13	18
Silt-sized 2-20 μm	39	7	3	1	6	5	13	7	18
Clay 0.45-2 μm	37	8	4	1	6	5	13	9	16
Clay <0.45 μm	41	6	6	1	6	5	15	8	12

Ortho. = orthophosphate; Mono. = P-monoesters.

$(P_{a-Fe})_N$  = NaOH-Na<sub>2</sub>EDTA extractable P associated with amorphous Fe/Al oxides.

$(P_{c-Fe})_N$  = NaOH-Na<sub>2</sub>EDTA extractable P associated with crystalline Fe oxides.

$(P_{other})_N$  = NaOH-Na<sub>2</sub>EDTA extractable P associated with other matters.

$(P_{a-Fe})_{resi}$  = Residual P associated with amorphous Fe oxides.

$(P_{c-Fe})_{resi}$  = Residual P associated with crystalline Fe oxides.

$(P_{other})_{resi}$  = Residual P associated with other matters.

**Comment:** In addition, the present discussion did not pay adequate attention to the linkage between aggregate size and various P forms. Although the proportion of P forms was relatively constant, their contents differed with aggregate size. What is its significance for the mangement of P in arable soils or other ecosystems? The data can be discussed in relation to some ecological issues at broad scales.

**Answer: We added the following statement:** P9889 Line 26: All the identified P forms were present in higher concentrations in < 2 μm soil fraction when compared to larger-sized particles. Small-sized soil fractions, such as soil colloids isolated in this study, are well-established as being efficient carriers of nutrients (especially phosphorus) (Haygarth et al., 2006). Therefore, soil managements, which control soil colloids loss from productive land (e.g. tillage and wind/water erosion) are crucial to restrain

any unwanted strong declines in soil phosphorus levels and thus help to retain the potential bioavailability of phosphorus over longer time periods.

**Other suggestions made by the reviewer:**

1. P9891, L7-8: The authors should explain why a large amount of orthophosphate (36-41% of total P) was extracted while only a trace amount of Fe was mobilized by NaOH-EDTA.

**Answer:** It indicated that the NaOH-Na<sub>2</sub>EDTA extracted orthophosphate was not occluded in the Fe containing minerals. These orthophosphate was probably derived from the surface of Fe containing minerals (e.g. Fe oxides) and was bond to other minerals.

**Revised in the text as follows:**

P9891 L11: The NaOH-Na<sub>2</sub>EDTA extracted P was not occluded in the Fe containing minerals (e.g. Fe oxides) but probably associated to the surface of Fe containing minerals and bond to other minerals. Therefore, a- and c-Fe oxides associated P present in NaOH-Na<sub>2</sub>EDTA extracts was probably attached to the surface of Fe oxides.

2. P9892, L2-4: If 43-98% of total Ca was dissolved in NaOH-Na<sub>2</sub>EDTA and DCB extracts (Table S3), why did Ca not retain a large proportion of P? Why should Fe be superior to Ca in the holding capacity of P in such an alkaline soil (pH 7.64)?

**Answer:** The total Ca accounted only for 3.6-8.2 g kg<sup>-1</sup> in different aggregate-sized soil fractions. In contrast, the total Fe amounted for 19.5-76.4 g kg<sup>-1</sup> in different aggregate-sized soil fractions. Therefore, this soil is clearly dominated by Fe-minerals compared to Ca-minerals. Furthermore, oxalate extracted P accounted for 53-62% of total P, but oxalate could only dissolve a very small amount of Ca (Ca<sub>ox</sub> ranges 0.16-0.19 g kg<sup>-1</sup>). It means that most of this 53-62 % of total P was likely bound to amorphous Fe oxides rather than to Ca containing minerals. Additionally, DCB extracted 70-75 % of total P, 47-53% of total Fe and 48-100 % of total Ca, which means that only 12-20% of total P (P<sub>DCB-P<sub>ox</sub></sub>) was bound to crystalline Fe oxides (6.31-28.4 g Fe kg<sup>-1</sup>) and to the 48-100% of total Ca (1.75-8.42 g Ca kg<sup>-1</sup>). The amount of extracted Ca minerals was significantly less than crystalline Fe oxides. Clearly, the majority of this 12-20% of total P was bound to crystalline Fe oxides not Ca minerals. Therefore, Fe is in our soils (Luvisol) superior to Ca in its holding capacity of P.

3. P9893, L4-5: I could not understand how the percent (12-18%) was derived, i.e. why this percent could be attributed to Ca-P?

**Answer:** This 12-18% of total P (Table 1) was the residual P after DCB and subsequently NaOH-Na<sub>2</sub>EDTA treatments. Because there were still Ca-minerals remaining in larger-sized soil fractions, the P-Ca minerals should potential have contributed to this 12-18% of total P. However, as discussed in the text, almost all the Ca-minerals were dissolved after these treatments in small soil fractions. The

majority of this P should be derived from other minerals, e.g. Fe bearing clay minerals. In our currently published work (Jiang et al., 2015), we found that some P in nanoparticles of this soil was most likely bound to Fe bearing clay minerals after DCB treatment according to the FFF (field flow fractionation)-ICP-MS (inductively coupled plasma mass spectrometer) and TEM (Transmission electron microscopy) results.

4. P9893, L22-24: The conclusion should better be more conservative. The released P after treatment with oxalate or DCB was not necessarily attached to the surface of oxides. It might be associated with other agents attached (e.g. Ca, see Table S3), or simply detached from clay surfaces. As mentioned above, the sequential extraction method could be problematic. The acidic oxalate and DCB could mobilize P from soil minerals, and thus the difference between PN and PN-I (or PN-II) was possibly not equal to Fe/Al-bound P in the NaOH-EDTA extracts.

**Answer:** We agree the conclusion should be more conservative. It is unavoidable that such chemical treatments (i.e. oxalate and DCB) could not exactly target for P bound to Fe oxides but also some other minerals. However, as discussed already, the amount of P-Ca minerals was very small in our soil. The majority of released P was still bound to Fe oxides.

**Revised in the text as follows:**

P9893, L22: The majority of NaOH-Na<sub>2</sub>EDTA extractable P (Pi and Po) was probably attached to the surface of amorphous Fe oxides and Al oxides, or alternatively inside of the Al oxides.

5. Table1: Data presented here probably refer to the results calculated by Equ (1-6). Perhaps it is better to explain this in the title of the table.

**Answer:** Yes, we have **revised in the text as follows:**

Table 1. NaOH-Na<sub>2</sub>EDTA 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 matter as shown in Eqs.1-6.

6. Figure 3: I am still puzzled by the figure. Were NaOH-P and residual P fractionated into different forms of P like orthophosphate and monoester? If so, the present figure might lead readers to misunderstand NaOH-P and residual P as counterparts of orthophosphate, monoester-P, etc.

**Answer:** The different P forms (i.e., orthophosphate, P-monoesters, P-diesters, Pyrophosphate and phosphonate) in this figure were from the NaOH-Na<sub>2</sub>EDTA extracts. For clarification, we tried to better **explain this in the title of Figure 3 as follows:**

Figure 3. NaOH-Na<sub>2</sub>EDTA extractable P, residual P content, and phosphorus forms / contents (mg kg<sup>-1</sup>) from the NaOH-Na<sub>2</sub>EDTA extracts in different aggregate-sized fractions as identified by solution phosphorus-31 nuclear magnetic resonance spectroscopy. The varying chemical P contents were de-

terminated by multiplying the proportion of spectral area by total concentration of the NaOH-Na<sub>2</sub>EDTA extractable P.

**The question from the associate editor:**

Additionally, please check the Fig 3: the P content in all particle size fractions is much higher than in Bulk soil (except sand). Because your soil does not consist to > 90% from sand (than it would be not a Luvisol), such P contents in the fractions or in the Bulk soil are not possible.

**Answer:** Our soil belongs to Luvisol with 15.7% sand, 65.6% silt and 19% clay (Jiang et al., 2014) determined by classical soil fractionation. However, the fractionation method used in our work to prepare the different aggregated-sized fractions (Sequaris and Lewandowski, 2003) is different from the typical soil fractionation method and explicitly avoids the destruction of small aggregates. The proportion of sand-sized (>20 µm instead of >63 µm), silt-sized (2-20 µm instead of 2-63 µm) and clay (<2 µm) fractions in our soil is 82.3%, 12.9% and 4.0% of total soil as mentioned in the manuscript (P9883 Lines 19-23), respectively. Thus the amount of sand-sized soil fraction in our soil is quite high. That is why P content in all particle size fractions is much higher than in bulk soil, except in the sand-sized fraction.

References

- Forsmann, D.M., and C. Kjaergaard. 2014. Phosphorus release from anaerobic peat soils during convective discharge — Effect of soil Fe : P molar ratio and preferential flow. *Geoderma* 223–225: 21-32. doi:<http://dx.doi.org/10.1016/j.geoderma.2014.01.025>.
- Haygarth, P.M., G.S. Bilotta, R. Bol, R. E. Brazier, P. J. Butler, J. Freer, L. J. Gimbert, S. J. Granger, T. Krueger, C. J. A. Macleod, P. Naden, G. Old, J. N. Quinton, B. Smith and P. Worsfold. 2006. Processes affecting transfer of sediment and colloids, with associated phosphorus, from intensively farmed grasslands: an overview of key issues. *Hydrol. Process.* 20: 4407-4413.
- Hedley, M. J., Stewart, J. W. B., and Chauhan, B. S.: Changes in inorganic and organic soil phosphorus fractions induced by cultivation practices and by laboratory incubations, *Soil Sci. Soc. Am. J.*, 46, 970–976, 1982.
- Jiang, C., J.-M. Séquaris, A. Wacha, A. Bóta, H. Vereecken, and E. Klumpp. 2014. Effect of metal oxide on surface area and pore size of water-dispersible colloids from three German silt loam topsoils. *Geoderma*. p. 260-270.
- Jiang, X., R. Bol., V. Nischwitz., N. Siebers, S. Willbold, H. Vereecken, W. Amelung, and E. Klumpp. 2015. Phosphorus containing water dispersible nanoparticles in arable soil. *J. Environ. Qual.*,doi:[10.2134/jeq2015.02.0085](https://doi.org/10.2134/jeq2015.02.0085).

Rick, A.R., and Y. Arai. 2011. Role of natural nanoparticles in phosphorus transport processes in ultisols *Soil Sci. Soc. Am. J.* 75: 335-347. doi:10.2136/sssaj2010.0124nps.

Séquaris, J.M., and H. Lewandowski. 2003. Physicochemical characterization of potential colloids from agricultural topsoils. *Colloids Surf. A: Physicochem. Eng. Asp.* 217: 93-99. doi:[http://dx.doi.org/10.1016/S0927-7757\(02\)00563-0](http://dx.doi.org/10.1016/S0927-7757(02)00563-0)