

## ***Interactive comment on “Colloid-bound and dissolved phosphorus species in topsoil water extracts along a grassland” by Xiaoqian Jiang et al.***

### **Anonymous Referee #2**

Received and published: 15 November 2016

The paper presents interesting and novel data as regards the speciation of P in soil extracts, based on results from three soil samples differing mainly in water saturation conditions. Several innovative techniques are used to characterize the distribution of P species among dissolved and colloidal phases, and most notably the  $^{31}\text{P}$ -NMR techniques which provide access to a great number of P organic species. In this respect, the paper is a valuable piece of work as it is the first time that such an inventory of inorganic and organic species is provided for soil extracts, including the colloidal and true dissolved phase. The speciation of P in soil solutions and the way this speciation may vary according to soil properties is clearly of broad international interest, as is of broad international interest the development and application of innovative and ac-

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curate analytical techniques to fully characterize the diversity of P forms both in soils and soil solutions. However, I found several weaknesses to the paper that should be addressed and at least partly corrected before its publication in Biogeosciences. The most important are summarized in the following general and more specific comments:

General comments :

Comment 1 : The paper does not give any information about the agricultural use of the sampled grassland sites. Are these sites used for cattle breeding. Do they receive P-containing manure? Are they, or were they, subject to inorganic P fertilization? Were the land use or P fertilization, if any, similar in the cambisol and stagnosol plots? The authors should provide information on those different points.

Comment 2 : Could the authors specify why they use Mill-Q and a pH set at 5.5 in their extraction experiments. Although I can understand that the aim of their study is to compare the behavior of different soils to colloidal extraction and not the impact of the nature of a given extractant and a given pH, I know from my own experience that the nature of the solution and the pH used during colloidal extraction may have great impacts on the composition of the colloids extracted and on the partitioning of P between the colloidal and dissolved phases. Therefore, a justification of the choices made regarding the extracting solution is necessary.

Comment 3 : Too little information is given with respect to the ultrafiltration procedure used for preparing the  $^{31}\text{P}$ -NMR spectroscopy samples. First, 600 ml is quite a large volume to ultrafiltrate. Most probably, more than one filter had to be used to ultrafiltrate such big volumes. Could the number of filters used be given? Second, of which material are the filters made of? Are they made of cellulose acetate and if so what are their organic (and phosphorus) blank(s) and the blanks of the overall ultrafiltration procedure?

Comment 4 : Could the authors explain why, in parallel of the ultrafiltration procedure they used to prepare  $^{31}\text{P}$ -NMR spectroscopy samples, they also mixed soil water ex-

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tracts with 0.025M NaOH and 0.05 M Na<sub>2</sub>EDTA solution. Was their purpose in doing so to compare these two preparation techniques to check if they were going to give similar (or different) results? Was there a risk that the ultrafiltration technique on its own could fail to give reliable results ?

Comment 5 : The authors should add a size scale in the top diagrams of Fig. 1, in which the OC and UV peaks are portrayed. Anyhow, the first peak on the left of these diagrams seems to occur for a particle size slightly higher than 20. Why then quote in the text (line 181) that the particles corresponding to this first peak are <20 nm in size. Why then also consider in line 186 that only two fractions are higher in particle size than 20 nm? If the same size scale as that shown in the bottom diagrams in Fig. 1 is transposed to the top ones, all the three OC and UV peaks occurring in the latter seem to be for particles of > 20 nm size. Therefore, I am not convinced in the current state of Fig. 1 that the first peak recorded in the analyzed samples correspond to particles below 20 nm.

Comment 6 : In all the top diagrams of Fig. 1 there is a shift between OC and UV peaks, the UV peaks occurring systematically at a lower elution time than the OC ones. What is the reason for this shift?

Comment 7 : I have problems with the idea promoted by the authors that the OC concentration of the first particle fraction would increase from samples 1 to 3. Indeed, the information provided by the top diagrams in Fig. 1 to which they refer lines 188 to 190 are intensities not concentrations. Would it not be equally possible that the OC concentration of the <20 nm particles is in fact constant in the three samples, but that the concentration of this size class of particles in the water extracts increases from sample 1 to 3 ?

Comment 8 : The authors argue that the occurrence of distinct Al and Fe peaks in the first size fraction of the Stagnosol could suggest that oxides are more readily involved in nano-sized soil particles under stagnant soil conditions. I find this interpretation sur-

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prising as stagnant conditions are expected to limit the stability of iron oxides. Should it be possible that Fe and Al peaks found in this fraction correspond not to oxides but to Fe and Al ions adsorbed onto, or complexed by organic matter? What proves that the Fe found in this fraction is Fe<sup>3+</sup> and not Fe<sup>2+</sup>. The authors should consider alternative hypotheses of that type here as they do not provide any direct (e.g. spectroscopic) evidence of the presence of Al and Fe oxides in their samples?

Comment 9 : The concentrations quoted in Table S1 are in mg/kg. How these concentrations were calculated ? To what refer  $\hat{A}$  kg  $\hat{A}$  in this table? To the amount of solution in which the particles are eluted ? To something else ? Please, give precision on that.

Comment 10 : The mechanism promoted by the author of a higher OC concentration in the first peak of the Stagnosol sample due to the release of OC from the larger colloidal fraction because of reductive dissolution of the iron oxides present in this fraction is plausible. However, the AF4 experiments were not performed under reducing conditions. Although this mechanism could probably occur in the true soil solutions under the water saturated conditions that usually prevail in the field in Stagnosol-type soils, I am sceptical about the fact that it could developed in the present case, as the experiments were apparently performed under aerobic conditions.

Comment 11 : The hypothesis brought about by the authors that the oxygen limitation and reduction regime of the Stagnosol would favor the dissolution of Fe oxides in Stagnosol colloids is not entirely convincing to me. Indeed, Table 2 shows higher Fe concentrations in S3 than in S1 sample colloids. Could it be possible that the Fe found in S3 colloids is in part Fe<sup>2+</sup> and not Fe oxides?

Comment 12 : I agree with the authors that the dissolution of Fe oxides in the Stagnosol could release Po in the soil solution, but the fate of this Po puzzle me. It seems implicit for the authors that this Po should be readily mineralized and transformed into Pi. However, Stagnosol being waterlogged soils, we expect a reduction of the microbial

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activity in these soils and thus of the mineralization rate of Po. I am also not convinced by the hypothesis promoted by the authors on line 276 that the formation of OC-Fe/Al-PO<sub>4</sub><sup>3-</sup> should be favored in these soils. Why should it be so, particularly if iron oxides are expected to be dissolved due to the reducing conditions that characterized Stagnosol as suggested by the authors earlier in the paper. I see a lot of contradictions and approximations here.

Comment 13 : I have difficulties to understand the conclusion of section 3.3 stating that “pedogenesis also affects the redistribution of different P species among different P colloids and the electrolyte phase”. I do not see in which respects the results presented in this study allow to put constraints on the pedogenesis of the studied soils and on the impact of this pedogenesis on the present P speciation results. In my opinion, other variables like land use, anthropogenic P inputs or the methodology used to extract colloids are likely to be as important as, and maybe more important than the pedogenetical history of soils in creating difference in P speciation among soils.

Comment 14: Why pyrophosphate of microbial origin should it be more abundant in Stagnosol than Cambisol, considering that the microbial activity should be enhanced in the more oxygenated Cambisol? I do not pick up authors’ arguments here.

Other, more specific comments :

Line 85 : How an organic carbon detector works. Could you specify or quote a reference in which the principle of the method is described.

Line 116 : Replace “ ; “ by “ . “

Line 119 : Replace “ ... for monitoring of Fe, aluminum (Al)... “ by “... for monitoring of iron (Fe), aluminum (Al)... “

Line 132-133. What do the authors mean by “the nano-sized colloidal particles after AF4 separation were smaller than < 20 nm”? According to Fig. 1, the colloidal particles recovered by the AF4 indeed ranged in size from 20 to 435 nm with peaks at 204 and

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435 nm ! Do you mean that the AF4 technique separated all colloids with a nominal size > 20 nm ?

Line 150. I suggest the authors start a new paragraph from “Solution 31P-NMR...” as they change of topics from that point, shifting from the description of how the samples were prepared to how the NMR spectra were obtained.

Line 169 : Replace “. . .test to test for identify. . .” by “. . .test to identify. . .”

Lines 183-184 : What more direct evidence have the authors that the third peaks in the fractograms could correspond to particle previously attached to the membrane during focus time ?

Lines 195-196 : Is the claim made here that the nano-sized colloids from the cambisol contain P, Fe and Al in lower (negligible) concentrations compared to the same fraction in the stagnosol so true ? Indeed, I calculated the OC/Al and OC/Fe ratios of both soil types and they are not so different : 58 and 93 for Al, and 74 and 105 for Fe. Everything looks like if the nano-sized colloid fractions were equivalent in composition in both soil types, the fraction being simply more concentrated in the stagnosol compared to the cambisol.

Line 202. Replace “Stagnols” by “Stagnosol” Line 205 : I agree that the UV signal is consistent with the OC peak distribution. However, I once again wonder about the reason why the UV peaks are shifted to somewhat lower elution time compared to the OC ones. Could the authors comment on that and provide explanation for this shift ?

Line 208-209 : I agree that the second-size fraction of the stagnic Cambisol present the highest Fe, A, Si and P concentrations of the three analyzed second size-fractions. Considering however ratios of OC/Al, OC/Fe, and OC/P

Line 218 : It is not clear to me why OC sorbed on iron oxides materials should be of nanometric size? Could the authors cite papers which prove this to be so.

Lines 237-238 : “This implies that the assignment of stagnic properties is related to

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its behavior in the colloidal particles and dissolved fraction". I find this sentence badly constructed. Do the authors mean that soils are classified according to the composition of the colloids they can release? I cannot believe that.

Line 243 (as regards Table 2): I wonder why TOC concentrations were not measured in the <300 KDa and < 5KDa fractions. Could the authors give an explanation for that? Lines 280-281. I do not see how Fig. 1 can be used to infer the proportion of clay-Fe oxides-OC-P associations in the 300 KDa-450 nm fractions. Could you explain?

Line 300: The statement made here that the majority of P in the <3KDa fraction of the Cambisol was  $P_o$  is quite "funny" in the light of what is said page 11 about the fact that the absence of NaOH-Na<sub>2</sub>EDTA most of the  $P_i$  is removed from the solution through sorption on the soil minerals. Quite clearly, the data cannot be used to assess the proportions of  $P_i$  and  $P_o$  as the methodology used biased these proportion. They just can be used to inventory the organic species present, which is already an innovative and very important objective.

Line 348-352. What direct proof do the authors have that pyrophosphates is bound to Fe oxides? Could and alternative interpretation be that orthophosphates form ternary complexes with  $Fe^{3+}$  or  $Fe^{2+}$  ions themselves bound to OC?

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