

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

### **Anonymous Referee #1**

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The manuscript discusses P speciation differences in soil extracts across a landscape gradient with varying soil type, elevation and water content. A number of interesting and quite novel hyphenated techniques were used, which, to the best of my knowledge, have not previously been employed together in such a manner. The ability to differentiate between P species and elemental associations in different colloidal size fractions is technically impressive; particularly as anything less than 0.45 microns in size is very often operationally defined simply as “aqueous P” elsewhere in the literature. The manuscript is easy to follow, well written and logically structured. The mobility and bioavailability of colloidal vs aqueous P is also certainly of broad international interest. However, the research does appear to be quite exploratory and descriptive in

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nature rather than hypothesis driven (no hypothesis is stated). The methodology and resulting dataset is very interesting but in my opinion the key conclusion, that soil type and water content affect P speciation in colloidal and aqueous fractions is relatively weak given the variety and complexity of the analytical techniques used. There is also some confusion as to the interpretation and relevance of the results with respect to natural drivers of P mobilisation e.g. iron redox cycling and leaching with pore water transport, due to sample handling which did not preserve field redox conditions. I feel that the manuscript is of interest to a broad audience and suitable for publication in biogeosciences, however, I think that parts of the manuscript, including the abstract and concluding paragraph, should be carefully and substantially revised to more clearly link the proficient analytical work to the applicability of the results.

Specific comments:

The extract used (MQ water) is quite harsh compared to natural waters such as rain water or pore water and would result in significantly greater release of P than that possible by contact with water in a natural environment, due to desorption and dissolution of poorly crystalline authigenic mineral phases. Living cells within the soil would also certainly undergo significant osmotic stress likely resulting in osmotic rupture and release organic and inorganic P found in intracellular components. The potential ramifications of these effects on the results should be clearly stated and discussed, as there are clearly implications as to the origin and mobility of identified P species in a natural context. Are the species identified in the size fractions indicated present in the natural soil or a result of alterations during the extraction procedure?

I have concerns with the way in which the results are framed within the context of oxygen availability and iron redox cycling. The first sentence of the abstract “Stagnant water conditions may release phosphorus (P) in soil solution that was formerly bound to Fe oxides” implies that the P release investigated is due to reductive dissolution of ferric oxides in the absence of oxygen. Undoubtedly, oxygen availability differences between the soil samples selected resulted in differences to iron speciation, particle size,

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organic carbon content and P speciation. The handling of the soil samples in the laboratory does not appear to have preserved the field redox conditions and likely resulted in considerable oxidation of reduced iron species during processing, particularly in the sampled Stagnosols. Oxidation of aqueous  $\text{Fe}^{2+}$  and colloidal ferrous particles can be very fast (seconds to minutes) therefore the extraction in presumably oxic MQ water for 18 hours almost certainly changed the composition and speciation of the colloids, which were later characterized. Although the importance of Fe oxidation and reduction processes on P speciation generally is highlighted in the manuscript, the impact of these processes during sample processing and on the final dataset is not discussed. The differences between the three soil types are convincing but I question whether the analyzed species and size fractions are representative of the soils themselves or differences in response to the extraction procedure based on different initial soil redox conditions. Extracting soils in MQ water, under oxic conditions, is not representative of P released during reductive dissolution, as implied in the abstract and in fact would result in the opposite process (oxidative precipitation of Fe hydroxides).

89. Inclusion of a site map would be useful here in the main manuscript rather than in the supporting information. A scale should also be included to establish the distance between the sampling sites.

101. How long were the samples stored at 50C? Long storage times prior to extraction and preservation could result in significant speciation changes. It is impossible to evaluate the importance of these changes if the storage time is not provided.

112. Please list the material of the 0.45 micron membranes.

119. There is no justification for the choice of analytes - Fe, Al, Si and Ca? The rationale for this may not be clear to some readers.

118. What were the limits of detection and precision for the analytes measured by ICP-MS?

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146. Was neutralization of the NaOH-Na<sub>2</sub>EDTA extracts with HCl performed to avoid break down of polyphosphate species? Perhaps the rationale for not doing so could be included here?

169 – “for identify” I believe this should read “to test for significant differences” or “to identify significant differences”.

170 – Which tests were employed to determine distribution normality?

178 – Analysis of Ca is not previously mentioned. Either calcium analysis should be included in the methods section, and the statement clarified i.e. what constitutes a low concentration? Or this statement could be removed here.

202 – The effect of pH, and differences between the sampled soils should probably be discussed here.

216 – This discussion needs to take into account the effect of the reactions that likely occurred during the oxic extraction procedure.

280 – clay-Fe oxides is an interpretation based on elemental analyses, it is not certain that the colloids identified contain clay minerals from the analyses conducted.

Table 1 – Dissolved or total organic carbon? If this refers to the bulk soil it is not dissolved organic carbon but total organic carbon? The table caption refers to uppercase letters but the letters indicating significant differences are lower case.

Table 2 – To help distinguish between bulk solid analyses and analysis of water extracts I suggest using mg kg<sup>-1</sup> for bulk soil analysis and mg L<sup>-1</sup> for water analysis. Also – TOC for bulk solid analysis and DOC for aqueous and colloidal analyses.

Table 3 – The formatting and alignment issues make this quite hard to read. “below detection limit” is noted but the detection limit is not defined?

Figure 1 – This figure is great, it really nicely shows the size fractions and their elemental compositions.

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