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# *Interactive comment on* "Sediment phosphorus speciation and mobility under dynamic redox conditions" *by* Chris T. Parsons et al.

**Anonymous Referee #1**

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GENERAL COMMENTS:

The study by Parsons et al. aims at investigating the effect of the redox potential on sediment phosphorus speciation and resulting changes in soluble phosphate. For mimicking fluctuating redox conditions, the study employs a bioreactor experiment with repeated cycles of anoxia/re-oxygenation by purging with suitable gas mixtures. The study confirms that anoxic conditions result in reductive dissolution of iron(oxyhydr)oxides in the sediment, which in turn results in a subsequent release of iron-bound phosphorus. However, the general approach as well as the finding of an increase in soluble phosphate and decrease in iron-bound P upon reduction of Fe(III) is far from being novel. The concept that the release of phosphorus from anoxic sediment can be attributed to the reduction of a FeOOH-phosphate complex can be traced back to a proposal by Einsele, which was later adapted by Mortimer (Einsele, 1936;

Mortimer 1941, 1942). Hence, the interesting aspect of this study is rather to try to elucidate the redistribution of released P between other P-bearing phases. The main point of criticism of this manuscript is that the novel aspect is not sufficiently emphasized - and, more importantly, not sufficiently discussed in detail.

Another example for the lack of clarity regarding the main message is the listing of the particular aims in the introduction. According to this list, the aims focus on determining (i) polyphosphate cycling; (ii) accumulation of autochthonous $P_o$ species; and (iii) rates of $P_o$ degradation. However, (i) data regarding the aims are visually present in one of six figures (no tables in the manuscript); (ii) the term 'polyphosphate' does not appear in any of the figures; (iii) polyphosphate accumulation was not confirmed and, more importantly, (iv) determining the accumulation of autochthonous $P_o$ species was not possible because "P contribution from individual algal additions ( 1.5 $\mu$mol P g-1) was relatively small compared to the total P mass in the reactor (61 $\mu$mol P g-1) and within the margin of analytical error associated with solid extractions" (p 17, l 373-375)!

Hence, the experimental design used did not match the research aim. Further, fractions other than $P_{Fe}$ which were found to display clear and significant trends over time were $P_{Ex}$ and $P_{Hum}$. Although it was not listed as being a focus of the study presented, the manuscript in fact focuses on these two fractions (see e.g. figures 4 and 5). However, the discussion fails to substantially address the chemical composition and nature of these two fractions and fails to describe related reaction mechanisms.

In view of the above and other significant shortcomings including weaknesses of the manuscript structure/organization, writing style, documentation and technical aspects (see e.g. the first comment below), I would not recommend Biogeosciences to publish the manuscript.

SPECIFIC COMMENTS:

1) To me the description of the operationally defined fractions and corresponding extraction conditions is insufficient and misleading. For example, the abbreviation $P_{CFA}$

is used for "$CaCO_3$ bound P“ (p. 10, lines 198-203) determined using the SEDEX acetate buffer. CFA actually stands for carbonate-fluorapatite. The SEDEX method focuses on the determination of carbonate-fluorapatite. However, the term ’carbonate-fluorapatite’ is not mentioned anywhere in the manuscript. Why did the authors not use the original fraction descriptions of the SEDEX protocol? Do the authors assume that $CaCO_3$ bound P plays a significant role at the field site or under the experimental conditions? There may be sufficient calcite, however the $P_{CFA}$ fraction remains constant throughout the experiment despite large changes in $P_{Aq}$ (Fig. 4; even detrital apatite shows more variability). This does not point to $CaCO_3$ bound P, this points to actual calcium phosphates because of their slow precipitation/dissolution kinetics under the experimental conditions.

2) Some available data sets are not presented / not discussed although these data sets could be useful to the reader. For example, the authors "postulate that solubility changes to humified DOC are driven by minor (+/- 0.3) pH changes between oxic an anoxic conditions..." yet recorded changes in pH are not presented (p. 16, lines 339-342). Another example are the collected ICP-OES data and the ion chromatography data. The majority of these data is not shown. Calcium and magnesium, for example, would be interesting ions for estimating the saturation state with respect to specific P species (together with the pH) or the inhibition of nucleation of P mineral phases.

3) The ionic strength together with the pH are essential variables in determining saturation indices and adsorption mechanisms. The ionic strength is mentioned once in the manuscript, but corresponding data are not shown (p. 7, lines 130-131: "Surface water was used, rather than distilled water, to provide background ionic strength and avoid osmotic shock to the microbial community.“). For the reader, the only possibility to gather information on the ionic strength are the terms "freshwater sediment“ and "freshwater marsh“ - which is insufficient.

4) In a broader sense, the study is intended to provide guidance in dealing with increased P loadings or for the "management of WWTP effluent“ (e.g. p. 22-23). The

experimental design has several limitations with resulting limitations in its applicability to field conditions, which include the given temperature (25°C) and light conditions (dark) and the sediment pH (7.2-7.5) and the ionic strength (freshwater), only to name a few. Such limitations should be mentioned if management recommendations are given.

TECHNICAL ISSUES:

line 64: Which phases are meant here in detail? ("these phases“ in the middle of the introduction seems to refer back to a sentence in the abstract)

lines 70-72: I suggest to explain the coupling of these biogeochemical cycles because they are suggested "to play important and complex roles in phosphorus mobility“.

line 90: missing comma; I would avoid brackets inside brackets here – and at other places in the manuscript.

line 91: I suggest citing the original source of the methods used, e.g. Ruttenberg.

lines 103-104: There are nested sentences which can be avoided. See also e.g. lines 107-110 and lines 166-169.

lines 119-121: Why aren’t the analyzed elements listed in full?

lines 123-124: Which software was used for phase identification?

lines 177-180: ’Method detection limit’ has been abbreviated before (e.g. line 174)

line 206: "Li et (Li et al., 2015) al“

line 252: Grammar

lines 379-381 and lines 392-395: Vague and poor sentences

line 396: Unclear structure of headings (e.g. this is placed after "Fe:P ratios“. To me, this belongs to "sequential chemical extractions and solid phase P partitioning“)

line 407-410: Vague sentence; in what respect "environmentally relevant“?

Section "hydrolytic enzyme activities“: This section deals with Figure 6. However, a reference to Figure 6 does not appear anywhere in this section. Figure 6 is split into a and b. It may make sense to include a,b,... in references.

FIGURE 2: It may make sense to label the depth interval used for the bioreactor experiment in b) and to be more consistent in using labels in general (e.g. "Figure 1: A)“, "Figure 2: a)“

FIGURE 3: Inconsistent labelling; some axis labels shown some not (e.g. Mn)

FIGURE 4: Did the authors analyze the 'control composition' for the fraction composition before equilibration?

FIGURE 4: Inconsistent axis labels for $\mathrm{P}_{Aq}$

FIGURE 6: Font size is too small in A); missing label for polyphosphate

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