

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

**Anonymous Referee #2**

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Parsons et al. studied speciation and mobilization of sediment P under fluctuating redox conditions using a bioreactor for the duration of 72 days. They reported that the mobility of P was controlled mainly by iron oxides and release of P to the aqueous phase occurred after completion of nitrate depletion. Remobilization of P into aquatic phase was limited since higher proportion of released P at anoxic conditions re-distributed among different P fractions. Mineralization of organic P was observed in the oxic condition where the activity of phosphomonoesterases was ~37% higher than that in the anoxic condition. Accumulation of polyphosphate was not observed.

I believe their study is valuable for understanding how the short-term fluctuating redox condition affects the P sorption/release mechanisms in relation to other chemical/physical elements, such as pH, Fe, Mn, C, N and S. The manuscript is well written, however, their aims of study (Line 79-87) don't match their major findings. Even though

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their aims were focusing on organic P cycling, their main findings were not likely related to organic P cycling, but the inorganic P sorption/desorption mechanisms related to redox chemistry. Their implications didn't include anything related to organic P cycling. Besides, I am not certain if their experimental design (individual algal additions) was reasonable to represent their study site for organic P cycling. Therefore, I recommend that the aims of the study be re-written. The paper is likely to be publishable, but requires some clarification and more detailed explanations in some parts.

A clarification about the extra step (1 M sodium bicarbonate, NaHCO<sub>3</sub>) the authors added to the SEDEX referred to the paper published by Baldwin (Line 204) is required since this P fraction is the most important fraction in their study (Line 413). The authors indicated that this extra step differentiates between P associated with metal-OM bridging complexes and truly reducible oxide associated P (Line 204). The authors called the P fraction extracted with the sodium bicarbonate as “Humic bound P, PHUM” (Line 208). However, the target P phase extracted with the sodium bicarbonate was not shown in the Baldwin paper. Baldwin observed that sodium carbonate removed highly colored extract, which indicates removal of part of OM. Thus, he assumed the sodium bicarbonate may have removed some OM associated P, however, he didn't mention anything about P associated with metal-OM bridging complexes (HMEP). Baldwin's sediment samples were rich in OM, whereas the sediment sample the authors used in their experiment was not rich in OM. If the authors observed colored extract as Baldwin did, I suggest that they mention it in the manuscript. I am not certain if it is applicable to express the P phase extracted by the sodium bicarbonate as “Humic bound P = HMEP” also due to the following reasons; 1) Li et al. (2015) reported that HMEP could be more recalcitrant than pure mineral Fe-oxides. If so, it is not likely extracted by the sodium bicarbonate. 2) Gerke (2010) reported that HMEP cannot be differentiated by fractionation methods, however, the formation of HMEP could be confirmed by measuring Fe content in the materials; comparison of pyroP extractable [Fe] and acid oxalate extractable [Fe] by McKegue (1967). These measurements may strengthen the authors statement. 3) It is well-known that in the Hedley's sequential fractionation,

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0.5 M NaHCO<sub>3</sub> (pH 8.5, 16 h shaking time) extracts some organic P (Hedley, White, & Nye, 1982). Since the sodium bicarbonate the authors used (1.0 M NaHCO<sub>3</sub>) is similar to the Hedley's extractant, it should extract some organic P as well as organic matter (OM), if the shaken time was long enough (the authors didn't show either the shaking time or pH of the extractant). Therefore, OM associated P may be organic P directly associated with OM. 4) The sodium bicarbonate extractant is also similar to the extractant used in the Olsen P test (0.5 M NaHCO<sub>3</sub>, pH 8.5, 30 min shaking time). The Olsen P extractant should extract labile Mg-Ps and Ca-Ps, such as monetite and brushite (Olsen, Cole, & Watanabe, 1954). Since the sediment sample used in the authors experiment had relatively high proportions of dolomite (8%) and calcite (19%), Ca bound P was expected to be a major form of P. However, PCFA was only 15% of total P present in their sample. Therefore, I assume PHUM possibly includes labile Ca-P minerals. It would be useful to measure the concentration of Ca and Fe in each extract to confirm this. 5) Even though the sorption sites in clays decrease with increasing pH, P sorption onto illite would occur at neutral pH (Manning & Goldberg, 1996). If pH goes toward alkalinity, P adsorbed by illite would be desorbed (Manning & Goldberg, 1996). The sediment sample used in the authors experiment was relatively high in illite (30%), therefore PHUM possibly includes P adsorbed by illite. I assume that the fraction most likely included various inorganic P forms including P associated Ca, Mg and/or clays as well as OM rather than HMEP. However, if the authors are able to explain/show that the bicarbonate extractant is able to remove HMEP, I think this step is crucial in the SEDEX and this should be one of their remarkable findings.

Even though the authors mentioned Fe/Mn-oxides in their abstract, discussion was made only for Fe-oxides but nothing for Mn-oxides.

The authors characterized forms of organic P in the sediment sample by solution <sup>31</sup>P NMR spectroscopy and analyze the rate of mineralization of organic P by various enzymatic approaches. The proportion of organic P in the sediment was found to be ~9 to 16 % with the increasing order of; monoesters > diesters > polyphosphate, which

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was equivalent of the enzyme activities. The accumulation of polyphosphate was not observed in their experiment settings. (1) Accumulation of polyphosphate or/and pyrophosphate is known to occur as a luxury uptake in algae and microbes (Hupfer, Gloess, & Grossart, 2007) and is often observed in the surface sediments (Giles, Cade-Menun, & Hill, 2011; Hupfer et al., 2007; Jorgensen, Inglett, Jensen, Reitzel, & Reddy, 2015; Li et al., 2015), however, the accumulation of poly- or/and pyrophosphate was not observed in their experiment. The authors commented this was because the experimental condition was not set in excess P (Line 373), despite the actual sampling site being consistently high in primary productivity (Line 369). I am not certain if the conclusion of the polyphosphate cycle in their experimental setting was valid. (2) Some peaks, especially at chemical shifts assigned as alpha- and beta-glycerophosphates, appearing in the monoester regions often belong to phosphodiester (Doolette, Smernik, & Dougherty, 2009; Jorgensen et al., 2015; Paraskova et al., 2014; Turner, Mahieu, & Condon, 2003). It is important to consider re-calculating these peaks when comparing the ratio of monoesters to diesters, if the authors didn't do it. (3) The recovery rate of total P by the NaOH-EDTA was not shown in the manuscript.

Below are some minor comments/suggestions:

Line 153: An explanation of the reason why the setting (i.e. temperature at 25 C and the dark setting) was chosen should be noted.

Line 192-194: I suggest moving these sentences to introduction or discussion sections.

Line 198: It is not clear which sediment profile was used for the SEDEX (I imagine it was the surface sediment; 0-4 cm). The number of samples used for the SEDEX should be noted. It would be useful to include a table showing a brief method (i.e. each extractant, pH, shaking time, number of wash, etc.) for readers, since the SEDEX method used in their experiment was modified.

Tables for basic physical/chemical characteristics of (1) sediment sample, such as pH, texture, TP, NaOH-EDTA extractable P, OM, N and other elements (i.e. Ca, Fe, Al, Mn,

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etc.) and (2) surface water sample such as pH and chemical contents would be useful to readers.

Line 209: PCFA should be expressed as Ca-bound P since the fraction includes not only CaCO<sub>3</sub>-associated P, but authigenic carbonate fluorapatite and biogenic apatite. Ruttenberg (1992) reported that the first step (MgCl<sub>2</sub>) can extract ~25% of biogenic CaCO<sub>3</sub> (i.e. loosely sorbed P onto CaCO<sub>3</sub>).

Line 339: The pH data obtained during the experiment during anoxic and oxic states would be useful for readers.

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