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

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Response to Anonymous Referee #1 regarding their review of "Sediment phosphorus speciation and mobility under dynamic redox conditions", which was published on February 14th 2017

We thank the referee for her/his thorough and critical review of our manuscript. The comments highlight the need to improve the clarity of the manuscript in places, particularly with respect to emphasizing the key findings, novelty and importance of our work. We agree with the majority of the reviewer's general and specific technical comments and suggestions, and are able to address them as detailed below. For those comments with which we disagree, in particular regarding differences between experimental and field conditions, we provide more supporting information about the in situ conditions at

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the sampling site.

General comments:

". . .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 (1941, 1942). Hence, the interesting aspect of this study is rather to try and elucidate the redistribution of released P between other P-bearing phases."

We agree that the finding of aqueous phosphorus release from sediments under anoxic conditions is in itself well established. We acknowledge this at the beginning of the manuscript, on lines 60-66, and indeed, cite Mortimer (1941) and other seminal works within this section. The novelty and relevance of the current study is, we believe, more extensive than highlighted by the reviewer. Specifically, the novelty of our work includes the following.

1. Acquisition of a comprehensive data set that describes the fully mass balanced redistribution of P between different solid and aqueous sediment pools as a function of changes in the redox state of the system. Many previous studies have shown aqueous P release from sediments under anoxic conditions and some have established the origin of the aqueous P, e.g. organic necromass (Joshi et al., 2015), microbial polyphosphates (Hupfer et al., 2007), or mineral bound P (Petticrew and Arocena, 2001). However, no previous studies have quantitatively investigated the redistribution of P among the mineral and organic fractions of a sediment during redox fluctuations. Most importantly, we demonstrate that only a very small proportion (4.5%) of P associated with reducible iron(III) (oxy)hydroxides actually ends up in the aqueous phase upon reductive dissolution of the iron(III) (oxy)hydroxides, even in carbonate-buffered sediments under slightly alkaline pH where P sorption is considered to be relatively

ineffective. Further, we demonstrate that polyphosphate accumulation and release are not major P cycling processes within this freshwater sediment (as reported previously in other redox oscillating environments). 2. Use of a controlled reactor system to simulate repetitive cycling between oxic and anoxic conditions. Oscillating fluctuations of redox conditions are ubiquitous in shallow sediments but are rarely investigated in laboratory experiments. Many experiments simulate a single oxidation or reduction event (e.g., Matisoff et al., 2016). To the best of our knowledge, the effects of successive oxic-anoxic cycles on P speciation, mineral association and mobility in freshwater sediments have not previously been investigated. The approach presented offers the possibility to determine cumulative effects of redox cycles, and to establish which (im)mobilisation processes are reversible. 3. Delineation of the interplay between redox conditions, mineralogical changes and activities of hydrolytic phosphatases. We demonstrate, for the first time, that phosphatase activities vary systematically with redox conditions, with higher activities occurring under oxidising conditions and lower activities occurring under reducing conditions. This trend appears to be specific to phosphatase enzymes: a hydrolytic enzyme of the cellulose degradation pathway shows the exact opposite trend. We propose that this observation reflects changes in enzyme production by the microbial community in response to phosphate scarcity during oxic conditions, because of sorption of phosphate to iron(III) (oxy)hydroxide minerals.

We agree that the above key points need to be more forcefully stated in the revised version of the manuscript.

“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 Po species; and (iii) rates of Po degradation.”

To clarify, our over-arching research aim was stated in the introduction on lines 79-81: “The aim of this study is to elucidate the microbial and geochemical mechanisms of in-sediment phosphorus cycling and release associated with commonly occurring short

redox fluctuations (days) at the SWI in shallow eutrophic environments."

Polyphosphate accumulation due to microbial activity has been proposed as a key process affecting P cycling under oscillating redox conditions in some environments, where polyphosphate can account for up to 10% of total phosphorus (Hupfer et al., 2007). For this reason, polyphosphate accumulation was investigated alongside other possible P cycling mechanisms. The time series 31P NMR analyses demonstrate that polyphosphate accumulation and release are not major processes within our experiment: polyphosphate never accounts for more than 1% of total P.

We do agree with the reviewer that polyphosphate cycling is only one of the many different processes investigated within this research and, especially given its negligible role in our experiment, it should not be highlighted as prominently in the introduction. This will be addressed by rewriting the Introduction of the revised manuscript, which will put more emphasis on the novel aspects listed in response the reviewer's first comment.

"...(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 Po species was not possible..."

The term polyphosphate is not shown in any of the figures, as it was never present in any of the samples at a concentration greater than 1%, thus, confirming that polyphosphate accumulation did not constitute a major P cycling process within this experiment in contrast to previous studies. Although this is noted within the manuscript on lines 443 to 446, we propose to include the statement "Polyphosphate was not detected at a concentration >1% in any of the samples analysed" within the figure caption for Figure 6 to clarify this point in the revised version of the manuscript.

We agree with the reviewer that accumulation of Po during the experiment due to algal additions is unlikely due to the small amounts of algal matter added and the relatively short experimental timescale (74 days). As pointed out by the reviewer, we state this

on lines 373 to 375 of the manuscript. In addition, we present two lines of experimental evidence suggesting that Po accumulation is not a prominent process within this sediment and that Po degradation is very rapid. These include:

1) The low concentration of Po compared to orthophosphate determined by 31P NMR (9% vs 91%) and through sequential extractions (7% PRes). 2) The results of phosphatase enzyme activities, which show the capacity for rapid Po hydrolysis under both oxidizing and reducing conditions.

We will modify the introduction to shift the focus away from polyphosphate and Po accumulation toward the key novel aspects. We also plan to remove the statement about Po on lines 446-447. âĂĺ

“Hence, the experimental design used did not match the research aim”

The goal of this research, as noted on lines 79-81, was to elucidate the chemical, mineralogical and microbial processes that control redistribution and release of P from the solid phase to the aqueous phase during oscillatory redox conditions. We believe that the experimental design and analytical methods used are appropriate for this aim, as evidenced by:

1) Production of the first fully mass balanced redistribution of P between different sedimentary pools during redox oscillating conditions. 2) Demonstration of reversibility of P transfers between solid and aqueous pools. 3) Assessment of the Po hydrolysis capacity of the sedimentary microbial community through the use of phosphatase enzyme activity assays.

“...the discussion fails to substantially address the chemical composition and nature of these two fractions (PEx and PHum) and fails to describe related reaction mechanisms.”

The chemical composition of the PHum pool is discussed in great detail within the manuscript. There is an entire subsection of the discussion devoted to the interpreta-

tion of the chemical composition, nature and reaction mechanisms associated with the PHum fraction (lines 396 to 416). If there are specific reactions or alternative interpretations of the PHum pool, which the reviewer believes we have missed within this discussion, we would be keen to include them in a revised version of the manuscript. Additionally, the rationale for the inclusion of the PHum pool within the extraction scheme and with respect to P binding mechanisms – based on the most current literature – is provided on lines 204-207 of the methods section.

Detailed discussion of the chemical composition of each of the phases extracted within the SEDEX method, including PEx, were not included in the manuscript as the method has been broadly used to study P speciation in sediments for approximately 25 years. Detailed descriptions of the phases targeted by the SEDEX extraction scheme, and the reaction mechanisms are provided within the original method by Ruttenberg (1992), which is referenced on line 199 in the methods section and again on line 372 in the discussion of the manuscript. However, to address the concern of the reviewer and to make the manuscript easier to follow for readers unfamiliar with the SEDEX extraction scheme, we will include brief descriptions of each of the pools in the original SEDEX method (i.e., PEx, PFe, PCFA, PDetr and PResi) within the Methods section. We further propose to revise the discussion section by explicitly including probable reaction mechanisms, where appropriate (e.g. adsorption, co-precipitation and the formation of ternary complexes).

Specific comments:

“1) To me, the description of the operationally defined fractions and corresponding extraction conditions is insufficient and misleading”

It was certainly not our intention to mislead readers with the description of the operationally defined fractions targeted by the SEDEX method. As stated above, we will include brief summaries of the chemical composition and P binding mechanisms associated with each pool extracted with the SEDEX method. With regards to the descrip-

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tion of the fraction extracted with acetic acid, Ruttenberg (1992) identifies this fraction as “authigenic carbonate fluorapatite + biogenic apatite + CaCO3-associated P”. We agree with the reviewer that simply referring to this fraction as “CaCO3 bound P” may be misleading and we will therefore revert to the original definition of Ruttenberg.

“2) Some available data sets are not presented / not discussed although these data sets could be useful to the reader.”

We agree with the reviewer’s point that more complete data could be useful to the reader. A large amount of additional data was produced during our experimental study, e.g. ICP-OES data from the aqueous fraction, ICP-OES data from the SEDEX method and ion-chromatography data. Not all the data are shown in the manuscript to avoid diluting the key points of the paper. We propose to include pH data within Figure 3, as these data are directly discussed within the manuscript, and to include all additional data sets in tabulated and graphical form within the supplementary material of the revised version of the manuscript. In doing so, the additional data will be available to the reader, but without detracting from the key messages of the project with respect to P cycling. Saturation indices for major P minerals were calculated with the available solution data using PHREEQC, at all time points during the experiment. The results of these calculations will also be included within the supplementary information of the revised version of the manuscript.

“3) The ionic strength together with the pH are essential variables in determining saturation indices and adsorption mechanisms...For the reader, the only possibility to gather information on the ionic strength are the terms “freshwater sediment” and “freshwater marsh” – which is insufficient”.

We will include the pH data within Figure 3 and the ionic strength in the “Experimental redox oscillation: Aqueous chemistry section” (294-352). Furthermore, we propose to include the calculated saturation indices for all the major P mineral phases within the supplementary information.

"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 (25oC) 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."

We fully recognize that there are (always) limitations to extrapolating experimental results obtained in the laboratory to field conditions. Nonetheless, the processes described in our study have, we believe, general implications for the management of internal and external nutrient loads in small lentic systems. Admittedly, referring to WWTP effluent in the implications section may be too specific given the focus of the bioreactor experiment on fundamental processes. We propose to replace the statement about WWTP effluent with a more general one about the role of external nitrate loading in the remobilization of legacy P from bottom sediments.

We also wish to emphasize that the temperature, light conditions, pH and ionic strength in the experiment actually closely resemble those found at the sampling site during summer/early fall. The pH in the experiments is buffered by the calcium carbonate naturally occurring in the sediment and matches values measured in the bottom waters of Cootes Paradise (see Figure 2 and lines 288-290). Similarly, the average temperature at the SWI measured at the sampling location in August 2014 is 23.8°C, while the absence of light is representative of processes taking place at or below the SWI, in particular because a thick mat of green filamentous algae covers the pond's surface during the growing season (as shown in Figure 1 A). We opted to mimic summer/early fall conditions, because sediments experience intense redox fluctuations during this period due to active bioturbation and pronounced diurnal cycles of photosynthesis/respiration. In addition, this is also the time of greatest organic matter input at the SWI. Thus, we strongly believe that the key processes identified within the reactor experiment repre-

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sent some of the key biogeochemical processes occurring within the topmost sediment at the field site, during the time of intense benthic activity and exchanges. We recognize that we must make this point more clearly in the revised manuscript

Technical Issues:

“Line 64: Which phases are meant here” – Agreed, this is unclear, we propose replacing “these phases” with “iron(III) (oxy)hydroxides” in the revised version of the manuscript.

“Lines 70-72: I suggest to explain the coupling of these biogeochemical cycles. . .” Detailed explanations of the importance of these coupled cycles were not provided for brevity. Instead the reader was referred to the references cited. In the revised manuscript a short paragraph will be added to summarize the major known pathways through which of carbon and sulfur affect P cycling.

“Line 90: Missing comma and brackets inside brackets” – Agreed this will be fixed.

“Line 91:. . .Citing the original source of the methods” – Agreed, we have cited the Ruttenberg method and others within the methods section and discussion but we will definitely add references to the appropriate methods here.

Lines 103-104, 107-110 and 166-169 – We agree with the reviewer, these nested sentences can be avoided and we propose to reword these sections to improve readability.

“Lines 119-121: Why aren’t the analyzed elements listed in full” – The full elemental list wasn’t provided for brevity. We accept the reviewer’s point that this list, and indeed the data, would be useful to readers. We propose to include the complete data for all elements in tabulated and graphical forms in the supplementary information.

“Lines 123-124: Which software was used for phase identification” – The software used was PANalytical’s Highscore+. This detail, including the version number will be added to the revised manuscript.

"Lines 177-180: 'Method detection limit' has been abbreviated before" – Agreed.

Line 206: "Li et (Li et al., 2015) al" –This referencing error will be corrected.

"Line 252: Grammar" – Agreed, we propose rewording to "Excitation fluorescence was set at 365 nm and emission intensity at 450nm was recorded at 5 minute intervals over a 6-hour period".

"Lines 379-381 and lines 392-395: Vague and poor sentences" – We agree with the reviewer and will rewrite the offending sentences in the revised manuscript.

"Line 396: Unclear structure of headings" – We agree with the reviewer, this makes more sense as a subsection within "Sequential chemical extractions and solid phase P partitioning". This will be corrected in the revised manuscript.

"Line 407-410: Vague sentence; in what respect "environmentally relevant" – We will rephrase this for clarity. The papers cited demonstrate that mixed Fe(III)-OM-phosphate and arsenate complexes can be synthesized in the laboratory. However, to the best of our knowledge, there is no direct evidence for the existence of these complexes in natural environments, largely because of the difficulty of measuring such complexes at low concentrations in structurally mixed and complex natural samples. Nonetheless, the recent spectroscopic evidence of synthesized Fe(III)-OM-phosphate complexes supports the hypothesis that these complexes can also form, and indeed probably form, in natural freshwater environments. We will clarify this point in the revised manuscript.

Section "hydrolytic enzyme activities" – No reference to Figure 6. - We agree with the reviewer: there should be a reference to Figure 6 within this section. This will be corrected in the revised version of the manuscript.

Figure 2: Label depth interval used in the bioreactor – We agree and will add this.

Figure 3: Inconsistent labeling; some axis labels shown some not (e.g. Mn) – We disagree that this is inconsistent. A second axis is only used when two sets of data

cannot be shown effectively on the same scale. For Fe and Mn, the same scale can be used and a common “concentration” label is applied. This is clearly explained in the figure caption. We do not intend to change the figure labeling.

Figure 4: P fractionation before equilibration is not shown – The objective of the experiment was to determine the redistribution of P cycling during redox oscillating conditions, therefore, the first sample analyzed was the one immediately starting the redox oscillations (i.e., the experimental time origin).

Figure 4: Inconsistent axis labels for PAq - We use both μM and mg P L-1 as some readers may be more familiar with one unit or the other. We do not propose to make any changes.

Figure 6: Font size, missing polyphosphate label – Font size will be increased. There is no polyphosphate label as polyphosphate was below the detection limit. This information will be included in the caption of Figure 6 as follows: “Polyphosphate was not detected at a concentrations >1% in any of the samples analyzed”.

References:

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Please also note the supplement to this comment:
http://www.biogeosciences-discuss.net/bg-2016-533/bg-2016-533-AC1-supplement.pdf

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