

Author's response to the comments of Peter Kraal and Tom Jilbert on the manuscript:

First of all, we would like to thank both reviewers for the time they put into evaluating this manuscript and their constructive and valuable comments. Both reviewers underlined their interest in the combined approach of water column and sediment sampling for a benthic P budget in the Peruvian OMZ. We try to clarify all issues raised by the reviewers below.

In response to the comments of Peter Kraal, received and published 16 Nov 2015:

- 1 It would be nice if the pore water PO₄ profiles are referred to before the freeze-thaw experiments as background to the resulting calculated PO₄ fluxes.

Author's response: The benthic chamber TPO₄ fluxes from in situ measurements and the diffusive TPO₄ fluxes calculated from the PO₄³⁻ pore water profiles are addressed in section 4.2.1. before the freeze-thaw experiments in section 5.2.2. We will provide a clearer link to the pore water profiles shown in Fig. 7 in section 4.2.1 in a new version of the manuscript.

- 2 P56, L21. A few more words could be spent to clarify the statements regarding phosphorite formation.

Author's response: We will briefly extend the information on the indications for recent phosphorite formation found in the study area in the abstract. Anyhow, phosphorite formation is addressed in more detail in chapter 5.2.3.

- 3 P57, L21-22. Perhaps some nuance is needed here. Under certain conditions (such as nutrient-rich upwelling regions off Peru and Namibia), extensive (microbially-mediated) CFA authigenesis has been found. And during burial below the oxygen penetration depth, reductive release of P from metal (oxyhydr)oxides triggers apatite formation, often in disperse form at low concentrations (sensu Ruttenger, Slomp). These are two very different, anoxic mechanisms, where the latter may be more representative for non-upwelling oceanic settings.

Author's response: This is a very good aspect. We will address specifics on CFA authigenesis in the new manuscript as suggested by the reviewer.

- 4 P68, L7. "except slightly increasing ratios close to the seafloor" Clearly state that this refers to the difference between the deepest water column sample and the sediment surface (as there is a general decrease between the deepest water column sample and the one immediately above it).

Author's response: We will change the wording in a revised manuscript accordingly.

- 5 P68, L9. Description of the trend at Stat VIII deserved a little more detail. Truncated profile, cyclicity?

Author's response: We will describe the sediment profile for the POC/POP ratios of Sta. VIII in more detail in the results section and will provide more explanations for the profile shape in the discussion section 5.1. Obviously the POC/POP profile is truncated, but there are no indications for sedimentary events in the ²¹⁰Pb profiles shown by Dale et al., 2015. More likely, the sharp increase of POC/POP ratios below 2 cm of sediment depth is driven by authigenic formation of phosphorites.

- 6 P68, L23-24. Unclear what is meant here; I do not see any consistent strong changes in the deepest water column sample.

Author's response: It is meant that there is a drop between the deepest water column sample and the first sediment sample at station VIII. We will clarify this in the new version of the manuscript.

- 7 P70, L6. "that could be triggered by the TPP", rephrase and mention mechanism/process

Author's response: This will be modified in the manuscript.

The measured benthic TPO₄ fluxes exceed the phosphate fluxes that could be generated from TPP degradation by a factor of 6, but the potential TPO₄ fluxes are still higher (Table 4).

- 8 P73, L21. Here, phrasing could be more clear: enhanced POC preservation and/or enhanced P release could lead to higher C/P in anoxic sediments compared to oxic. Current phrasing is convoluted while an answer is not (and cannot) be provided regarding the main driver.

Author's response: The last sentence of the section will be rephrased according to the reviewers comment.

- 9 P75, L21-27. It seems from this that the authors assume that terrestrial P, i.e. P associated with riverine suspended particles, would not show up at all in the PIP fraction on the filters from the water column samples? If riverine particulate matter sinks through the water column (or do the authors assume all riverine input is lateral?), and consists at least in part of Ca-P and oxide-associated P, why would it not (partially) be part of the measured PIP on the filters? Even though it is a minor P source, the authors might want to elaborate slightly on why riverine P is treated as a completely separate P input.

Author's response: We were aiming to estimate the maximal effect of terrestrial P input to the sediments with this approach. Riverine transported material from the continent is likely underrepresented on our water column filter samples due to fast sinking speed of such particles and/or a laterally dominated transport. However, we do not exclude that a small fraction of the riverine transported material can be found on our filter samples. Anyhow, the results of the calculations show that terrestrial P input is of minor importance for the presented P budget.

- 10 P76, L12-18. Could sinking of fish debris through anoxic waters not provide a rapidly sinking source of both apatite and organic matter to the seafloor (biological fish remains, collagen etc. in fish bones)? Then, would fish debris necessarily leave a signature of very low C/P ratios? If these fish debris are indeed missed during water column sampling (or perhaps have a strong seasonal character), the associated OC would also be missed in the budgets, which would have an impact on the argument of the theoretically required low C/P ratio of incoming particles. Perhaps C/P ratios alone are insufficient to dismiss a potential role for fish debris as (additional) PO₄ source? The authors show nice links between PO₄ fluxes and sedimentary bacterial (biological) activity, which can be used to hypothesize on the likely source(s) of PO₄. Perhaps it would be better to focus on the evidence for the contribution of bacteria, to the point where other P sources are not necessarily required to close the budgets.

Author's response: We are convinced that an imprint of fish debris in the sediments which have not been sampled on the water column particle filters must lead to differences in the

POC/TPP ratios between the water column and sediment ratios. Since this difference is not observed it is likely that fish debris can be ruled out for closing the P budget during the sampling campaign.

However, if we only consider the bacterial P release as additional P source to the sediments, it is very likely that questions about the other mentioned sources arise. Hence, we want to make sure to discuss potential other sources briefly and show that the role of bacteria are key to the understanding of the P-budget.

- 11 78, L13-14. In fact, highest freeze-thaw P release was found in sediments with abundant foraminifera rather than microbial mats (Stat VIII). This deserves a bit more attention here, as it might put the potential role of bacteria in more context?

Author's response: This is a good point. However, the PO_4^{3-} concentrations after the freeze-thaw experiments of the stations V and IV, where sulfide-oxidizing bacteria are still abundant, are only slightly lower compared to station VIII. Hence, we assume that the occurring sulfide-oxidizing bacteria at station V and VI as well as the foraminifera observed at station VIII are contributing phosphate to the pore waters. However, it remains to be shown how these mechanisms play out in detail (e.g. nutrient concentration thresholds, time scales, P release from *Marithioploca*-related bacteria and foraminifera) and the impact on benthic P release in oxygen and nitrate deficient environments on longer time scales.

- 12 P80, L1-3. If foraminifera represent such an efficient sink of BW PO_4 , it would be good if the authors provide their preferred mechanism by which the internally-stored PO_4 makes it into authigenic apatite. Would this be a matter of release after death fueling apatite formation rather than uptake by living forams? What type of redox-dependent PO_4 uptake/release behavior do forams display?

Author's response: This is another interesting aspect, but unfortunately the mechanisms how the P release from foraminifera work in detail remains unknown and requires more detailed experimental work (e.g. are the foraminifera alive or dead releasing the P, redox-dependent P uptake and release?) and will be addressed in more planned experimental work in the study area in the near future. There are two expeditions planned to the Peruvian OMZ where detailed experiments will be carried out in order to answer this type of questions.

- 13 P80, L18-26. This is crucial information regarding potential PO_4 release mechanisms and should be included in the discussion. The conclusions should not contain such crucial new information, but rather should concisely synthesize the findings and interpretations already presented in the results and discussion.

Author's response: We will take this into account in the revised manuscript and suggest changes on P77, L13-17 and P80, L18-26.

All technical corrections will be considered in a revised version of the manuscript.

In response to the comments of Tom Jilbert, received and published: 22 Nov 2015:

Major:

- 1 One of the main challenges associated with the approach employed here is that the fluxes being measured are generally not in steady state, and a single sampling moment (i.e. one cruise) will struggle to tell the full story. The authors have acknowledged this and indeed conclude that their budget cannot be closed for this reason, but I agree with Peter Kraal's comment (re. P80 L18-26) that more specific contextual information about the variable redox regime of the study site should be included earlier in the paper. The authors refer to the studies of Guitierrez et al., 2008 and Schunk et al., 2013 in section 2 but perhaps it would be good to show in graphical form (e.g. incorporated into Fig. 1) how much the redox conditions can actually change at these sites, and how frequently. For example, can potential loading-unloading cycles for the bacterial P 'capacitor' the authors postulate be identified from past data?

Author's response: Due to the lack of time series data available for longer time scales and more water depth than presented in Gutiérrez et al. (2008), we decided to not duplicate any figure in this manuscript. However, we will provide more detailed information on where to find information for redox changes in the water column in the text of the revised manuscript (e.g. Noffke et al, 2012; Scholz et al., 2011).

- 2 I recommend that the authors present not only the various C/P ratios (e.g. Fig. 2) but also the raw C and P data in graphical form (these are currently given in table form and only in the supplement). This is important because in both the water column and sediments, trends in C and P concentrations may help to indicate transformations (e.g. breakdown of organic matter, precipitation of CFA), which are relevant for the interpretation of the data.

Author's response: We will add a new figure to the manuscript.

- 3 In the case of the water column data, I miss a conclusive statement from the authors about what they believe the PIP phase on their filters actually is.

Author's response: More detailed information will be added concerning this aspect. Nevertheless, a final conclusion on the composition of PIP cannot be made based on the available data set.

According to Labry et al. (2013) we expect the PIP phase to be comprised of inorganic P phases originating from abiotic particulate phosphorus as well as inorganic P phases from that are biogenic origin. Abiotic PIP comprises mineral associated P, e.g. from terrestrial sources. The inorganic phosphorus from biotic particulate phosphorus is composed of orthophosphates, pyrophosphates and polyphosphates incorporated into organic cells.

- 3.1. The authors refer to the paper of Sanudo-Wilhelmy et al. which describes P adsorbed on the surface of living *Trichodesmium* tissue, probably associated with hydrous Mn oxides. There are several questions which follow from this: How representative are the conclusions of that study in a high-productivity upwelling system such as this one, considering the different primary producer assemblages? And if there is indeed a major fraction of surface-adsorbed P associated with surface-water POC, is it realistic that P will be preserved in such a form as this material sinks through the water column?

Author's response: This is indeed a very interesting aspect. Sanudo-Wilhelmy et al. (2004) suspect that the finding of surface P-adsorption might be a general feature comprising all phytoplankton groups. To date, this statement has, unfortunately, neither been confirmed nor disproved by other studies. However, if it applies, there shouldn't be any general differences between low nutrient and upwelling areas. On the other hand, it doesn't seem likely that Mn-oxides play a major role off Peru. Mn-oxide concentrations were not measured on the filter samples, but SEM-analyses of the filter samples (data are not presented here) indicate that the overall concentrations are very low. In addition, Mn-oxides are not contained in surface sediments, indicating that they are continuously dissolved when sinking through the water column. The adsorbed P should be released during transport, but given the low concentrations the effect on our measured C/P ratios is likely negligible.

Generally, one should assume that remineralization in the water column leads to a decrease in the reactivity of the organic matter. However, our data do not reveal evidence that POP is transformed to PIP during transport. Statements about the quality of the organic matter or changes in reactivity would remain purely speculative.

- 4 The water column POC data from the offshore sites (Table S1) suggest export of ~5% of surface-water POC to the deep waters at Station VI (see POC at 10m vs. 240 m) and ~20% at Station VIII. What can the authors say about the quality of the exported POC, and what does this imply for the fate of any surface-adsorbed P? Furthermore, how would hydrous Mn-oxide bound P be expected to behave while sinking through the anoxic water column?

Author's response: The example the reviewer chose for estimating and comparing the POC export from the POC concentrations is biased. The POC concentration at 10 m water depth at station VI is by far the highest concentration compared to the other POC concentrations found at the same water depth (stations I, III and IV) and represents an outlier in our data set, which will explicitly be marked as such in a new version of the manuscript.

As outlined above (comment 3.1) we don't believe that Mn-oxide-bound P plays a major role in this context, because of the low concentrations. However, any Mn-oxide-bound P would be released in the anoxic water column due to the continuous dissolution of Mn-oxides.

- 5 It is indeed remarkable that POC/TPP is so close to Redfield throughout the water column. Could there be a role for conversion of POP to polyphosphates as suggested by Diaz et al. (Global Biogeochem. Cycles 26, 2012) or to CFA (Jilbert and Slomp, GCA 107, 2013), during the decay of organic matter in the water column? If P bearing molecules are preferentially broken down, and P is then stored in these forms, POC/TPP could stay quite constant as observed here. In summary, I think a discussion of these various options for the PIP phase is essential, including statements about the expected extraction behavior of the candidate phases (e.g. are polyphosphates expected to count as POP or PIP?).

Author's response: On the basis of our dataset, such a conversion can only be observed within the sediments, especially at station VIII and at some stations between the bottom water sample and the surface sediment sample (e.g. station I, IV, VI and VIII) as described in the manuscript. Here is likely a shift in the POP and PIP concentrations. The POP concentration drops while the PIP concentration increases, which could be a hint to such a process. Due to the fact, that we have not conducted sequential extraction it is not possible to follow up precisely which PIP phase (e.g. polyphosphates or CFA) is formed.

- 6 In the case of the sediment data, I would also like to see the raw plots of TPP, POP and PIP to see if there is evidence for transformations with depth, such as the precipitation of CFA as observed in many open ocean studies (Ruttenberg and Berner, GCA 57, 1993). As stated by Peter Kraal it is important to distinguish between different mechanisms of CFA formation and with all the data available here it is possible to say something more about this.

Author's response: According to comment 2 of the reviewer, we would like to include an additional figure similar to Fig. 2 that shows the water column and sediment raw concentrations of TPP, POP, PIP and POC. On the basis of that figure we will further explore on CFA formation mechanisms in section 5.2.3.

- 7 A further concern I have about the sediment data is the way in which the burial fluxes of P have been calculated. This has been done using average P concentrations in the top 10 cm and mass accumulation rates (Page 66). In the supplemental data it can be seen that TPP concentration decreases from the sediment surface downwards, so the ultimate burial flux is probably better calculated from the value at 10 cm rather than an average including the surface sediments. In fact the authors state that a previous related study (Dale et al., 2015) employed exactly this approach to determine carbon budgets. How would the P budget change if the same was done here?

Author's response: The numbers given in the manuscript were calculated from the average P concentration of the first 11 cm of sediment depth (11 cm is due to our sampling resolution). However, using the P concentration at 11 cm sediment depth would not lead to significant changes of the P burial fluxes. Only at the station V the burial flux would change slightly and the P deficit would deviate for less than 10% from the value given in the manuscript. Since there are no changes at any other station and only a change of less than 10 % for station V, we would like to stick to the calculation using the average P concentration of the first 11 cm of sediment depth which was also applied in Dale et al. (2015).

Minor/technical corrections: We thank the reviewer for his minor/technical corrections and will address these in the revised manuscript.

- 1 Page 61, Lines 16-20. What was the pH during analysis? The way this is phrased, it sounds like you carried out the analyses at neutral pH but normally this is not done. Please clarify.

Author's response: The analysis was carried out at low pH. The NaOH was added to the sample solutions to slightly raise the pH. It was done because the slope of the calibration curve was to flat for our low concentration measurements. However, due to the reagents added to the sample solution, the pH remained low.

- 2 Page 62, Line 25 onwards. Related to my earlier comment, it would be good to state somewhere which P phases are expected to dissolve in the 1M HCl (pre-combustion) extraction. Especially in this study where intracellular polyphosphate pools, and surface-adsorbed P, may be quantitatively important, the expected extraction behavior of different phases should be clarified.

Author's response: Please find the author's response related to that comment above (comment 3).

- 3 Page 73, Lines 10-20. Here I would state more clearly the role of Fe in sedimentary P cycling in oxic conditions i.e. the observation that POC/TPP in oxic sediments is typically 10-50 is primarily due to the association of P with Fe (oxy)hydroxides in surface sediments after release from decaying organic matter. Also check the reference given as Baturin (2007). In the reference list the only article with this first author is Baturin and Savenko, *Oceanologia* 37, 1997.

Author's response: We will clarify this in the revised manuscript and replace Baturin et al. (1997) with Baturin (2007).

- 4 Page 77, Lines 1-10. Again, add some more contextual statements about the expected role of Fe in P cycling in the OMZ environment. Iron availability in the surface sediments should vary greatly with water depth through the OMZ but this is not expressly discussed here.

Author's response: This is a good point. We will extent the information on Fe oxyhydroxides in the sediments in the revised manuscript accordingly.

Fe oxyhydroxides are expected to be important carriers for phosphorus from the water column to the sediments. Due to their dissolution in the sediments, the adsorbed P is released to the pore waters. However, in the Peruvian OMZ oxygen concentrations are already very low in the water column. In consequence, similar to Mn-oxides, a large part of the Fe oxyhydroxides is already dissolved in the water column and, as such, cannot be an important P source to the sediments (see P budget calculations).

- 5 Page 80, Lines 1-3. Once again I agree with Peter's comment, that the mechanism of the proposed foraminiferal P uptake should be discussed in more detail. If true this could be an exciting new process in sedimentary P cycling so it deserves more attention

Author's response: Please find the author's response in comment 12 of P. Kraal.