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Biogeosciences Discussions

Interactive comment on "Impact of seasonal oxygen deficiency on the phosphorous geochemistry of surface sediments along the Western Continental Shelf of India" *by* Josia Jacob et al.

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Response to the comments by the Anonymous Referee #3 (RC C3313)

Referee's general comment: This study focuses on the phosphorus geochemistry of surface sediments from the western and eastern continental shelf of India. The authors specifically focus on the effect of seasonal variations in bottom water oxygen on sediment P forms. The major conclusion is that a significant decline in surface sediment concentrations of Fe-bound P occurs during periods of hypoxia on the western

shelf. This decline corresponds with an increase in dissolved PO4 in the water column. On the eastern shelf, in contrast, such seasonality is not observed because there is no hypoxia there. While the western shelf has been studied earlier, these are the first data on the eastern Indian shelf that I have seen so far.

I have one major concern, however: The authors report large changes in the P speciation and organic carbon contents between seasons. These also involve P components that are are not expected to respond to seasonality such as detrital P and authigenic Ca-P. The same holds for sediment organic carbon: a loss of several wt% over a season due to degradation is not possible. Thus, it seems likely that there is a large spatial variability in sediment composition the region, and that, like in other shelf regions, the surface layer is frequently resuspended and transported elsewhere, precluding simple seasonal comparisons of the surface sediment. More compelling evidence for the suggested release mechanism from the shelf could be obtained by studying the porewater composition in both seasons (dissolved Fe2+ and PO4) with depth in the sediment. This could be combined with depth profiles of sediment P species. Besides providing more mechanistic insight, the link between the sediment processes and water column chemistry could then be made more quantitative.

Author's response: We acknowledge the refree for the valuable suggestions and comments on the manuscript.

Out of the five phosphorus species analysed from the surface sediments and presented in this manuscript Pbio, PFe, Paut and Porg are usually classified as reactive species, while Pdet is non-reactive (Ruttenberg, 1992; Hensen, 2006). The reactive species are considered to have been either biologically available or was associated with some bioavailable forms of phosphorus before getting buried in the sediments. These reactive phosphorus species are either productivity or redox sensitive (Hensen, 2006; Ruttenberg, 1992). Paut forms a sink for phosphorus after it forms secondary phosphorus phases to form CFA (carbonate fluorapatite) from more mobile phosphorus forms which usually happens in the deeper sediments. The mechanism of the formation of CFA or phosphogenesis is thought to be mediated by an initial primary authigenic mineral phase (Hensen et al., 2006). Hence, the response of the reactive phosphorus species PFe, Paut and Porg in the surface sediments of the WCSI to the variations in the hydrographical and productivity characteristics of the WCSI during LSM and SIM as reported in this manuscript is obvious.

The refree suggests that the spatial variations in the phosphorus species can also be due to physical processes such as re-suspension, dispersal etc due to the currents operating in the region. However, such factors are not expected to cause seasonality in the concentrations of the reactive phosphorus species. But can lead to spatial re-distribution of the phosphorus species in a particular season. The physical processes seem to be responsible for the spatial re-distribution of the non-reactive Pdet from the central WCSI during LSM to the entire outer shelf during LSM. This will be discussed in the revised version of the manuscript.

Enhanced deposition/sedimentation of organic matter is a characteristic feature of hypoxic zones. They are also characterised by greater preservation of the deposited organic matter (Diaz and Rosenberg, 2008; Middelburg and Levin, 2009). In an earlier study on the total and labile organic carbon (TCHO and PRT) of the surface sediments (using the same 0-1cm layer of sediment samples used in the present study) along the WCSI during LSM and SIM, revealed marked seasonality. The total and labile carbon was higher and concentrated along the regions characterised by intense oxygen deficiency during LSM compared to SIM (Jacob et al., 2009a). In section 4.1 of the manuscript, the higher TOC, TN and TP observed in the surface sediments of the WCSI during LSM along the regions experiencing intense oxygen deficiency is discussed. In alternating oxic-anoxic conditions the degradation of organic matter is more extensive than permanently anoxic conditions (Aller, 1994; Aller and Aller, 1998). As mentioned before the physical processes can lead to some resuspenson or transportation locally but cannot lead to the observed seasonality in the geochemical characteristics of the sediments. Hence, the reported seasonality in the organic carbon, organic nitrogen

and total phosphorus can be expected from the WCSI owing to the vast variations of the productivity and hydrographical characteristics of the region.

As suggested by the reviewer, the pore water composition and depth profiles of the phosphorus speciation will be considered for a future extension of the present study.

Repose to the specific Comments of the refree

Comment - Page 6090: Line 3: please be more specific: the biogeochemistry of what?

Response - By ‘Biogeochemistry’ we meant the biogeochemical processes in general or to be more precise the biogeochemical cycling of carbon, nitrogen, phosphorus and other biogenic elements. This will be corrected in the revised version of the manuscript.

Comment - Line 15-19: Apart from the Fe-bound P fraction, the surface sediment P speciation typically will not change on seasonal time scales. Thus, changes in the authigenic and detrital fractions as observed here likely reflect spatial variability not temporal variability.

Response - Out of the five phosphorus species analysed from the surface sediments and presented in this manuscript Pbio, PFe, Paut and Porg are usually classified as reactive species, while Pdet is non-reactive (Hensen, 2006 ; Ruttenberg, 1992). The reactive species are considered to have been either biologically available or was associated with some bioavailable forms of phosphorus before getting buried in the sediments. These reactive phosphorus species are either productivity or redox sensitive. Paut forms a sink for phosphorus after it forms secondary phosphorus phases to form CFA (carbonate fluorapatite) from more mobile phosphorus forms which usually happens in the deeper sediments. The mechanism of the formation of CFA or phosphogenesis is thought to be mediated by an initial primary authigenic mineral phase (Hensen et al., 2006). Hence, the response of the reactive phosphorus species PFe, Paut and Porg in the surface sediments of the WCSI to the variations in the hydrographical and productivity characteristics of the WCSI during LSM and SIM as reported in this manuscript is obvious.

As the refree suggests that the spatial variations in the phosphorus species can also be due to physical processes such as re-suspension, dispersal etc due to the currents operating in the region. However, such factors are not expected to cause seasonality in the concentrations of the reactive phosphorus species. But can lead to spatial re-distribution of the phosphorus species in a particular season. The physical processes seem to be responsible for the spatial re-distribution of the non-reactive Pdet from the central WCSI during LSM to the entire outer shelf during LSM. This will be discussed in the revised version of the manuscript.

Comment - Line 18. Correct the spelling of “fluorapatite”. Are the authors sure that this is the phase present in their sediment? Wouldn’t it be safer to call this “detrial apatite” or simply detrital P?

Response - ‘Detrital fluorapatite bound phosphorus (Pdet) will be corrected to detrital phosphorus in the revised manuscript wherever it is mentioned in the manuscript

Comment - Line 23-25: have the authors calculated how large the change of P in the sediment should be to explain the change observed in the water column? What about changes in release of P from organic matter?

Response - Higher concentrations of DIP (dissolved inorganic phosphorus) more than expected from the degradation of organic matter, is observed along the WCSI where the seasonal oxygen deficiency intensifies to anoxia (Naqvi et al., 2006). The present study provides observational evidence for the release of PO4 from the sediments to the overlying water column which explains the higher DIP along the region observed during intense oxygen deficiency. However, the calculations of phosphate fluxes from the sediments is beyond the scope of the present work since it lacks information on porewater data, diffusion coefficients, adsorption constants, rates of sedimentation etc. which will be included in a future extension of the present work.

Comment - Line 26: The data for the eastern continental shelf are part of this study and should be presented as such. The way the abstract is now phrased, it looks like these are data from other previously published studies.

Response - The abstract will be rewritten in the revised version of the manuscript. The work done along the ECSI will be more emphasised and it will be made clear that it is a part of the present work.

Comment - Page 6091, Line 3: what evidence do you have for labile organic matter? How are preservation of labile organic matter and phosphorus geochemistry related exactly? This is a surprising result because in an oxygenated area you would expect to find less preservation of organic matter.

Response - As described under section 1 (pg 6092; lines 17-23) the hydrography of the ECSI is influenced by enormous freshwater discharges into the region. The ballasting effects of the lithogenic materials introduced by the rivers accelerate the removal of newly fixed organic matter from the euphotic layer to the sediments. This mineral organic association leads to an increase in sedimentation rates and subsequently to a better preservation of organic matter along ECSI (Ittekot et al., 1992; Dileep Kumar et al., 1998). The respiration rate experiments in the subsurface waters of the Indian Ocean showed lower ETS (Electron System Activities) activities in the Bay of Bengal than in Arabian sea and hence particulate matter undergoes a lesser degree of oxidation in the water column through its incorporation into rapidly sinking organic matter (Naqvi et al., 2006). A comparative study of the total organic carbon and the labile carbon (in terms of the biochemical components – total carbohydrates and proteins) in the surface sediments of the WCSI and the ECSI revealed greater labile carbon in the sediments of the ECSI by a factor of three than the WCSI (Jacob et al., 2008; Jacob, 2009). Comparison of pore water sulphate concentrations in the sediment cores from Krishna-Godavari basin (K-G basin) along the ECSI and off Goa along the WCSI showed higher sulphate reduction rates along the K-G basin (3.6 to 15.8 nmol cm-2day-1) than along off Goa (0.11 to 0.94 nmol cm-2day-1). The attributed reason for the observation was that the lower exposure time to oxygen for the organic matter in K-G sediments has preserved reactive organic compounds required for sulfate reducers and possibly methanogens (Mazumdar et al., 2007). Hence, eventhough ECSI is oxygenated throughout the year because of the higher sedimentation rates there is greater preservation of organic matter in the sediments.

As expected from the hydrographical characteristics of the region, Pdet was the major phosphorus species along the ECSI. But since the region is also characterised by greater preservation of organic matter, the surface sediments had higher abundance of Porg (which was not expected as the productivity along the region is very low).

Comment - Line 19: There is also enhanced release of P from organic matter under anoxia. See the cited references and Ingall et al., 1993 GCA). This should be discussed.

Response - Higher DIP (dissolved inorganic phosphorus) was observed in the shelf waters of the WCSI experiencing intense seasonal oxygen deficiency (anoxic) which could not be explained only by the degradation of organic matter (Naqvi et al., 2006). The present study provides observational evidence for the release of PO4 from the sediments to the overlying water column which explains the higher DIP along the region observed during intense oxygen deficiency.

Comment - Page 6091, Line 19: Change to “Van Cappellen”

Response - The suggested correction will be incorporated in the manuscript.

Comment - Page 6092, Line 9: “the N/P ratio”. An average? Please specify.

Response - N/P ratios were computed by Naqvi et al., 2006 from the regression line of the plot between the observed DIN (dissolved inorganic nitrogen) and DIP (dissolved inorganic phosphorus) in the suboxic waters of the WCSI (Naqvi et al., 2006)

Comment - Line 10. Provide a reference for “Richard’s stoichiometry”

Response - The Reference is : Richards, F.A.: Anoxic basins and Fjords, In: Chemical Oceanography, Volume 1, Riley, J.P., and Skirrow, G., Academic Press, New York, USA; 611-645, 1965. This will be given in the revised version of the manuscript.

Comment - Line 13. Specify what type of “redox conditions prevail”.

Response - By redox conditions we meant intense oxygen deficiency leading to anoxia along the WCSI during when phosphorus is released from the sediments by the reductive dissolution of iron oxides and diffused into the water column.

Comment - Line 15: Reductive dissolution by itself does not lead to a transfer of P from the sediment to the overlying water, as suggested here. The P is released from the Fe-oxides in the sediment and then is lost through diffusion (or bioirrigation).

Response - As suggested it would be made clear in the revised version of the manuscript that reductive dissolution of phosphorus bound to Fe-oxides due to the prevailing redox conditions and the subsequent release into the water column by diffusion leads to the higher phosphate in the shelf waters during LSM. Bioturbation may not be important since the benthic population along the shelf during LSM was very less (from our observation) apparently because they could not survive the physiological stress caused by the oxygen deficiency.

Comment - Lines 24-and further: Again, it should be made more clear that the work presented for the eastern continental shelf is part of this study. Here, it is first stated that the study is about the western continental shelf (WCSI). Then, at the end of the paragraph on page 6093 it suddenly becomes clear it is also about the eastern continental shelf and that this the first time that such data for this region are presented.

Response - The significance of the work done along the ECSI will be emphasized while presenting the aim of the study in the revised version of the manuscript.

Comment - Page 6093. Line 10. What is meant by “terminal end of”?

Response - “Terminal end of” will be corrected to “end of summer monsoon”

Comment - Line 18. Please explain why these can be considered as “inner shelf”

Response - The main objective of the present work was to understand the impact of oxygen deficiency on the phosphorus geochemistry of the surface sediments of the WCSI for which we collected two samples (one each from the inner shelf and one from the outer shelf) from seven latitudes covering the entire WCSI. But due to technical reasons and the rough weather during LSM the vessel could not be stopped for sampling at shallower stations. Hence we had to limit our sampling to 50m water depth which the nearest coastal sample we could obtain. The seasonal oxygen deficiency intensifies closer to the coast. From our study it was found that the outer shelf experienced hypoxia which becomes more intense along the inner shelf were suboxia is observed. Anoxia is observed much closer (<50m water depth) to the coast where we couldnot get the samples. Hence the sampling depth is mentioned particularly in manuscript while distinguishing the samples as from the outer shelf and inner shelf. Moreover the width of the shelf along the study area (8-22°N) and the bathymetry is not uniform (Nair, 1995) hence for a uniformity of the sampling depths, samples representing the inner shelf was taken from 50m water depth.

Comment - Page 6094, Line 22: The primary reference for the SEDEX procedure is Ruttenberg (1992) – that reference should be added.

Response - As pointed out by the reviewer the primary reference for the SEDEX procedure is Ruttenberg, 1992 (Ruttenberg, K.C.: Development of a sequential extraction method for different forms of phosphorus in marine sediments, Limnology and Oceanography, 37, 1460 – 1482, 1992) which will be included in the manuscript.

Comment - Page 6094: Kraal et al. (2009; GCA) recently showed that the exposure of carbonate poor sediment samples to air may lead to oxidation artefacts and changes in sediment P speciation as detected by SEDEX. Can the authors exclude that this is important here?

Response - The total inorganic carbon (TIC) content of the surface sediments of the

WCSI used for the present study was 7.16% $\pm$ 2.12 (averaged for both the seasons $\pm$ SD) in the outer shelf and 3.66% $\pm$ 2.21 in the inner shelf (Josia, 2009b). Since the sediments had considerable amount of TIC, the above said artefacts do not seem to be important here.

Comment - Page 6095: Line 7: is this truly fluorapatite? see earlier comment.

Response - From line 7 (Page 6095) detrital flouorapatite will be deleted and Pdet will be given as detrital apatite bound phosphorus.

Comment - Page 6096. Line 4. Temperature is not a “physico-chemical parameter”. Please rephrase.

Response - Line 4 will be rephrasesd as “The distribution of properties such as ……..”

Comment - Page 6098, Lines 10-16. + Figures 7 & 8. And further. Most of the differences in P speciation between sampling periods are likely due to spatial variability. As a consequence, presenting them in the context of seasonal changes related to hypoxia is not meaningful. It also would be good to add the P speciation data (in ppm or umol/g) in a table.

Response - The response to this comment is given earlier. The phosphorus speciation data (in ppm) will be presented in a table in the revised version of the manuscript.

Comment - Page 6102: It is not clear why the ancient deposits are relevant here.

Response - The discussion has been extended to the geological time periods to explain the fact that in contrast to the present day observations, the ECSI was more productive to have even phosphorite deposits. Whereas the WCSI had remained productive for longer geological time periods such reports from the ECSI is referred to give the reader a broader implication of the topic.

Comment - Page 6103. Lines 19-21. This finding that seasonal oxygen deficiency leads to enhanced P release may not have been shown for this region before, but otherwise is not new. Please identify what truly new things we can learn from this work.

Response - Published works on the influence of the seasonal hypoxia along the WCSI on the sediment biogeochemistry of the region are very few. This manuscript presents the response of the phosphorus geochemistry of the surface sediments to the varying productivity and hydrographical characteristics of the WSCI during and before the development of the seasonal hypoxia. The present study also provides observational evidence for the release of PO4 from the sediments to the overlying water column during intense seasonal oxygen deficiency observed along the WCSI (which has been earlier documented from many other hypoxic zones). However the phosphate flux could not be calculated from the present study but it would be taken as a future scope of the study. The manuscript also documents the first data set on the phosphorus geochemistry of the surface sediments of the ECSI. Hence, this manuscripts adds substantially to the present understanding of the biogeochemical processes along both the eastern and western continental shelves of India.

Comment - Table 1: are all numbers given here significant?

Response - The numbers in table 1 will be given as whole numbers after removing the decimals.

Comment - The English needs to be improved. Some examples: Page 6090. Title: change "phosphorous" to "phosphorus" Line 4: remove "the" before "seasonal" Line 28: rephrase "where any kind of: : :has not been reported yet" to "where seasonal oxygen deficiency

Response - The manuscript will be edited for English and the corrections suggested will be incorporated to the revised version of the manuscript.

Comment - Page 6092. Line 1. Change to "an intensification" and "since the 1970s"

or "since the early 1970s" or "since 1970" whatever is applicable. Line 3. Change to "along the WCSI" Line 5. Here both past and present tense are used in one sentence.

Response - The corrections suggested will be incorporated to the revised version of the manuscript.

We hope that our responses are satisfactory in addressing the major concerns and comments of the refree on the manuscript.

Sincerely

Josia Jacob on behalf of the co-authors

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