Biogeosciences Discuss., 7, C3752–C3761, 2010
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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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Received and published: 11 November 2010

Response to the comments by the Anonymous Referee #2 (RC C3052)

Refree's general comment: The western continental shelf of India experiences acute oxygen depletion in near bottom waters on a seasonal basis. This manuscript focuses on the influence of this phenomenon on phosphorus geochemistry of surface sediments in the region. The authors find seasonal changes in phosphorus speciation in surface sediments, which they attribute to the prevalence of bottom-water anoxia. The conditions observed along the east coast of India are found to be quite different because of a different hydrographic regime. The results presented add substantially to what is known about the biogeochemistry of this region. However, I have two major concerns about the data. The first one is about iron measurements. It is not clear from the Methods section if "clean" protocols were followed during sample collection and processing. Did the vessel have a clean lab/container for handling such samples? I suspect that was not the case, which explains some very high iron values (exceeding 100 nM) at sea surface. If so, the iron data are not usable.

The second comment is on the way excess phosphate in water was computed (i.e. the difference between the LSM and SIM concentrations). While during the SIM the water column is well oxygenated, the bottom water oxygen concentrations are close to zero during the LSM. Thus, most of the difference in phosphate concentrations could well be due to remineralization of organic matter rather than diffusion from the sediments.

Author's Response: We acknowledge the reviewer for his/her comments and suggestions on the manuscript and also for appreciating the results presented in this manuscript.

For the analysis of dissolved Fe in seawater samples maximum care was taken to follow clean protocols. The details of the method adopted for the sampling and analysis is as follows. Water samples for the analysis of dissolved Fe were collected using precleaned 5 litre Teflon-coated Go-Flo bottles (General Oceanics) attached to polyvinyl chloride-coated stainless steel CTD-rosette sampler. Upon recovery, the samples were filtered under nitrogen pressure, through pre-weighed and acid washed 0.45μm membrane filters (Millipore) mounted on to Teflon filter blocks, to separate dissolved and particulate fractions. The filtrates were stored after acidifying with conc. HCl to pH 2-3. The analyses of Fe in the filtered water samples were done using ammonium pyrrolidine dithiocarbamate-methyl isobutyl ketone extraction (Brooks et al., 1967) and subsequent measurement using Graphite Furnace Atomic Absorption Spectrophotometer (GFAAS, ZL-4110). Working standards of iron (2-10 ppb) solution were prepared by

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diluting the stock solution (E-Merck) with Milli-Q water in 1% HNO3. To check the accuracy of the analytical method we used a river water reference material (SLRS-4) from National Research Council Canada (iron concentration 103±5 ppb). The analytical precision obtained for triplicate reference material was better than 5%. The methods followed will be described in detail in the revised version of the manuscript.

As mentioned by the reviewer, very high values of dissolved Fe (>6 ppb) was observed along the inner shelf particularly along 15°N of the WCSI during LSM. But high dissolved iron in the surface waters of the coast off 15°N has earlier been reported by Rejomon, 2005 and Rejomon et al., 2008. They have also reported very high concentration of Fe in the zooplankton (13,749 and 14,583 ppm along the inner and outer shelf off 15°N respectively) from the region. The coastal state off 15°N (Goa) is well known for mining activities and also exports more than 10 million tonnes of Fe-Mn ore per year (Parulekar et al., 1986). Thus the high dissolved Fe in the seasurface waters is due to the iron ore bearing landmass and the associated surface runoff from the nearby Mandovi and Zuari estuaries to the coastal waters off Goa (Sundar and Shetye, 2005). A detailed discussion of this would be provided in the revised version of the manuscript.

The seasonal oxygen deficiency along the WCSI intensifies (from hypoxic to anoxic) progressively from the outer shelf to the coast. The present work was done on the surface sediments overlain by hypoxic (150m water depth) and suboxic (50m water depth) bottom waters. Low DO (<10 μM) and high NO2 (>4 μM) were observed along the intermediate waters (30 - 40m water depth) indicating intense oxygen deficiency and denitrifation along the inner shelf during LSM. Naqvi et al., 2006 evaluated the stoichiometric ratios of DIN/DIP along the shelf waters of the WCSI experiencing varying degrees of oxygen deficiency (hypoxic, suboxic and anoxic). The DIN/DIP ratios observed in the hypoxic waters (13.74) were close to Redfield ratio. They observed DIN/DIP ratio (-79.1) for the suboxic waters slightly higher than expected from Richard,s stoichiometry (Richard, 1965) for the case when there is no oxidation of NH3 by nitrate (-84.8).

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In the anoxic waters, much greater DIP was observed which could not be explained merely by degradation of organic matter by sulphate reduction. Based on these observations Naqvi et al., 2006 proposed that DIP is released from the sediments to the overlying water column by the reductive dissolution of iron (III)-oxy hydroxides bound phosphorus (PFe) in the sediments when intense reducing conditions prevail along the shelf. From their observations, when the environment progresses from suboxic to anoxic conditions NO3 will be completely exhausted while PO4 in the water column will be >2.15. But from the present study, PO4 in the suboxic inner shelf was >2.2 (Fig.2) which is greater than observed earlier for the suboxic waters of the region. An enhanced flux of phosphate together with iron from the sediments into the water column is a well-documented phenomenon in hypoxic/anoxic zones (Diaz and Rosenberg, 2008; Middelburg and Levin, 2009). The present study provides the first observational evidence for the mobilisation of PO4 from the sediments of the WCSI during intense seasonal oxygen deficiency observed along the region in LSM.

Repose to the specific Comments of the refree

Comment - Page 6091, line 8: oxygen deficient WATERS

Response - The suggested correction will be incorporated in the revised version of the manuscript

Comment - Lines 26, 27: “Western Continental Shelf of India” already abbreviated in line 21.

Response - The suggested correction will be incorporated in the revised version of the manuscript. The abbreviation WCSI will be retained and the expanded form will be deleted.

Comment - Page 6092, line 3: Delete “closer”

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

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Comment - Lines 19-20: Do these figures apply for the ECSI or the whole of Bay of Bengal?

Response - The figures are given to provide an approximate idea of the huge amount of freshwater and sediment discharges from the major rivers draining from the Indian landmass to the Bay of Bengal from the published works, to explain the hydrographical characteristics of the region. The depositional settings for most of these rivers extend from the coastal plain to the shelf edge and finally discharge the freshwater and sediments into the deep ocean (Schwartz, 2005). In the revised version of the manuscript either the explanation for presenting these figures for the ECSI can be given or ECSI can be replaced by Bay of Bengal for making it more clear.

Comment - Line 20: Low SALINITY water

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

Comment - Page 6093, line 10: Delete "terminal"

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

Comment - Lines 14, 15: Change to "except 8°N and 22°N, where samples were taken only during LSM and SIM, respectively"

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

Comment - Page 6095, line 10: were ANALYZED for phosphate

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

Comment - Page 6097, section 3.1.2: Data from the ECSI are from only one season when upwelling-related hypoxia is not expected anyway.

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Response - Even if, upwelling-related hypoxia is not expected, the general hydrography observed along the region in terms of the physico-chemical parameters during the sampling period is discussed.

Comment - Section 3.2: I am surprised by the seasonality in the composition of sediments. Changes in iron speciation are understandable as they may be regulated by the re-dox chemistry of overlying waters, but the sedimentary TOC and TON contents in the samples recovered by a grab are expected to be determined by processes that integrate over much longer time scales.

Response - 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., 2009). 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). In the manuscript, the Section 4.2 and 4.3 discuss the response of the various phosphorus species to the varying hydrographical and productivity changes along the region during LSM and SIM. Hence marked seasonal behaviour was observed in all the geochemical parameters analysed in the surface sediment samples (0-1 cm) collected from the region during LSM and SIM. Moreover, seasonality in the organic carbon fluxes from the euphotic later to the sediments are also observed even in the sediments of the deep Arabian Sea with higher fluxes during SWM than during SIM (Rixen et al., 2000; Gauns et al., 2005). Higher sedimentation rates (0.06 to 0.66 cm/yr) have also

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been reported from the study region (Somayagulu et al., 1999). If the 0-1 cm sediment layer was an integral of several years (as the concern expressed by the refree), the geochemical parameters analysed would not have expressed the observed seasonal behaviour.

Comment - Page 6100, line 1: Pleistocene.

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

Comment - Line 17: LOW productivity

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

Comment - Page 6102, lines 11-18: The surface sediments examined in this study are of recent origin. I do not think the discussion of conditions during the Cretaceous is 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, line 2: Change "both the" to "the two".

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

Comment - Fig 2, Fig. 3 and Fig. 5: sampling points may be shown as in Fig. 4

Response - The sampling depths for the analysis of the physico-chemical parameters (temperature, DO, nitrate, nitrite and phosphate) was uniform for both the WCSI (both the sampling periods) and the ECSI. The sampling depths are clearly mentioned un-

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der the materials and methods section (section 2.1; p 6093; Line 24) hence it does not seem to be logical to give the sampling points again in the respective plots. The reason for giving the sampling points in Fig. 4 for the distribution of dissolved iron is clearly mentioned under section 2.1 (p 6094; Lines 6-8). The sampling depths for measuring dissolved Fe was not uniform during both the sampling periods and also it was not analysed from all the standard depths as in the case of other physico-chemical parameters analysed.

We hope that our reply will satisfy the concern expressed by the reviewer on the quality of the data and the interpretation of the results. The suggestions of the reviewer on language corrections will be incorporated in the revised version of the manuscript.

Sincerely,

Josia Jacob on behalf of the co-authors

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Interactive comment on Biogeosciences Discuss., 7, 6089, 2010.