

Interactive comment on “Beyond the Fe-P-redox connection: preferential regeneration of phosphorus from organic matter as a key control on Baltic Sea nutrient cycles” by T. Jilbert et al.

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REVIEWER: This is a very interesting and well-written paper dealing with an important topic in marginal seas. Especially in the Baltic Sea the P-cycle needs more attention when considering the variable redox-conditions and cyanobacteria blooms, respectively. Therefore, I recommend publication in Biogeosciences with only some minor revisions as given in the comments below. In particular, I would like to see some more details about the flux calculations (interference of PO₄ adsorption on Fe-oxides at oxic sites) and at least one statement about the term “Hypoxia” from a geochemical view.

AUTHORS: We thank the reviewer for the positive comments. Details of the flux calcu-

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lations are now given in the caption to Figure 2. We address the geochemical relevance of ‘hypoxia’ in the discussion associated to Figure 4 (see below for more details on both points).

REVIEWER: Specific comments:

REVIEWER: Abstract: Although, the preferential remineralisation of P seems to be depth dependent, I would suggest putting stronger focus on redox conditions. In my opinion, the apparent correlation with depth is due the site selection. For instance, if you would take samples in the Aland Sea, you will find a water depth comparable to the Gotland Basin but different redox conditions.

AUTHORS: The abstract has been changed accordingly.

REVIEWER: Introduction: Very often you are using the term “Hypoxia”. Do you really think that this biological classification is of significant relevance for your geochemical study? In my opinion, this border value of 2 mL/L or about 90 μM O₂ does not change that much for the redox cycles. Obviously it is important for organisms but if you think e.g. about Fe²⁺ it will be oxidized at 1 mL/L or 3 mL/L. Please comment on this also with respect to the Results and Discussion section.

AUTHORS: Our use of ‘hypoxia’ stems from the fact that this has become a widely accepted generic term (and definition) for oxygen stress in the Baltic, and in coastal seas worldwide. Indeed, this study was performed within the framework of the “HYPOxia mitigation for Baltic Sea Ecosystem Restoration” (HYPER) project. We acknowledge that the 2ml/L threshold is of little relevance for geochemical processes in bottom waters. However, as seen in Fig. 4, even ‘mild’ seasonal hypoxia in the bottom waters (ie. 1-2 months with bottom water O₂ ~2ml/L) is enough to generate a strong response in Fe and P behavior in the surface sediments at site BY2, because of the upwards migration of the redox zones within the sediment. We have included discussion about this in the revised Section 3.1. Also, we are careful to provide the true bottom-water oxygen concentrations at the various sites that we study, and we do not use the hypoxia threshold,

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but rather the sediment geochemical behavior, to divide the sites into the two groups.

REVIEWER: Methods: In which way did you handle the interference of H₂S during photometric PO₄ determination? Is it possible that you used PO₄ data from the ICP-OES?

AUTHORS: The phosphate data reported in the manuscript are derived from the photometric method. The samples were acidified immediately upon subsampling, as indicated in the text. We know from comparison of ICP-OES-derived sulfur and colorimetric sulfide analysis of Baltic Sea porewaters that the acidification protocol removes sulfide, leaving sulfate as the only S phase in these samples. Furthermore, ICP-OES-derived phosphorus matches nearly perfectly with photometric phosphate data. Therefore we are confident that no such sulfide interference effect is possible in this case.

REVIEWER: Please also add the accuracy of your measurements – only precision is not sufficient. Which reference materials are used?

AUTHORS: In all instances where we refer to precision (based on duplicate measurements), we also now include an indication of accuracy and the relevant reference materials.

REVIEWER: Concerning the acid digestions: -Does the acid mixture completely dissolve the sediment at 90°C? Did you use an open or closed system?

AUTHORS: This method has been used as standard in our laboratory for several decades and successfully dissolves all sediment components in most cases (including in this study). The Teflon bombs are closed during the initial 90°C heating. This is now indicated in the text.

REVIEWER: - is it really true that you evaporated the acids until complete dryness (“precipitate”)? Such a procedure would cause the partial formation of “refractory” minerals (e.g. Al oxides) and thus an underestimation of especially 3+ elements.

AUTHORS: No, the acid was allowed to evaporate until a gel-like substance was visible

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at the base of the bomb. This is now indicated in the text.

REVIEWER: Results and Discussion: Chapter 3.1

I miss some details about the calculation of the fluxes (e.g. possible sources of error), which can be added for instance in the methods section. At oxic sites, I am uncertain whether the calculation really works only by using the bottom water and uppermost pore water value. In which way did you consider that some upward diffusing PO₄ is possibly trapped by Fe oxides between 0.5 and 0 cm? Please comment on this.

AUTHORS: Details of the mathematics of the flux calculations are now provided in the caption for Figure 2. It is true that at oxic sites, there may be some uptake of phosphate onto iron oxides between 0.5 and 0 cm, thereby reducing the gradient and lowering the flux. However, the most oxic sites have such low fluxes of phosphate anyway (due to strong sorption to iron oxides throughout the uppermost few cm, e.g. Sites BY2 June and GOF5) that this difference would be negligible. Furthermore, at many sites with a high phosphate flux due to seasonal iron-oxide dissolution at the time of sampling, the gradient appears to become steeper toward the sediment-water interface (implying no such removal effect at the core-top).

REVIEWER: What is the reason for the extremely high bottom water concentrations of PO₄ at sites F80 and GOF6 (Table A)?

AUTHORS: These sites are extremely rich in organic material and have very high porosity. The abundant phosphate released from organic matter diffuses easily out of the sediment to generate high bottom water phosphate concentrations. In the case of GOF6, this flux is also enhanced by dissolution of Fe-oxides at the time of sampling.

REVIEWER: Chapter 3.2 In Figure 1 and Table A you show some sites which are not included in Fig.5. What is the reason for this selection?

AUTHORS: As indicated in the text, we do not include the flux ratios from the Group 1 sites in Figure 5, because the seasonal variability caused by retention and release of

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phosphate by Fe-oxides will overprint the flux of phosphate from organic matter breakdown (hence also overprinting the N:P flux ratio). Furthermore, several of the sites sampled with rhizons were not subsampled for solid-phase analysis so only appear in the figures reporting porewater data.

REVIEWER: P667/L5: Do you see any indications for preferential release of P related to C and N in deeper sediments? This older material should have other C:P and N:P ratios.

AUTHORS: We are still investigating the characteristics of diagenesis deeper in the sediments at these sites. When looking at the longer records, it will of course be necessary to consider the twin effects of changes in the initial C:P ratios through time, caused by variable bottom-water redox conditions (see Fig. 7) and the ongoing breakdown of organic matter which may alter the initial signal after burial. Note that many ancient sediments show similar ranges of C:P variability to the values we find, and sharp transitions between periods of contrasting redox conditions (eg. Kraal et al., 2010), suggesting that these signals are largely fixed soon after burial of organic material.

REVIEWER: P667/L11: As shown by Dellwig et al. (2010) GCA, vertical PO₄ profiles are influenced by strong coupling to the cycles of Mn and Fe at the redoxcline. Therefore, it is important to know the position of the sediment traps and the O₂ concentration as the relation between Mn, Fe, and P is restricted to a limited depth interval.

AUTHORS: This issue is now addressed in Section 3.2. The two sediment traps reported in the Emeis et al. (2000) study were positioned at 140 m and 230 m depth, respectively and this is stated. The Dellwig et al. (2010) study shows an increase in suspended P and Fe (as "MnOx-FeOOH-PO₄" and "FeOOH-PO₄") from the redoxcline (~120 -140m) downwards, with an indication that the lower boundary of this suspended Fe-P peak may extend many tens of meters deeper than the redoxcline (Fig. 3 in Dellwig et al.). Hence both traps reported in Emeis et al. could have collected non-organic P, influencing the N:Ptot and C:Ptot data in that study.

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REVIEWER: Chapter 3.3 This chapter appears like a review and I miss supporting data from the present study. Therefore I would suggest some shortening.

AUTHORS: As suggested by both reviewers, this section has been substantially shortened. Most of the opening paragraph summarizing relevant literature has been removed, while one of its more important statements has been moved to the introduction.

REVIEWER: Chapter 3.4 P672/L22: Site LF3 appears a bit different when compared with sites LF1 and 2 (Fig. 8).

AUTHORS: Indeed, LF3 is somewhat deeper than LF1 and LF1.5, and qualifies as a Group 2 site at the present time while the others are Group 1 sites. However, the profiles in Figure 7 clearly show that LF3 is shallow enough to be sensitive to multidecadal variability in the halo/redoxcline depth, in the same way as LF1 and LF1.5 are.

REVIEWER: Chapter 3.5 I would like to see a bit more discussion about upwelling e.g. in the Gotland Basin, which is likely of importance for the P cycle (e.g. Nausch et al. ECSS 2009).

AUTHORS: Section 3.5 has been restructured to include the Nausch et al. reference and to mention summer upwelling alongside winter mixing as a potential vertical transport mechanism bringing P to surface waters.

REVIEWER: Table A: Bottom water oxygen concentrations should be added. It is a bit difficult to see them in Fig. 2.

AUTHORS: These have been added.

REVIEWER: Fig. 2: What is the reason for some SO₄ scattering? Analytical errors or artifacts during sampling?

AUTHORS: We think that this is an artifact of the analytical method that we used. We currently are investigating this. However, the scatter is not an issue for the interpretations in the present paper.

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REVIEWER: Fig. 3c: Is it really possible to calculate Fe fluxes for oxic sites with your method?

AUTHORS: The calculation simply uses the observed concentration gradient to estimate a flux across the sediment-water interface. Of course, the reactivity of Fe²⁺ diffusing out of the sediments would cause it to oxidize rapidly in the bottom waters of oxic sites; but then during strongly oxic conditions there would be no flux anyway because there is no dissolution of Fe-oxides at the surface (see BY2 June in Figs. 3c and 4). Only during seasonal episodes of hypoxia do we expect Fe²⁺ to really 'flux-out' of the sediments at such sites (see BY2 Sept in Figs. 3c and 4). At such times the transport of Fe²⁺ upwards across the sediment-water interface may outweigh the rate of oxidation of Fe²⁺ in the bottom-waters, leading to a temporary accumulation of Fe²⁺ despite the presence of dissolved oxygen.

REVIEWER: Fig. 4a: Which year?

AUTHORS: Means of 1995-2009. This is now indicated.

REVIEWER: Fig. 4b: Is the upper gradient due to diffusion or oxidation of Fe²⁺? What is Fe-P, iron bound P?

AUTHORS: The definition of Fe-P is given in the methods section as being the fraction of P extracted by the citrate-bicarbonate-dithionite solution; hence, yes, iron oxide-bound P.

REVIEWER: Fig. 5a: Where are the fluxes of sites 1-7?

AUTHORS: As indicated above, the fluxes from Group 1 sites are not shown in Fig. 5 as these are influenced by seasonal variability in Fe-P dissolution. The purpose of the figure is to highlight the influence of preferential remineralization of P on ammonium: phosphate fluxes.

REVIEWER: Fig. 7: Please exchange "Corg and Porg concentration data" by "Corg and Porg contents".

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AUTHORS: Done

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