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Comment

Interactive comment on “Benthic phosphorus and iron budgets for NW-African slope sediments; biogeochemical processes and the importance of bioturbation” by K. Küster-Heins et al.

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Received and published: 28 July 2009

General comments: Extended chemical analysis of porewater and solid material from three sediment cores taken on the continental margin of NW Africa were examined to unravel the local geochemical conditions that control benthic P and Fe cycles and to identify, understand and quantify the processes that affect the (re)distribution of P in surface sediments. Applying a simple balance approach authors were able to show that particle mixing probably due to bioturbation must be considered for the interpretation of the sediment data. The study could be of interest for marine biogeochemist but need thoroughly revised before it is acceptable for publication. The major problem

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of this study is that applied methods not allow a concise discussion of the interrelating processes of benthic P fluxes like sorption, organic matter mineralization, microbial uptake, biotic or abiotic iron reduction, formation of P minerals. Also the influence of bioturbation remains vague due to the lack of any direct evidence (detection of organisms) or involvement of lab experiments. The manuscript would strongly benefit from a re-focusing of the study aims and a condensing or sharpening of the discussion section (see specific comments).

We thank the anonymous Referee for the careful and detailed reviewing of our manuscript. Despite of very helpful specific comments, in principle we do not understand the general critics on our work. We have used high quality pore water and solid phase data to describe the relationship between phosphate and iron in sediments. The comparison of such data based on the applied methods and the calculation of release and transfer rates is a successful approach for identifying and interpreting relevant biogeochemical processes. Especially for the inspected processes in our case study lab experiments are not necessarily taken into account.

Specific Comments: 1) The title of the study is a bit misleading or to promising. It should be considered that benthic phosphorus and iron budgets are just shown for three sediment cores and that biogeochemical processes and bioturbation are not investigated in detail. My suggestion is: “A simple balance approach for the interpretation of P distribution in sediment cores from NW African continental margin” or something similar.

The scope of our study was not to provide benthic phosphorus and iron budgets for the whole NW African slope sediments, therefore we include ‘for three NW African slope sediments’ in the title.

2) Although the introduction is written in a concise way it needs to be clarified if the study provides really something new for the scientific community or if it is just an evaluation of known things. The latter seems to be true.

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Of course, our manuscript presents an extensive dataset obtained in NW African slope sediments. There is no known publication that focused on a detailed discussion on phosphorus and iron cycling in fully marine deep-sea sediments. Up to now, there exists no study where results of two different methods of pore water extraction are presented, therefore their comparison should be something new.

3) P. 5377, Line 24. Since the squeezing method led obviously to substantial changes of chemical composition of pore water chemistry the data obtained by this method should be omitted. Note, that also manganese might be oxidised using the squeezing method (p. 5378, Lines 6–7). Since manganese data are not presented in this study this sentence can be deleted anyway.

Manganese data are shown in Figure 2.

4) P. 5378, Lines 4–6. For what purpose diluted samples were acidified with 1% HNO₃. Probably, not to measure total sulphur (following sentence) or to repeat nitrate analysis?! This sentence should be deleted.

The acidification is important for preservation of the pore water samples for ICP-OES analytic.

5) P. 5378, Lines 11–12. I assume that the porosity was calculated? And, please indicate the source of diffusion coefficients. “temperature- and substance-dependent” can be deleted.

We will include a reference in the revised version of our manuscript.

6) P. 5378, Lines 14–15. It might be useful for the readers to give some information about the used model Explicit. What was modelled (if steady state conditions can be assumed or not?). The cited references seem to be inadequate.

We modelled a fit to pore water iron data for site GeoB 9519 (see Figure 8). Why are the cited references inadequate? Schulz (2006) describes the Explicit mathematical solution. The program is available to be downloaded from our home page:

<http://www.geochemie.uni-bremen.de/downloads/>. Examples are published in Zabel, M. and Schulz, H.D., 2001, and by Schulz, H.N. and Schulz, H.D., 2005.

7) P. 5379, Lines 2–6. What does it mean: “. . . , good to fair correspondence was obtained for cores 9510 and 9515, . . . substantial difference for core 9518.”? Please give numbers.

The total recovery of the sequential extraction calculated as the sum of P extracted from all five steps relative to bulk P (cf. Figure 3). The sequential extraction recovers on average 99% (9510), 90% (9519) and 83% (9518) of bulk P.

8) P. 5379, lines 9–10. It should be clarified if the leaching solution was filtered before of P analysis.

We will clarify it in the method section of the revised version; leaching solutions were filtered through 0.2 μm membranfilter.

9) P. 5382, Lines 1–5. What about the precision of this method? Are there any other (non-bio)turbative processes like growing and rising gas bubbles?

The precision of the applied method is ensured. There is no evidence for additional (non-bio)turbative processes.

10) P. 5382, Line 11. Are any oxygen data (oxygen profiles) available from the sediment surface? If not, I would just delete “under oxic conditions”. Since nitrate is detectable in the upper zone “oxic” might be replaced by “aerobic” alternatively.

Oxygen penetration is estimated to be about 1 cm (Wenzhöfer, F. and Glud, R.N., 2002. Benthic carbon mineralization in the Atlantic: a synthesis based on in situ data from the last decade. DSR I 49(7): 1255-1279). We will replace it in the revised version.

11) P. 5382, Line 13. “The total release of P by this process is hard to quantify”. This also holds true for the other mentioned P releasing processes below. I recommend condensing the whole section 4.1 substantially. All speculative parts should be deleted,

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for instance the last para in this section: “Our data clearly indicate . . .”. It was stated that sulphate reduction can be neglected (p. 5383, Lines 4–5). Are any sulphate data available for the overlying bottom waters? If so (net) sulphate consumption rates can be calculated by the second derivation of sulphate concentration gradients or by using the computer program Profile V1 (Berg, P., N. Risgaard-Petersen, and S. Rysgaard. 1998. Interpretation of measured concentration profiles in sediment pore water. *Limnology and Oceanography* 43(7):1500–1510.). Since fixation of Iron by sulphide is argued later in the text (p. 5386, Line 13) there must be sulphate reduction or is sulphide coming from deeper layers?

In principle correct, but the only possible way is to determine release rates by applying Fick’s First Law of diffusion. Therefore our calculations are essential and are indicative and not speculative. Results from the adjacent gravity core 9519 indicate the SMT below 7 m sediment depth, sulphide is released in deeper layers. Therefore the sulphate gradient in the upper 20 cm is low and can be neglected close to the sediment surface. We know the computer program V1, but bottom water sulphate data are not available.

12) P. 5384, Line 28. Please specify “moderate time scales”.

Moderate time scales= several 1000 years.

13) P. 5385, Line 1. What a decrease of Corg could be expected in case that bioturbation or other mixing processes are absent, above all at this low levels? Can be also assumed that rising of gas bubbles is of importance in investigated sediment layers (e.g. M.P. Haeckel, B. Boudreau and K. Wallmann, Bubble-induced porewater mixing: a 3-D model for deep porewater irrigation, *Geochim. Cosmochim. Acta* 71 (21) (2007), pp. 5135–5154.)?

We do not understand this question. However, the release of organic P could be easily transferred to the decrease of Corg by using C:P ratios (Table 6). Because this calculation base on diffusive flux rates results are independent of mixing processes. Gas bubbles can definitely be excluded.

14) Section 4.2. This discussion is a bit confusing or long-winded. Please condense and highlight the main points. In particular, p. 5385, Lines 3–23 needs to be revised in order to increase the readability of the text.

We will revise it.

Technical Corrections: P. 5375, Line 9. Replace “P-cycle” with P cycle. Please check also the rest of text to delete the dashes (e.g. P. 5375, Line 19; Line 28, P. 5376, Line 4, etc.). We will replace it in the revised version of the manuscript.

P. 5376, Line 23 and also in the rest of the text the unit wt% was given for matter contents. Probably it means % of dry matter?! Wt% (mass percentage) denotes the mass of TOC in a sediment sample as a percentage of the mass of the entire sample of dry sediment.

P. 5377, Line 3. Write “NW Africa” instead of “NW-Africa”, see also the title. We will replace it in the revised version of the manuscript.

P. 5377, Line 8. Write “in situ”. We will write “in situ” in the revised version.

P. 5377, Line 11. Write “squeezing” instead of “squezzing”, please check also the rest of the text, e.g. p. 5378, Line 6 and Figure 2 (but squeezer data should be deleted anyway), We will correct it in the revised version.

P. 5377, Line 17. Delete concentrations behind “alkalinity”. We will delete concentration.

P. 5377, Line 18. “retrieved” might be replaced with “gained”. We will replace ‘retrieved’ with ‘gained’ in the revised version.

P. 5380, Line 6. Values should be rounded: 23–26 and 30–39. We will round the values in the revised version.

P. 5380, Line 24. The numeration of single fractions needs to be changed: first: “NH₄Cl-extractable biogenic P”, then “oxide-associated P”, . . . We will change the

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numeration.

Figures and Tables are nicely drafted so far, but it must be clarified for Table 4 if P concentration is related to dry sediment. Figure 2: solid lines were used instead of dashed line for P and Fe concentration profiles, and please indicate the charge of the species: SO_4^{2-} , NO_3^- , etc.. I assume that phosphate is present in the protonated form in your system; SRP (soluble reactive phosphorus) might be an alternative? Concentration in Table 4 is related to dry sediment; we will include it in the revised version. We will change the figure caption for Figure 2, and include the charge of the species.

Interactive comment on Biogeosciences Discuss., 6, 5373, 2009.

BGD

6, C1287–C1293, 2009

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