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Comment

# ***Interactive comment on “Diagenesis and benthic fluxes of nutrients and metals during experimentally induced anoxia in the Gulf of Trieste (northern Adriatic Sea)” by N. Koron et al.***

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## General comments

Koron et al. use a benthic chamber experiment to investigate the effect of controlled imposition of anoxia on biogeochemical processes in bioturbated sediments of the Gulf of Trieste. The experimental approach involves bulk solid-phase and porewater sampling before, during and after controlled intervals of anoxia. The field data are complemented by a reactive transport model, which is used to calculate diffusive fluxes and to infer the response of various transformations to the changes in redox conditions. The authors observe rapid dissolution of surface-sediment Fe and Mn oxides in the

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early stages of anoxia, as suggested by porewater Fe and Mn accumulation in the first month of the experiments. The solid-phase data imply changes in the relative degradation rates of C, N and P in response to anoxia. Most notably, after 2 months of anoxia the Corg/Porg ratios throughout the upper sediment column are a factor >2 higher than before the start of the experiment, suggesting preferential remineralisation of P from organic matter under anoxia. I appreciate that this is one of several papers reporting related aspects of the same project, and the fundamental approach of the project – to impose anoxia in coastal sediments and monitor various aspects of the system's response – is exciting. However I feel the division of data has left this manuscript lacking some important components which are required to support the authors' conclusions. I also raise a number of issues concerning the modeling approach, and there are additional aspects of the discussion which require clarification. Finally, I would urge the authors to divide the discussion more systematically in order to make the manuscript more accessible for readers, perhaps using subheadings. I hope the authors are able to provide suitable responses to my comments in order to improve the manuscript for publication in Biogeosciences.

### Specific comments

- To my mind, a number of important data and descriptive/interpretive information are missing from the manuscript (listed in comments 1-5). Where possible, these should be provided.

1. The mixed layer depth (L) as a consequence of bioturbation should be stated in Section 2.1 as this impacts on interpretation of the solid phase and pore water profiles.
2. The sensor data from the experiment with the EAGU would be very useful, as would any time-series which are available for the seasonal evolution of bottom-water oxygen close to the site. I could not find the referenced Riedel et al., 2013 paper in BGD but I presume that study will present these data. It is important to show (at least for one experiment) that anoxic conditions were achieved once the chamber was closed, and that

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oxic conditions were re-established during the recovery period. I note that two of the recovery periods were programmed in the late summer (August, September). In section 2.1 the authors state “A density gradient in late summer can result in bottom water layer hypoxia and even anoxia (Faganeli et al., 1985)”. Can the authors guarantee that oxic conditions returned during these recovery periods?

3. Is there any quantitative information about the recolonization by bioturbating organisms during the recovery intervals?

4. Because of the complexity of sedimentary diagenesis, pore water and solid-phase datasets need to be as complete as possible to allow confident interpretations of the processes controlling the observed profiles. In a study of the diagenetic response to imposed anoxia, pore water sulfate and solid-phase Fe and Mn are important variables to measure, as these represent the electron acceptors most likely to become active in organic matter breakdown in the absence of oxygen, plus they are involved in various secondary redox reactions. I notice that Metzger et al. (this issue) present sulfate data. Were these the same incubations and could the data be presented here also? Was solid-phase Fe and Mn measured at all (e.g. as in Ogrinc and Faganeli 2006)? Finally, although the authors measured nitrate, and discuss the results, these data are not presented. I would urge the authors to present the nitrate data if they wish to discuss it.

5. One of the clearest outcomes of the experiment is the enrichment of Corg/Porg throughout the sediment column after 2 months of anoxia. It would be very interesting to know what happens to Corg/Porg after one year of anoxia, but this data is not shown and no reason is given for its absence. Please address this.

- The following comments (6-8) concern the reactive transport model and the interpretations derived from its results:

6. The authors state that bioturbation after 1 year of reoxia may explain some offsets between the model and field data (Section 3.4). This implies that bioturbation was

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not imposed in the model during normoxia and reoxia. If so this needs to be explicitly stated, because it limits the ability of the model to capture the processes taking place in the sediments at these times.

7. The model also does not describe sedimentary and porewater P transformations in sufficient detail to capture the observed patterns in the pore water profiles. Most importantly, there is no description of the interaction between P and Fe-oxides and its redox sensitivity. Instead, PO<sub>4</sub> adsorption to unspecified phases is calculated using a simple linear isotherm. Hence, the subsurface pore water PO<sub>4</sub> peaks observed in many of the profiles are simply missed by the model.

8. Considering the above two points, I have major reservations about using the model to calculate diffusive fluxes, for all species, but especially for PO<sub>4</sub>. If the authors calculated PO<sub>4</sub> fluxes from the raw data, they may see large fluxes at times of pronounced subsurface phosphate peaks which would alter the conclusions of the paper. These peaks are not only observed during the '1 yr recovery' experiment as implied at the end of Section 3.2 and thus cannot be explained only by bioturbation. PO<sub>4</sub> peaks are seen in all profiles except for 'normoxia' and '1 yr anoxia'. I suspect these are related to the dissolution of Fe and Mn oxides at various depths as the redox zonation changes in response to imposed anoxia.

- The remaining comments (9-12) concern various other aspects of the discussion which require clarification.

9. Page 11741, Lines 22-26:

"sedimentary Corg/Norg ratios and Corg/Porg ratios generally increase with depth in surface coastal marine and estuarine sediments (Hedges and Keil, 1995). This is usually considered as an indication of preferential mineralization of organic nitrogen and phosphorus in sediments and that the more labile fractions have lower Corg/Norg and Corg/Porg ratios than the bulk sedimentary OM (Hedges and Keil, 1995; Ingall and Jahnke, 1997)"

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I checked the Hedges and Keil reference and found no mention of C/N and C/P relationships, while Ingall and Jahnke deal only with respiration rates and benthic P fluxes. In fact, sedimentary C/N is usually used as a determinant of organic matter sources (e.g. Müller and Mathesius, *Paleo3*, 145, 1999), and the diagenetic effect with increasing sediment depth is largely controlled by resorption of  $\text{NH}_4^+$  and organic nitrogen by clay minerals (Müller, *GCA*, 41, 1977). Meanwhile, variable sedimentary C/P is indicative of redox-dependent cycling of P by bacteria, as stated in the Ingall and Jahnke reference and investigated in more detail recently by Steenbergh et al. (*L&O*, 56, 2011). So focusing on the relative degradation rates of P or N-rich compounds in a discussion of sedimentary C/N and C/P does not tell the full story.

10. Page 11743, Lines 7-15:

“The results clearly show Fe and Mn reduction processes since the concentrations of dissolved species notably rise. . . . These processes are energetically more favourable than sulphate reduction (Froelich et al., 1979) and even though the DET results (Metzger et al., 2013) indicate that sulphate reduction is the preferential anaerobic microbial process in early diagenesis in these coastal sediments, Fe and Mn reduction can proceed in some microniches.”

The authors should make clear that the reduction of Fe and Mn oxides may proceed coupled to organic matter remineralization or  $\text{H}_2\text{S}$  oxidation. Hence, it is not only the energetic favorability of dissimilatory Fe/Mn oxide reduction which will determine the porewater profiles of Fe and Mn, if  $\text{H}_2\text{S}$  is present. I suspect that reaction between Fe/Mn oxides and  $\text{H}_2\text{S}$  following vertical migration of the sulfate reduction zone may be the cause of the porewater Fe, Mn and  $\text{PO}_4$  peaks observed in the data.

11. Page 11743, Lines 20-25:

“In anoxic conditions, Ca and Mg pore water concentrations indicate lower carbonate dissolution or even carbonate precipitation as previously postulated for surface anoxic sediments of the Gulf of Trieste (Cermelj et al., 2001; Ogrinc et al., 2003).”

What mechanism do the authors propose triggers carbonate precipitation under anoxia... increased alkalinity due to enhanced sulfate reduction? This should be discussed in a bit more depth.

12. Page 11744, Lines 4-8:

“When oxic conditions reappears P precipitates quickly as authigenic carbonate fluorapatite,  $\text{FePO}_4$  or it is adsorbed onto Fe-hydroxides (Ogrinc and Faganeli, 2006)”

The data presented in this study are insufficient to discuss carbonate fluorapatite precipitation, and especially changes in its rate upon redox transitions. I am aware that the Ogrinc and Faganeli (2006) study shows that porewaters at this site are supersaturated with respect to carbonate fluorapatite, but there is no sequential extraction data for authigenic P phases in that study or the present manuscript. By what mechanism should the rate of apatite precipitation change upon redox transitions?

Technical corrections

In general, I would recommend to introduce more structure to the discussion, maybe including subheadings to deal clearly with each topic.

In the description of the model (Page 11736, Lines 9-10 and 19-24) some symbols are missing. Eg.,  $\omega, \beta$ .

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