

# ***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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Received and published: 31 October 2013

We appreciate and accept the criticism of both referees and have revised the manuscript accordingly. The suggestions of the referees have improved a quality of our paper. All changes are marked red in the original article. We hope that the paper is now appropriately corrected and suitable to be published 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

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and pore water profiles.

The following sentence was corrected on page 5, lines 1-2: "Sediment in the southern part of the Gulf is composed mainly of silty sand that is high in biogenic carbonate, populated mostly by brittle stars, sponges and tunicates and actively bioturbated by polychaetes and bivalves down to the depth of 10 cm (Ogrinc and Faganeli, 2006)."

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 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).

The data are presented by Metzger et al. (this issue). The following sentences were added on page 6, lines 4-6 to the reference of the data: "Temporal O<sub>2</sub> variations are reported by Metzger et al. (this issue) where it is evident the decrease in O<sub>2</sub> concentrations from initial values of 190  $\mu\text{mol l}^{-1}$  to values close to zero after 7 days."

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? Yes. The oxic condition was reestablished during the recovery periods. This was assured by the exchange of oxygenated water present at the sea bottom carefully removing the benthic chamber.

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

Unfortunately, there is no quantitative information about the recolonization by bioturbating organisms during the recovery intervals.

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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?

Since these are the same incubations, we could not duplicate the datasets. However the following sentence was added to refer to sulfate data presented in Metzger et al. (this issue) on page 10, lines 20-22: "Vertical distribution of NO<sub>3</sub><sup>-</sup>, NH<sub>4</sub><sup>+</sup>, PO<sub>4</sub><sup>3-</sup> and dSi concentrations during incubation experiments are presented in Fig. 2 and 3, while sulfate concentrations are presented by Metzger et al. (this issue)."

Was solid-phase Fe and Mn measured at all (e.g. as in Ogrinc and Faganeli 2006)?

The solid-phase Fe and Mn were not measured. The data are reported by Ogrinc and Faganeli (2006) for the same sampling site.

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. Vertical distribution of nitrate concentrations is now presented in Figure 2.

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.

Unfortunately, these measurements were not performed and thus not presented.

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

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reoxia may explain some offsets between the model and field data (Section 3.4). This implies that bioturbation was 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.

This is now described on page 12, lines 17-22: “In diagenetic models bioturbation could be treated as a diffusion-like process and thus the biodiffusional coefficient ( $D_b$ ) should be used in diagenetic model.  $D_b$  coefficient depends on the infauna size and distance between burrows (Aller, 1982). Since we have no quantitative information about the recolonization by bioturbating organisms during the recovery intervals, it was not possible to determine the  $D_b$  coefficient and include it into the diagenetic model.”

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,  $PO_4$  adsorption to unspecified phases is calculated using a simple linear isotherm. Hence, the subsurface pore water  $PO_4$  peaks observed in many of the profiles are simply missed by the model.

We agree with the reviewer comments and corrected the text accordingly. The corrected text is included on page 12, lines 22-26: “Another process that could influence the  $PO_4$ - distribution in pore water and is not included in the model is the interaction between P and Fe-oxides and its redox sensitivity. Higher  $PO_4$ - peaks were observed in all profiles except for normoxia and 10 months anoxia indicating dissolution of P-bearing Fe oxyhydroxides at various depths as the redox zonation changes in response to imposed anoxia.”

8. Considering the above two points, I have major reservations about using the model to calculate diffusive fluxes, for all species, but especially for  $PO_4$ . If the authors calculated  $PO_4$  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

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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.

Now the diffusive fluxes were calculated also from the raw data and included in Table 2. The following sentences were added on page 8, lines 12-15: "Diffusive fluxes of NH<sub>4</sub><sup>+</sup>, PO<sub>4</sub><sup>3-</sup> and dSi across the SWI were estimated from the concentration gradient between bottom water and the uppermost pore water sample (0-0.25 cm depth from cores sliced for pore water extraction by centrifuging) using Eq. 1."

The comparison between fluxes was also performed. Surprisingly, the comparison between modeled and measured PO<sub>4</sub> concentrations appeared reasonably good, except in 2 cm layer in 9 days anoxia and 1 month recovery (could be also an analytical artefact) and, obviously, in 1 year recovery experiment in heavily bioturbated sediments. We think that the calculated diffusive fluxes from diagenetic equation could better represent the fluxes than simply use of the First Fick's Law and rather coarse (insufficient) resolution of pore water gradients (0.5 or 1 cm) near the sediment-water interface. The following text was added on page 13, lines 11-29: "The comparison between modeled diffusive fluxes and those calculated from the concentration gradient between bottom water and uppermost pore water sample (0-0.25 cm) using Fick's first law was performed (Table 2). It was found that PO<sub>4</sub><sup>3-</sup> diffusive fluxes calculated from the raw data were not comparable with the model ones and usually always higher except in normoxia and 10 months anoxia experiments. Higher fluxes were also observed for NH<sub>4</sub><sup>+</sup> in normoxia, 9 days and 2 months anoxia experiments indicating more pronounced release of NH<sub>4</sub><sup>+</sup> during remineralization as described by the model. The highest discrepancy in dSi fluxes was observed in 10 month anoxia experiment where the model fluxes are almost 4 times higher compared to the fluxes calculated from the gradient between bottom water and uppermost pore water sample. Although higher

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NH<sub>4</sub><sup>+</sup>/PO<sub>4</sub><sup>3-</sup> flux ratios were observed with the raw data, the ratios exhibit the same pattern if different experiments are compared. A marked NH<sub>4</sub><sup>+</sup>/PO<sub>4</sub><sup>3-</sup> flux ratio was observed between different anoxic experiments. The highest ratio of 540 was observed in 10 month anoxic experiment followed by 1 month and 9 days anoxic experiments (ratio of 44 and 11, respectively). The opposite trend was observed in Fe fluxes with the highest flux of 16.6 μmol m<sup>-2</sup> day<sup>-1</sup> observed in 9 days anoxic experiment (Table 2). The lowest NH<sub>4</sub><sup>+</sup>/PO<sub>4</sub><sup>3-</sup> flux ratio was observed in 2 months anoxic experiment in parallel to the observed influx of Fe in sediments. These data indicate the importance of simultaneous release of PO<sub>4</sub><sup>3-</sup> and dissolved Fe at the transition from oxic to anoxic conditions observed in the 9 days anoxic experiment, while in other anoxic experiments OM remineralization influence the rate of PO<sub>4</sub><sup>3-</sup> generation.

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)” 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 NH<sub>4</sub><sup>+</sup> 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

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tell the full story.

We agree with the reviewers comments. The reference was not properly used and was deleted from the manuscript. The following sentences add a more precise discussion related to redox-dependent cycling of P by bacteria on page 14, lines 14-22: “The utilization of these compounds by sulfate reducing bacteria then results in the mineralization of sedimentary OM (Burdige, 2002). Consequently, the sedimentary Corg/Norg and Corg/Porg ratios generally increase with depth in surface anoxic coastal marine and estuarine sediment (Blackburn and Henriksen, 1983; Ingall and Jahnke, 1997). This is frequently considered as an indication of preferential mineralization of organic nitrogen (Macko et al., 1993) and phosphorus (Ingall and Jahnke, 1997) as well as a consequence of limited ability of prokaryotes to accumulate phosphorus in anoxic conditions and slow microbial degradation and enhanced preservation of Corg in anoxic sediments (Ingall et al., 1993; Steenbergh et al., 2011).”

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 H<sub>2</sub>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 H<sub>2</sub>S is present. I suspect that reaction between Fe/Mn oxides and H<sub>2</sub>S following vertical migration of the sulfate reduction zone may be the cause of the porewater Fe, Mn and PO<sub>4</sub> peaks observed in the data.

We agree with the reviewer and corrected the text accordingly. The following sentence was added on page 16, lines 5-6: “In addition, the fast abiotic reactions between Fe and Mn oxides and H<sub>2</sub>S can produce additional Fe and Mn in pore waters (Yao and

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Millero, 1993;1996).<sup>^</sup>

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.

Sulfate reduction is the main process influencing carbonate precipitation under anoxia. It was added on page 16, line 11.

12. Page 11744, Lines 4-8: "When oxic conditions reappears P precipitates quickly as authigenic carbonate fluorapatite, FePO<sub>4</sub> 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.

No sequential extraction for authigenic P phases was performed in this and any of the mentioned study. This extraction (SEDEX, Ruttenberg1992) can be useful bearing in mind that this scheme, like all sequential schemes, is operationally defined and needs corroborating evidence to identify separately quantified sedimentary P reservoirs (Ruttenberg, 2004) because different reservoirs can overlap. The following sentences were added on page 16, lines 28-31: <sup>^</sup>In this context, sequential extraction (Ruttenberg, 1992) would help to quantify the different form of P bearing in mind that this scheme, like all sequential schemes, is operationally defined and needs corroborating evidence to identify separately quantified sedimentary P reservoirs (Ruttenberg, 2004).<sup>^</sup>

By what mechanism should the rate of apatite precipitation change upon redox transi-

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tions? The mechanisms involved in marine precipitation and subsequent concentration of apatite are not completely understood. Experimental studies of authigenic apatite formation under controlled conditions documented nucleation of apatite on calcium carbonate, apatite formation in sea water and effect of carbonate substitution on apatite solubility (Ruttenberg, 2004). Two processes seem important in this context (Slomp et al., 1996 a; b) in the low sedimentation environments, (like in the Gulf of Trieste), where most organic mineralization occurs at the sediment-water interface (Cermelj et al., 2001): the release of phosphate from decomposing organic matter and adsorption onto Fe-hydroxides precipitating in the oxidized sediments and subsequent release of phosphate during the reduction of Fe-hydroxides in anoxic sediments which is then included in precipitating apatite. In reoxidation the fast lowering phosphate concentrations can be due to apatite and FePO<sub>4</sub> formation and adsorption onto Fe-oxyhydroxides (Ogrinc and Faganeli, 2006). Differences in precipitation kinetics were not studied. In addition, the direct and indirect role of microbes may be important for apatite precipitation (Krajewski et al., 1994).

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

The discussion is now more structured by adding more subtitles.

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

Symbols are now included in the text (page 8, lines 8 and 24)

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Interactive comment on Biogeosciences Discuss., 10, 11729, 2013.

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