

## ***Interactive comment on “Artificially induced migration of redox layers in a coastal sediment from the Northern Adriatic” by E. Metzger et al.***

**E. Metzger et al.**

edouard.metzger@univ-angers.fr

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Review of “Artificially induced migration of redox layers in a coastal sediment from the Northern Adriatic” (E. Metzger et al., Biogeosciences Discussions, 2013) by Peter Kraal (Department of Earth Sciences – Geochemistry, Faculty of Geosciences, Utrecht University, The Netherlands).

General: With great interest I have read “Artificially induced migration of redox layers in a coastal sediment from the Northern Adriatic” by E. Metzger et al. The authors present geochemical data and visual observations that capture the benthic (redox) evolution of the Gulf of Trieste seafloor over a period of 10 months, using a benthic chamber setup that isolates part of the seafloor and thus induces oxygen depletion. Geochemical data consist of high-resolution pore-water profiles of Mn(II), Fe(II), SO<sub>4</sub>(-II) and alkalinity.

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Visual observations include qualitative dissolved sulfide analysis using sulfide-sensitive tape (coloration), and images of the seafloor and benthic chambers over time. The results show oxygen depletion, migration and mortality of macrofauna, and upward migration of redox fronts (Mn(II), Fe(II), SO<sub>4</sub>(-II)) during the incubation experiment. The study is well-designed and the data seem robust. The data nicely illustrate the sequence of processes that are associated with the development of anoxic benthic conditions; the “migration of redox zones” follows well-established understanding of anoxia-driven sedimentary geochemical changes. What makes the study of interest in my opinion is the combination of geochemical analyses and visual observations (e.g. faunal mortality) in a time-series experiment, and the interesting results regarding sedimentary sulfide sources (the importance of faunal decay at the surface sediment compared OM decomposition deeper in the sediment). The manuscript is generally well-written, but the order in which conclusions and the supporting data are presented in the discussion section is a bit awkward: many sentences leave the reader pondering how a certain conclusion came about, with the supporting evidence being presented afterwards without connecting phrases. But this is mostly a matter of wording and order. "We thank the reviewer for these very positive statements and for the precise comments on the discussion that helped to reorganize our findings and reasoning. Another shortcoming I felt was the lack of solid-phase data to support the suggestions about the role of FeS and Fe (oxyhydr)oxides (which can be determined with relatively simple geochemical analyses), but I guess there is only so much one can do for a study. This point is discussed further within the comments about the Discussion section."

Furthermore, I am interested to know whether the authors think that the collected high-resolution profiles may enable them to perform flux calculations using Fick's Law? This might provide an interesting additional illustration of the geochemical evolution of the mobility of dissolved species during incubation; the vertical migration of the Fe and Mn profiles will definitely strongly affect calculated fluxes. "Actually we ran “Profile” in order to get those fluxes. But after reflexion, we thought that, given the lateral heterogeneity and the fact that the chamber was not precisely designed to quantify benthic

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fluxes as the referee 2 points out, the results would not be very significant and could induce potential readers to take them as a reference for comparison, which would be a mistake. Nevertheless, here are the results for Mn: DET Name Incubation time (days) Flux (nmol cm<sup>-2</sup> s<sup>-1</sup>) N18 0 -1.7 10<sup>-5</sup> N47 0 -0.09 10<sup>-5</sup> A7-5 9 -1.3 10<sup>-5</sup> A7-10 9 -3.3 10<sup>-5</sup> AM-53 29 -0.39 10<sup>-5</sup> AM-10 29 -0.62 10<sup>-5</sup> AY-53 330 -1.8 10<sup>-5</sup> AY-22 330 -0.05 10<sup>-5</sup> The results show a lot of heterogeneity and, ultimately, the qualitative description of the profiles reveals more about the vertical migration of the Mn redox zone than the efflux at the interface."

Overall, I support publication of this work, provided the authors sharpen the discussion section. Below I have included specific comments to the manuscript. PLEASE NOTE THAT THESE COMMENTS ARE ALSO AVAILABLE AS A MORE READER-FRIENDLY PFD ATTACHMENT

Abstract p1,L18. transient anoxic conditions "done"

p1,L20. associated with "done"

p1,L26. Is alkalinity (why capital A?) a redox-sensitive species? "In anoxic sediments, HS<sup>-</sup>, NH<sub>3</sub>, and several other redox species contribute to alkalinity. In that sense alkalinity can be considered as a redox-sensitive species."

p1,L28. anoxia was established "done"

p1,L29. Specifically mention the oxidation mechanism to explain the rusty color formation. "The two first sentences of this paragraph were rephrased including more details about oxidation of Mn and Fe. See text below: "After 7 days, anoxia was established at the bottom waters within the chambers. Mn and Fe started diffusing towards the anoxic water column until they reached upper oxygenated levels. Being reoxidized, Mn and Fe precipitated, giving a rusty color to the seafloor" p1,L30. Decomposition of macro-organisms at the sediment-water interface done"

p1,L31. What is "important" production? "This is a good point. The sentence was

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rephrased to specify that sulfide was recorded up to the roof of the chambers as follows: “Decomposition of macro-organisms at the sediment-water interface generated a production of sulfides within the entire height of the chamber, leading to a downward flux of sulfide into the sediment, where sulfides were quickly oxidized by metallic oxides or precipitated as FeS.”

p1,L32. downward flux of sulfide into the sediment "done"

p2,L1. sulfide was below detection "done"

p2,L4. residence time in the water column "done"

p2,L5. Because you have no solid-phase data, I would suggest using “availability” of (reactive)Fe. “Content” implies you will link amount of Fe to sulfide concentrations. "Agreed and changed"

## 1. Introduction

In general (for the whole manuscript), be consistent with elements, introduce them with their full name and then use the abbreviation from then on. Currently, full names or abbreviations appear in various places in the document. p2,L10. mechanisms or factors instead of “parameters” "ok"

p2,L12. associated with (mass) mortality "ok"

p2,L13. In most cases "ok"

p2, L14. water circulation is restricted "ok"

p2, L14. residence times of what? "Of water. . ."

p2, L14. The particular morphology of semi-enclosed basins "done"

p2, L16. Aren't estuaries often somewhat restricted? Or are the specific examples not restricted in any way? Currently, it seems you are saying estuaries by definition are not restricted. "The authors agreed that estuaries are not open oceans. However,

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the examples cited here are quite large settings with important water exchanges with the watershed and the ocean and are situated in temperate waters. The fact that, locally and temporally, the residence time and oxygen demand would increase enough to consume drastically dissolved oxygen is less likely than in a lagoon, where conditions for oxygen depletion are more common and can be better understood. The sentence was slightly changed as follows: "However, this phenomenon is not exclusive to semi-enclosed settings. Many estuaries where residence time of water is supposedly relatively short also show severe hypoxia" The paragraph shows a sort of progression from enclosed settings to open ones (lagoons-estuaries-coastal seas)"

p2, L19. furthermore instead of "also". Furthermore, continental seas such as the Baltic Sea and Black Sea, and the Gulf of Mexico... "Ok"

p2,L20. Explain "progression of anoxia", please be more specific. "Changed by "increase of occurrence and geographic extent of anoxic events"

p2, L21. the evolution of hypoxic events in the North Sea (and where in the North Sea?) "changed and completed by "In the Oyster Grounds (central North Sea)"

p2, L24. a decrease in anoxic events has been reported since the 1990s "done p2, L26. phosphorus "changed

p2,L28. First phosphorus, now phosphate, please be consistent. "changed"

p2, L28. Again, what is "important"? Significant, large, appreciable...? "Gallicism. "Large" was chosen. Going into details in the text seems not to be relevant "

p2, L28. In what form is it available in the sediment? "Mainly as shellfish pseudo faeces. The Thau lagoon produces about 20% of French shells and the mode of production is quite unique with suspended rods where shells (mainly oysters) are fixed. This method increases shell growth by increasing the efficiency of filtering but leads to the concentration of pseudo faeces and the clearing of water column (enhancing macrophyte primary production at the bottom). Large stocks of nutrients are cumulated in

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some areas of the lagoon, ready to be mineralized. When water circulation weakens, sulfide starts diffusing into the water column (see Metzger et al, 2007; Metzger et al, 2013) "

p2, L29. the Thau Lagoon "changed"

p2, L29. What does "summer conditions" mean? "(i.e., increased temperature and lack of wind)", which leads to less water circulation and stratification of the water column

p2, L30. Phosphorus "ok"

p3, L5-6. Include a transition between the paragraphs. What is the open question you are addressing? After all the info, what curiosity drove the collaborative Adriatic project in general and this manuscript in particular? "The first sentence of the paragraph was rewritten as follows: "Aiming to better understand how anoxia affects benthic macrofauna and meiofauna survival and how fast the impacted zone regains a new ecological equilibrium, a series of in situ experiments was conducted in the Northern Adriatic (Mediterranean Sea), an area repeatedly affected by seasonal hypoxia." Another sentence was added before the listing of our aims at the end of the introduction in order to clarify better those objectives: "Benthic meiofauna and foraminifera preferentially inhabit the top layer of the sediment. However, these organisms partly live in microhabitats within the sediment, that correspond to the major redox zones. Some species, with a deep infaunal microhabitat, are able to live under anoxia (Jorissen, 2003; Schönfeld, 2001). Sulfide, however seems to be a barrier for vertical migration of foraminifera (Moodley et al., 1998). Our hypothesis was that during our experiment, not only the pore water chemical composition would change, but the vertical distribution of meiofauna as well"

p3, L11. delete "this issueb" "all occurrences of "this issue" were changed by "2013"

p3, L14. favoring vertical separation between redox sensitive elements done p3, L15. iron (Fe) and manganese (Mn) (oxyhydr)oxides (surface sediments often contain fresh

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hydrous ferric oxide rather than ferric oxides such as goethite and hematite), "indeed" and use element abbreviations from here on. "done"

p3, L18. What does "vertical extent of their diffusion" mean?

p3, L19. elements that are not redox-sensitive. "Cadmium is not redox but redox-sensitive because it is influenced by redox conditions, so we retained the original wording Also, Cd may not be a good example as mildly and strong reducing sediments show Cd enrichments as it precipitates as CdS (and perhaps coprecipitates with FeS). Several studies showed that cadmium can be remobilized when redox oscillation occurs (e.g. Gobeil et al, 1987, 1999; Point et al, 2007; Metzger et al, 2007. . .). We agree that, in the case of anoxia, Cd would be buried as CdS or coprecipitated with FeS, but before sulfate reduction occurs, cadmium can be mobile in anoxic waters. We wanted to illustrate that anoxic events would impact trace metal mobility in one sense or another during the event or the recovery from it."

p3, L20-23. Diffusive release of elements does not automatically confirm "changed vertical succession of redox zones", it shows reductive dissolution. Either the authors need to rephrase and make it simpler, or include the data that really confirm such a changed succession. "The term "succession" is unfortunate. We meant here that the vertical extent of redox zones changed during the experiment. Such change led to a successive release of reduced species in the overlying water. "

Also, is the succession changed by changing redox conditions, or just the vertical extent of redox zones? "Of course reductive dissolution explains the release of reduced compounds to the porewater, but the disappearance of oxic compounds allows their diffusion up to the overlying waters, enhancing benthic fluxes."

p3, L24-25. Can bioturbation perhaps also enhance exchange between surface sediment and water column, increasing the release of reduced species into the water column? "In general, bioturbation favors oxygen penetration into the anoxic sediments,

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resulting in an oxidation of reduced compounds such as pyrite. However, the presence of organisms can sometimes create a rapid transfer of reduced porewaters to the surface, leading to the release of reduced compound before they have a chance to be oxidized. Some studies showed that diffusive oxygen uptake increased because of bioturbation (e.g. Lagauzère et al, 2011). "

Also, as bioturbation is not part of the study focus, why include this sentence in the introduction? It gives the stage to questions that are not addressed. "Then we agree with the reviewer that this question is not really in the scope of our study, so the sentence was deleted."

p3, L26. When do seasonal hypoxic conditions occur? I assume summer, but it's good to be explicit. "Late summer in general. Added."

p3, L27. How do they impact the recycling of metal oxides and bioturbation? It may be somewhat obvious, but needs to be mentioned. Only a little bit of extra info is needed, but it is important to guide the reader. Again, be explicit. p3, L29. How are the fisheries harmful? And how does the impact (which is not described) highlight the vulnerability, what is the link? Is "highlight" really the appropriate term here, maybe "illustrate" is more appropriate? "The sentence was rephrased to give more information: "Moreover, the region is impacted by intense trawl-fishing activities, enhancing the vulnerability to benthic perturbation"

p3, L31. at 24 m water depth "done"

p3, L33. during a series "done"

p4, L5. for the studies [...] that were conducted within the larger collaboration we simplified the sentence here as follows: "to provide the geochemical constraints for the studies focusing on the faunal response to anoxia"

## 2. Materials and Methods

p4, L11. check spaces in notation geographic location "done"

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p4,L11. This site was selected because of a minimal risk of damage to equipment at this location by commercial fisheries. "changed"

p4, L14. How can a shoal be “deep”? Please explain? "A shoal is a relief of the seafloor. This means that the average depth around it is much deeper than 100 m. I think the value is 300 m on the northern side and down to 1000 m on the southern side" p4, L14. longer residence time, and of what? Of water. Added.

p4, L19. the benthic macrofaunal community "done"

p4, L23. mostly diatoms "done"

p5, L2. What does the acronym EAGU stand for? "Experimental Anoxia Generating Unit. Added"

p5, L3. guarantee optimal isolation "done"

p5, L4. the sidewalls were pushed "ok"

p5, L15. Here sulfide sensors are mentioned, but the data are not featured in the manuscript? Am I missing something? Because concentrations were below detection for the whole experiment? Would it be worthwhile to show the flatline sulfide profiles in Fig. 1, to further emphasize the lack of measurable sulfide in the water column? "Indeed, sulfide was below detection for the whole experiment. A flatline over the x-axis does not bring much. A sentence was added in the results section to mention that sulfide was always below detection limit"

p5, L24. 1.5 % w/w "done"

p6, L5. in the chambers as well as the precise location of the sediment-water interface "replaced"

p6, L17. 0.01 mol L<sup>-1</sup> (personal preference, I guess) "we agree to change"

p6, L31. Can the authors provide quantitative information on the accuracy and preci-

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sion, or relative standard deviation or something similar? "included."

p7, L1. 0.01 mol L<sup>-1</sup> (personal preference, I guess) "done"

p7, L15. sodium hydrogen carbonate done

### 3. Results

p7, L17. No mention of the probe sulfide data? "A sentence was added: "Sulfide concentration for both probes was below detection limit during the whole experiment (0.3  $\mu$ mol L<sup>-1</sup>)."

And, as mentioned, I think it might be useful to include flux calculations for Fe and Mn for the different sampling points as well, in light of the nice high-resolution data obtained in this study. Of course, there are drawbacks to calculated fluxes, but despite these the comparison of fluxes calculated in the same manner may be informative on redox behavior of Fe and Mn around the SWI? Perhaps the authors have a strong preference to omit such calculations, in which case I am very keen to learn their arguments. "This point is discussed above, directly after the referee's overall comment "

p7, L21. Fig. 1 "done"

p7, L27. The lines are mixed up in the caption of Fig. 1. "The problem lies not in the caption. The dotted line corresponds to the probe placed farther from the interface (5 cm). The mistake was within the text. Corrections were made."

p8, L4. Remove extra space between "experiments." and "Results" "done" p8, L7. I would suggest that the authors use generic probe names that are less confusing to the reader (e.g. Normox I and II, Day 9 I and II, etc.). That is, unless these codes are used across different studies/manuscripts. "The codes reflect one experiment and one probe. This code cannot be simplified if we want to allocate one sulfide tape from figure 5 to one DET profile from figures 2, 3 or 4. Thus, we plan to publish additional data from those DET and need to be consistent about sample nomenclature. "

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p8, L8. Do not start a sentence with an abbreviation. "ok"

p8, L12. Probe numbers are A7-10 and A7-5, I believe (from Figure 2). "indeed, changes were done"

p8, L22. Concentrations of about 179 and 1087 "ok"

p8, L28. An interesting feature of the sulfate profiles is a general increase with depth below the immediate sediment subsurface for 1 month and 10 months. Could this fit with the idea that OM decomposition at SWI is an important oxidant sink, perhaps the authors can discuss this further? "Indeed. . . this point is discussed below"

p8, L31. There seems to be a step in the SO<sub>4</sub>(-II) data at ~ -5 cm (N-46), any idea what caused this? "That could correspond to the interruption of a series of measurements. The profile was realized during 2 days of measurements. The second day, data were more scattered and could have induced a small gap of the final results; we opted to leave it like this since we could not correct better the data on the basis of our standards."  
"

p8, L32. "basically shows the same pattern". Well, the onset of the SO<sub>4</sub>(-II) decrease has shifted upwards substantially (6 to 1 cm depth) for A7-22. "The sentence was rephrased as follows: "Spatial variability seems to be higher for the "9 days" DETs. DET A7-22 (lower panel) shows a decrease of sulfate from 1 cm below the interface, whereas no decreasing trend is present in DET A7-4 (upper panel). Minimal SO<sub>4</sub>(II) concentrations are about 29 and 27 mmol L<sup>-1</sup> for DET AW-4 and AW-22."

p9, L7. What happened to the data from probe AY-46? "The figure was completed with the missing data that were analyzed in another run. Unfortunately, the results are a bit more scattered but they do give the same trend"

p9, L11-23. Avoid the excessive use of the term "respectively", reorder text to achieve this. "ok"

p9, L21. Below the SWI up to what depth? "The first cm. . . sentence changed: "From 1

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cm above the SWI to the first cm below, alkalinity increases slightly up to 7 and 6 mmol L-1 for DET AM-44 and AM-51”

p9, L24. contrasting patterns "ok"

p9, L26. With a relatively high amount of scatter, ideas about the source of this scatter? "The sediment is quite heterogeneous, explaining a part of the scatter, especially in the lower part of the profile (from 7 cm depth) where the alternation of increase and decrease has a period of more than two values. In general, and here in particular, sometimes a bubble can affect the weight of the sample because evaporation is fast and we ignore how it affects alkalinity before the gel is stabilized by the reagent. The technique is very sensitive to the dilution and therefore to the mass of gel. If the gel is less easy to handle (for example, and without any apparent reason, the gel can be more or less sticky), the time from sampling to stabilization increases and uncertainty grows. The pipetting can play a role as well (if a drop of the reagent falls on the edge of the eppendorf it will be taken into account in the weight but will not be in contact with the gel..."

p9, L28. Maybe notable that 3.5 mM is actually a decrease compared to 1 month? "Indeed, conditions seem to be comparable to the initial ones in the overlying waters. After months, it seems that the products of the degradation of organisms that contributed to the increase of alkalinity in the 1 month chamber diffused and have been diluted, reoxydized and/or precipitated as discussed later in the manuscript."

p9, L31-32. white tape was used to seal the agarose pieces behind the membrane, in order to protect them from particles and bacteria., and to prevent the agarose pieces from falling out of the probe "replaced"

p10, L1. Was the PVC tape washed after deployment? Precipitation of Fe and Mn (oxyhydr)oxides can also cause coloration of probes, gels and perhaps PVC tape. In the case of DGT analysis of sulfide (using coloration by formation of AgS), gels are always soaked overnight in reducing agent to remove interference by Fe or Mn (oxy-

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hydr)oxides. From my own experience, probes can be partially (the part sticking out of the sediment, in particular) coated with dark grey-brown-orange coatings in systems where reducing conditions occur in the sediment and Fe (oxyhydr)oxides precipitate under less reducing conditions at the SWI. In the case of this study, the fact that the coloration only occurs after 1 month (when O<sub>2</sub> is zero) offers a strong suggestion that it is indeed sulfide, but I am interested in how possible interferences were dealt with. "We agree with the reviewer that rust can bring coloration to the tapes. We observed in many cases from other studies the same coating, which mostly appears as a line just above the SWI and indicates iron diffusion towards the overlying waters and precipitation as (oxyhydr)oxides. In our study this could be the case since washing solely involved using a moist paper towel. However, the conditions suggest that such interferences would be minor because the coloration appears in anoxic waters. Since our observations are qualitative here, general conclusions should not be altered. We thank the reviewer for pointing this out. It may help for future studies"

#### 4. Discussion

p10, L16. I think the authors should reconsider the order of the discussion section. It now starts out with explaining the constraints of the study, and mentioning that within these constraints, good data were obtained. Every study is constrained in some way (and this is detailed in the M&M section), in my opinion this does not need elaborate discussion. In particular, starting the discussion this way takes away a lot from the main findings. These now feature after section 4.1, which also holds a lot of information that is more suitable for Materials and Methods (M&M). If the authors want to discuss the limitations or constraints, perhaps this can be included in section 4.4? With regard to the discussion, I think the focus should be on the two main findings: migration of Fe and Mn peaks under anoxia and sulfide production at sediment surface (influx into rather than efflux out of sediment). These should clearly emerge as focal points that every reader takes away from this study. No matter what the authors decide regarding the setup of the discussion, here are some specific comments: p10, L20. Rephrase "our

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experimental anoxia” p10, L22. “multiply core sampling”? p10, L26. to conduct manual in situ profiling; automated in situ profilers were too large for the chambers (what kind of automated probe profiling setup should I be thinking of here?) p10, L28. a dataset that captures the evolution p11, L1. obtain p11, L2. profiles at 2 mm resolution (delete rest of sentence) p11, L4. were used for each type of analysis, to investigate lateral heterogeneity (this really is M&M) p11, L11. is known to rise under anoxic conditions (due to what?) p11, L13-15. This is M&M.

"This section was deleted and some elements of it now appear in the last section of the discussion or in the M&M section"

p11, L16. The following section(4.2) in part triggered my comment regarding the order of reasoning. It starts with discussion of another study, then there is a conclusion (without mentioning the actual data that support it, or figures), then the evidence is provided. Especially because of the lack of connecting phrases (such as: for instance, this is illustrated by, or (semi) colons), the line of reasoning becomes hard to follow. This occurs a few times in the discussion section of this manuscript (e.g. p11, L24-25; p12, L18-19; p13, L18-19 and should be addressed throughout the discussion. Perhaps it is personal preference, but ideally a discussion section runs like this: (i) finding including supporting evidence (for instance: The upward shift in dissolved Fe and Mn peaks (Fig. 2) suggests migration of redox zones under induced anoxia, (ii) further information for elaboration (more data and links between parameters) or context (other literature). If support follows after a conclusion, link the two by using above-mentioned connecting phrases or symbols. This will greatly enhance the clarity of the discussion in my opinion. No matter what the authors decide, here are some specific comments:

p11, L24. What results show this? "The sentence was rephrased including more specifically mention of the results “Manganese profiles from the “normoxic” DETs show a chemical gradient across the SWI indicating that manganese diffuses upward towards the SWI and the overlying waters” p11, L28. I do not follow how the fact that the

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Fe peak is below the Mn peak (because Mn dissolve under less strongly reducing conditions) suggests that Fe is not oxidized by free oxygen? The authors should mention sequential depletion of oxidants with depth, and address why their data indicates that oxygen will be fully depleted by Mn oxidation (I assume?) before Fe oxidation occurs. But what about close to the SWI, where dissolved Fe is very low? Can Fe precipitate as Fe (oxyhydr)oxide there by direct reaction with oxygen? "Iron profiles show almost no gradients and sometimes negative ones. At our level of precision, nothing indicates that iron diffuses close to the interface. Of course it is possible, especially in such a heterogeneous sedimentary environment. However, any mention of it would be speculative. Nevertheless, Hines and coworkers (1997) showed that iron reduction rates were the highest near the interface when stratification of water column occurred. In winter conditions they were minimal on the top cores. Here we are probably in "winter" conditions. Of course it could be different if we sampled after the marine snow event reported later during our field work. "

p11, L30. The oxygen consumption rate should be included in the results (as could, perhaps, the rates of Fe and Mn diffusion, as mentioned earlier). "It was included"

p12, L5-6. I believe some caution is advised here, as the SO<sub>4</sub>(-II) profile reflects the balance between consumption and supply from seawater. Without further supporting evidence, I do not think the authors should make assumptions about the relative importance of OM degradation pathways (which in any case have no important bearing on the major findings in this study and thus could easily be omitted in the humble opinion of this reviewer). The sentence was rephrased to stick closer to the facts: "Sulfate concentrations (Figure 3) decrease below 5-cm depth showing very slight gradients (at most  $\leq 10\%$  of sulfate consumed 12 cm below the SWI). The white tapes showed a very slight discoloration only in scattered zones within the sediment. In other shallow-water environments these qualitative probes showed a dark grey/brown coloration when sulfide concentrations reached millimolar amounts, a few centimeters below SWI (e.g. Thau lagoon, Jézéquel et al, 2007, Metzger et al., 2013; Arcachon Basin, Metzger,

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unpublished data).”

p12. L17-18. Repetitive, p11 L30 "simplified"

p12, L30-32. “This indicates” in L32 links back to sulfide production in L30, but is now separated by rates. Restructure. Done: “However, in these experiments respiration of the enclosed macrofauna led to a rapid oxygen decrease in the chamber (i.e. anoxia after maximum 4 days), with calculated oxygen uptake varying from 40 to 80 mmol m<sup>-2</sup> d<sup>-1</sup> (table 2).. Those studies also showed that sulfide was produced within the chamber less than one day after oxygen had been totally consumed”

p13, L9-11. Maybe repeat where Piran is relative to the study site. Also, could the authors give an indication of the rates they allude to? "The sentences were completed accordingly: “Sulfate reduction rates reported by Hines et al. (1997) showed lower values in our study station than in a station from the Bay of Piran located a few kilometers southeast of the buoy (our station) and closer to the shore (Hines et al., 1997), potentially reflecting a larger sediment grain size and a lower organic carbon content at our station. Note, however, that these authors showed that in late summer (September 1993), when the water column was stratified and oxygen saturation at the bottom was 45%, sulfate reduction rates near the buoy increased from about zero to 300 nmol cm<sup>-3</sup> d<sup>-1</sup> in the top layer of the sediment. In our “9 days” experiment, oxygen concentration at the sea floor was about 200 μmol L<sup>-1</sup>, corresponding to a saturation rate of about 80 % suggesting very low sulfate reduction rates, especially near the SWI”

p13, L19-20. Again, link sentences: a typical pattern [...]; after closure oxygen was quickly depleted [...] "We are aware that this section starts from literature findings and that things are structured unusually. Here we want to point out the fact that we assumed the system to follow a certain pattern when it did not, this is the reason the paragraph is written such way."

p13, L20. depleted, dropping below the detection limit in a few days "ok"

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p13, L21. tended to start accumulating about one day after oxygen was depleted "ok"

p13, L28. What is meant by "use of metallic oxides"? "reductive dissolution of (oxyhydr)oxides. Added in the text."

p13, L28. under hypoxic conditions "changed"

p13, L30. a temporal succession in the release of reduced manganese, iron and sulfur "replaced"

p13, L32. Following this conceptual model "ok"

p14, L4-5. With regard to order: the whole section 4.3 has so far been background, after which the measured profiles are introduced. I would turn this around: profiles suggest this and that, which is in line with the general model of redox of evolution sediments. The key statement in this section seem to be contrasting profiles (heterogeneity, L10) and upward shift of Mn (L14), which should take center stage. "The section was changed accordingly"

p14, L25. Sulfate reduction is not "visible", it is suggested by the normalized SO<sub>4</sub>(-II) profiles (or are you referring to the black layer formed at the surface of the sediment cores in Fig. 6G?). "Here we refer only to sulfate profiles. The point is to indicate later in the text that without the direct observation of the sediment and the use of the sulfur sensitive tapes, we would have missed a very important feature that is of the highest importance to interpret meiofaunal behavior in Langlet and Grego papers of the present issue. However, the sentence was slightly changed to clarify this: "The sulfate profiles point to sulfate reduction below 6 cm depth in the "Normoxic" profiles. After "9 days", sulfate reduction is suggested to occur only a few millimeters below the SWI. In the following weeks, the sulfate gradient becomes steeper, with a decrease of about 3 and 5 mmol L<sup>-1</sup> in the first 2 cm observed in the "1 month" and "10 months" profiles, respectively."

p14, L28-30. In my opinion, these closing statements deserve a more prominent place

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in your discussion, also because the intro clearly mentions that this study was designed to provide constraints for the interpretation of faunal data. "The discussion about the relationship between geochemistry and meiofauna evolution during the experiment is developed in the foraminifera papers. They suggest that foraminifera react more to the organic carbon dynamics than to the upward shift of manganese and iron redox fronts. In purpose we leave this discussion to these papers. However a sentence was added to give some major trends: "Copepods drastically decreased with anoxia duration. No more living organisms were found after one month (Grego et al., 2013a) while foraminifera kept high densities all over the experiment (Langlet et al., 2013b) suggesting that copepods were more sensitive to redox conditions than foraminifera"

p15, L2. Why does the direct link between SO<sub>4</sub> and alkalinity (as sulfate reduction generates bicarbonate) necessarily reflect the "dominant" role of OM mineralization? "The link between alkalinity and sulfate decrease was established in many environments (Aller, 1994; Metzger et al., 2007; Mucci et al., 2000). This implies that when alkalinity increases just below the SWI that sulfate reduction is important and dominates anaerobic OM mineralization such as in Thau lagoon. Here the results suggest the opposite of what we wrote. The sentence was deleted."

p15, L9. concentrations of free sulfide "ok"

p15, L10-13. As mentioned, could the authors comment on the likelihood that precipitation of Fe or Mn (oxyhydr)oxides might have contributed to the coloration of the PVC tape? We left, during the whole "10 months" experiment, PVC tapes inside the chamber. We clearly saw the discolouration of tapes due to rust development. The tapes were uniformly deep grey/brown except near the SWI, where a layer of rust was observed on top of it. However, the pale scattered patches observed within the PVC tapes could point to the development of metallic oxides precipitates.

p15, L15-19. Perhaps the very interesting section on vertical position of sulfide production and the links to macrofauna deserve a separate discussion section? "the section

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4.3. was split to highlight the special sulfide feature"

p15, L23. outside the chamber "ok"

p15, L25. With regard to the possibility of FeS formation and Fe (oxyhydr)oxide precipitation, simple geochemical extractions of selected samples could provide answers where mere observation or interpretation of porewater data only provide hints. Of course, there are limits to what can be done in a single study, consider this the reviewer's wish list. In general, I am of the opinion that studies with DET/DGT gels suffer from a lack of background solid-phase data; it is made to seem as if the novel, high-resolution measurement of porewater species can stand without solid-phase information, an attitude I do not favor personally. "We agree to the reviewer that without more information about the solid phase, it is difficult to discuss processes involving equilibrium between solid and dissolved phase. This is why the discussion of the section 4.1. is quite short and is broadly based on the Hines et al. (1997) paper. However the paper deals about processes that take place out of equilibrium, and the description of the evolution of porewater during the anoxia experiment is in the opinion of the authors worth publication because it is rarely observed in experiments realized in situ. We agree that DET/DGT studies often neglect the solid phase in trying to achieve a good understanding of what they measure exactly (especially when DGT are deployed). I think this comes from the fact that it is difficult to compare different spatial scales especially when the results indicate the presence of microenvironments. However improvements help today to achieve microscale solid analyses without very expensive equipment (e.g., x- $\mu$ fluorescence. . .) and we will no doubt be able to see more systematic good use of such approaches in the future.

p15, L30. They migrated to the sediment surface and died in the absence of oxygen at the SWI "ok"

p15, L32. Remove extra space between "sampled cores" and "showed" "ok"

p15, L33. Can the authors explain how a straight OC profile (not shown) automati

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cally indicates that OM is supplied due to macrofaunal mortality? "The sentence as we wrote it says the opposite that we actually wanted to say. Indeed, the profile does not give a clue about OC enrichment due to benthic mortality. We rewrote the sentence: "The organic carbon (OC) content in the sampled cores showed no clear vertical trend that could suggest any organic matter supply due to macrofaunal mortality" By the way, this example points out how difficult it can be to conciliate pore water data and solid phase results when transitory conditions are discussed.

p16, L1-2. I doubt the relevance and necessity of this sentence. "With the clarification of the sentence just above, the authors believe that the sentence now makes sense."

p16, L23. Please be precise and consistent with the type of sediment (silty sand in Introduction, sandy sediment in Discussion section 4.3, muddy sandy bottom in Conclusions), it has important consequences for the reader's understanding of transport rates and redox behavior. Ideally, the grain size distribution (D50) could be provided to end all uncertainty? "The porosity of the sediment is about 0.6, which is characteristic of sandy sediment (added in the "study area" section). We do not have granulometry results. However, a silty sand is still sand so it is not incorrect to say sandy sediment. We changed the conclusion to put silty sand again."

p16, L24. I would not say that sulfide precipitation is 'purification' per se, and would thus avoid the term auto depurative. Sounds snazzy, but also offers little insight in my opinion. "A sentence was added hereafter to precise how the presence of free sulfide in pore water is important for the meiofauna survival. Here is the sentence : "While S(-II) is a toxin that, already at micromolar concentrations, impairs biological processes necessary for organisms metabolism (Bagarinao, 1992; Giere, 2008; Moodley et al., 1998), it seems that the control of pore water S(-II) content by the sedimentary lattice was one of the key parameters allowing long-term survival of benthic foraminifera under anoxia"

p16, L26. The experimental constraints (currently 4.1) could be included here. "agreed"

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p17, L1. macroepifauna "ok"

p17, L9. seems to mimic (no need to toot your own horn with a term like “admirably”, right?) "indeed. It was deleted" p17, L21. I would prefer consistent terminology, referring to the upward migration of redox zones in the sediment. "done"

p17, L24. What is “important sulfide production”? "Changed to: “Our experiment shows that despite of important sulfide release to the water column (i.e. saturation of H<sub>2</sub>S sensors above the SWI)”

Table 2. Capitalization of names "done"

Fig. 1. Incorrect legend in caption (switched). "The legend is correct (see changes made in text above)"

Figures in general: Capitalization first words in captions. "done"

Please also note the supplement to this comment:

<http://www.biogeosciences-discuss.net/10/C5995/2013/bgd-10-C5995-2013-supplement.pdf>

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