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

Anonymous Referee #2
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This manuscript is one of a series of manuscripts derived from a multidisciplinary project in the Northern Adriatic Sea; it reports on a simulation of bottom-water anoxia that used benthic chambers equipped with sensors that measure oxygen and sulfide over time in the enclosed water column. Diffusive Equilibrium in Thin films probes (DET should have been spelled out) were employed to measure the distribution of porewater constituents in the enclosed sediment at the end of a simulation.
DET acronym was spelled out
The aims of this particular sub-project were to “describe the geochemical evolution of the enclosed bottom water and sediment pore water during three incubations lasting from nine days to ten months; to understand the behavior of the main redox fronts during the onset of anoxia; and provide the geochemical constraints for the studies focusing on the response to anoxia of various studied faunal compartments”.
The first aim is straight forward, assuming that geochemical evolution means the way the composition of the bottom water changes over time.
Actually, bottom and pore waters. This has now been better specifiied in the text.
The second and third aims are not so clear. What precisely is “behavior of the main redox fronts”, and what is meant with “geochemical constraints for the studies of response of various studies faunal compartments”? I can guess that the second aim is related to how the sequential use of terminal electron acceptors during diagenesis (the Froelich paradigm) influences the depth in the sediment that separates the stability fields of reduced and oxidized components of a given redox couple, but I am not sure that this is in fact what the authors had in mind.
The referee assumes correctly. We changed “redox fronts” by “redox species (i.e. : O, Mn, Fe and S)” in the text.
The third aim is problematic because we are not offered information about the nature of the “faunal compartments”, nor about their responses or how these could be constrained by the results of this study. As it happened, infauna crawled out of the sediment, died, and ultimately decomposed, but it seems doubtful that this is the faunal response intended in the formulation of aim number 3.
In order to better specify the aim number 3, a paragraph was added before the enumeration of the objectives giving some information about infaunal organisms’ dependence on pore water composition. The goal 3 was rephrased to make it clearer as well.

The project used three benthic chambers of a design called Experimental Anoxia Generating Unit (EAGU) (this acronym should have been spelled out – I had to look it up in another paper) that were equipped with sensors to measure dissolved oxygen and sulphide in the enclosed water. As I understand it, this chamber was designed primarily for studying the behavior and survival/mortality of benthic infauna according

to their tolerance of changing oxygen levels. There is no indication that the chambers are optimal for measuring fluxes of chemical substances, which requires a certain degree of control over the hydrodynamic regime of the enclosed water. For example, there is no indication that the water was stirred. If the absence of stirring was a deliberate choice, the reasons for it should have been given.
Indeed, the goal of the study was not to measure benthic fluxes. The authors are aware of the fact that such long-term experiments make pointless the measurements of benthic fluxes since some of the chemicals diffusing to the overlying waters such as ammonia would end up to be more concentrated above the SWI (within the chamber) than below, this leading to a change in the direction of the flux. The absence of stirring was a deliberate choice since we wanted to simulate an event of prolonged absence of ventilation as could occur in extreme climatic conditions suggested by some paleoenvironmental records in the Mediterranean for example. A paragraph was added in the M&M to develop this justification.
There is a large body of literature describing the design and performance of benthic chambers. For example, Hall and co-workers in Sweden used benthic chambers to measure in-situ fluxes of oxygen, nutrients, metals, alkalinity, and transport tracers at the sediment-water interface. (Hall, Per OJ, et al. "Oxygen uptake kinetics in the benthic boundary layer." Limnology and Oceanography 34.4 (1989): 734-746, and several other papers). These papers discuss the importance of design variables such as stirring vs. no stirring with respect to the transport of solutes and gases across the sediment-water interface. Another important paper from the Swedish group is Tengberg et al. "Intercalibration of benthic flux chambers I. Accuracy of flux measurements and influence of chamber hydrodynamics." Progress in Oceanography 60.1 (2004): 1-28. I realize that the purpose of the present study was not to measure fluxes, but the authors' apparent unawareness of this body of useful knowledge when they designed their study is surprising. Besides, the boundary layer also affects benthic organisms (e.g. Jørgensen, B.B. (2001). Life in the diffusive boundary layer, in: Boudreau, B.P. et al. (Ed.) (2001). The benthic boundary layer: transport processes and biogeochemistry. pp. 348-373, and many other papers by Jorgensen and co-workers.)
We are aware of such literature, but found it not context-specific since our goal was not to measure fluxes and the system was not stirred. The paper from Tengberg and coworkers is very interesting and shows very well how the shape of the chamber induces variable pressure at the bottom of the chamber. If we had stirred the chamber, its square shapet would have indeed been a problem.
One of the authors of the present study led a joint effort to make a state of the art of technologies available in 2003 to conduct in situ surveys and determine benthic fluxes in particular (Viollier et al., JEMBE, 2003)
We added some of references the referee mentioned in the paragraph cited above to better show the deliberate choices according to specific hypothesis and goals.

A second question about the design of the benthic chambers is whether they were darkened to avoid the influence of benthic photosynthesis on the oxygen regime at the sediment water interface. There is no mention of it in the paper, so I assume they were not darkened.
The chambers were made of Plexiglas and were transparent. Of course, transparency evolved (became gradually reduced) during the experiment since the

outside of the chamber was colonized as shown on the plate (last figure). We did not want to avoid photosynthesis because we wanted to mimic a natural system.

Not knowing much about the transparency of the water column at the study site, I cannot say if this was important or not. Was the light level at the site measured, and was the apparent decision not to use darkened chambers the result of such measurements? In any event, as revealed in the paper, the sediment surface was covered by microalgae, mostly diatoms, so some degree of oxygen production by photosynthesis certainly seems possible.

The visibility at the study site (24 m depth) was very poor, however light could penetrate. The influence of light was probably higher at the beginning of the experiment (see above) and could explain some of the variability of oxygen measurements during the first week of incubation. It was probably not important thereafter since the chambers were covered by debris that sedimented and then by epigrowth such as sponges.

From “progressive orange coloration of the seabed” it is inferred that reduced iron diffuses to the sediment surface and is oxidized. The coloration suggests that oxygen is present at the sediment surface, which is consistent with benthic photosynthesis and a stagnant boundary layer. (For an example of the importance of this phenomenon, see Jahnke, R. A., et al. "Benthic primary productivity on the Georgia midcontinental shelf: Benthic flux measurements and high-resolution, continuous in situ PAR records." Journal of Geophysical Research 113.C8 (2008):

The paper is very interesting indeed. We agree that, at the beginning of the experiment, the rust observed can be favored by additional input of oxygen from the microphytobenthos. Unfortunately no PAR measurements were performed inside the chambers. The results showed higher oxygen content for the probe closer to the sediment, corroborating such a hypothesis.

A third aspect of the design is the placement of oxygen and sulfide sensors on the interior walls. What was the reason for placing them precisely 0.4 cm and 5.0 cm above the sediment water interface? And why were not some of the sensors placed in the sediment instead of in the water column? A time series of oxygen and sulfide in the sediment pore water could have provided valuable information.

We assumed, according to previous experiments using the EAGU system, that oxygen would be removed very quickly from overlying waters and that sulfide would increase in bottom waters. A preliminary experiment realized one year before also suggested this scenario. So we decided to raise the position of the probes in order to have an idea of the stratification of the water column. Unfortunately we missed the sulfidic level within the sediment. However, the lack of coloration of the PVC sensors suggests that the sensors would have recorded sulfide only if they were placed by chance in some microenvironment. In addition, we wanted to avoid inserting the probes within the sediment to limit the influence of lateral heterogeneity that is important within the sediment. Finally, we have had very negative experience with inserting sensors into the sediment (broken tips…)

Incidentally, why are the data from the sulfide sensor not shown?

Sulfide sensor results were always at the detection limit; a sentence was added in the results section.

Now some comments on the results. Looking at the data presented in this manuscript, I was struck by the difference between the two sets of observations from the control site just outside the chambers, what is here called the “normoxic experiment”. The distributions of dissolved manganese and iron at this site (fig. 2) reveal an extreme degree of spatial heterogeneity. The upper and lower rows of panels in fig. 2 are replicate observations – two DETs per chamber for Mn and Fe. These data reveal that the distributions of iron and manganese are equally heterogeneous in the porewater of the sediment inside the chambers. The heterogeneity makes it difficult, if not impossible, to draw firm conclusions from the data set presented. The heterogeneity was revealed by the DET, a tool that measures on a much smaller spatial scale than the chamber itself.

This is the reason why we tried to describe manganese and iron behavior as evolution of their production zones during time. For sulfate, the heterogeneity seems to be lower. This could be explained by the fact that the source of electron acceptors is the sedimentary lattice for Mn and Fe, while the source of electron acceptors for sulfate reduction is a dissolved species. The heterogeneity of the solid phase explains the variability of PVC coloration since the residence time of sulfide produced from sulfate reduction is controlled by the quantity of potential oxidants (i.e. metallic (oxyhdr)oxides.

Had the water in the chamber been stirred, the water column data could have been treated as averages, and could have provided an interesting and useful comparison with the DET data.

In principle we agree to the referee's idea, but then we would have not mimicked a stagnant system (see discussion on this issue earlier in the response).

A weakness of this study is that it does not provide information on the composition of the solid phase sediment. Yet, as revealed in the paper by Koron et al. (part of the same project), sediment samples were collected and preserved, so it would have been relatively simply to obtain an idea of the vertical distributions of major components such as reducible forms of iron and manganese, and iron sulfides in addition to sediment texture, porosity, and organic carbon. The DET data show high concentrations of ferrous iron in the porewater as well as concentration maxima that indicate the depth where the soluble iron is being produced, but they do not provide information about eventual vertical heterogeneity in the solid phase sediment components. In view of the extreme horizontal differences in sediment properties that was observed, there is reason to think that the vertical variability may be equally important.

We agree to the referee and Hines et al. (1997) showed this. We believe according to our results that lateral heterogeneity could be even higher than vertical: sediment was heterometric (some particles were centimetric); a lot of burrows were observed; very different porewater profile replicates, etc…

Since pore water changed with time during incubation, and since the sediment is probably very heterogeneous, it would have been difficult to connect results from the solid and the dissolved phase, especially when spatial resolution is not the same from DET and solid extractions. This is why Koron et al. (this issue) deals with solid and dissolved phase from the same core samples. But still, the difficulty to achieve a comparison between solid and dissolved phases remains because transitory conditions were recorded from porewaters.

Indeed, the sulphate data in fig. 3 reveal that prominent concentration minima developed in the porewater as the experiment progressed. The concentration minimum implies that the rate of sulfate reduction is higher at about 20 cm below the sediment water interface than higher and lower in the sediment column, i.e. the highest rates of sulfate reduction take place within the sediment column and not at the sediment water interface. The reason why sulfide does not appear in high

concentrations in the porewater is likely because it is precipitated as a ferrous sulfide by the abundant soluble reduced iron in the porewater – at least until the sediment runs out of reducible iron. I am curious why the sulfate minimum developed at 20 cm depth: could it be that the sediment at that depth was organic rich, i.e. that the sulfate distribution reflects vertical heterogeneity in the solid phase sediment? Are there other ways to understand the development of this minimum? Vertical profiles of sediment properties might have provided some clues.
The referee probably meant 20 mm. These results would suggest indeed highest sulfate reduction zones at this depth. We believe as well that the low concentrations of sulfide in porewaters is controlled by the presence of oxides, as explained in the discussion. We did not measure reactive metal oxides from the solid phase. Hines et al 1997 showed that even if sulfate reduction was maximal in the top 2 cm of sediment during anoxia, Mn and Fe reduction still occurred. They showed that dissolved iron was depleted on top but still present below, while dissolved Mn was at its maximum on top of the core. All these facts confirm the important role of Mn recycling on the sulfide content in porewaters.
Overall, other than the local spatial variability in sediment properties, I find little in this paper that could not have been predicted from present understanding of sediment diagenesis and sediment water exchange processes. I refer the authors to Aller's work on the Long Island Sound, an environment where the bottom water fluctuates seasonally between oxic and anoxic. A good example is Aller, Robert C. "The sedimentary Mn cycle in Long Island Sound: Its role as intermediate oxidant and the influence of bioturbation, O2, and Corg flux on diagenetic reaction balances." Journal of Marine Research 52.2 (1994): 259-295. Likewise, the papers by Hall and coworkers mentioned above contain information that could have been used to predict the sequence of events in the Adriatic experiments.
This is true up to a certain point (the reference has now been added and commented in the discussion (section 4.2.). To our knowledge, however, the behavior of sulfide was not really documented before. The opposite gradient from the one month chamber was striking, and the fact that after 10 months despite a sulfate reduction rate apparently equivalent according to equivalent sulfate concentration decrease with depth. The present study points out the importance of biomass of benthic infauna in the intensity and duration of sulfide production during anoxia. In addition this paper gives important clues to help understand meiofauna survival and its population dynamics in this context. See Langlet et al. this issue. A separate section in the discussion was created to highlight this aspect of the study.
All that being said it is always valuable to confirm experimentally, especially in situ and in other natural settings, what other studies seem to evidence.