

Interactive comment on “Artificially induced migration of redox layers in a coastal sediment from the Northern Adriatic”

By E. Metzger et al.

Anonymous Referee #3

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Review of “Artificially induced migration of redox layers in a coastal sediment from the Northern Adriatic” by Metzger et al. bg-2013-328

This study reports geochemical evolution of sediment, and effect on benthic fauna, during prolonged anoxia using benthic chambers on the seafloor of the Northern Adriatic for 9, 30 and 315 days of incubation. The main results of the study were that decomposition of benthic macro-organisms on the seafloor generated important production of sulfides within the chamber, which generated a downward flux of sulfide towards the sediment where sulfides were quickly oxidized by metallic oxides or precipitated as FeS. Sulfide was found to be no longer detectable in the water column and pore water at the end of the experiment. The authors therefore claimed that sulfide enrichment in the water column in coastal systems is strongly controlled by the biomass of benthic macrofauna and its decay during hypoxia, while its residence time in the water column is controlled by iron content (as solid oxides or as dissolved reduced cation) within the sediment. I have a number of problems with this paper.

First, there have previously been several similar in situ experiments in other marine environments studying negative redox turnovers at the sediment-water interface (SWI), which the present authors appear not to have cited appropriately and may not even know about. These previous experiments include studies by Balzer (1982 in GCA), Balzer et al. (1983 in Oceanol. Acta) and Balzer (1984 in L&O) in the Eckernförde Bight, southern Baltic Sea; studies by Rolf Hallberg and coworkers, including Nils Holm and Anna-Greta Engvall, near the Askö Laboratory in the NW Baltic proper; studies by e.g. Anderson et al. (1986 in L&O), Rutgers van der Loeff et al. (1984 in L&O), Sundby et al. (1986 in GCA) and Skoog et al. (1996 in GCA) in the Gullmar Fjord, western Sweden; and studies in Chesapeake Bay, USA, by e.g. Boynton and coworkers. Many of these studies reported fluxes of sulfide from sediment to water column (measured in benthic chambers) as a result of a negative redox turnover, and the sulfide accumulated in the chambers. Some of them reported dying benthic fauna at the SWI due to the induced oxygen depletion, and it may be that some of these papers reported that the dying fauna contributed to the sulfide production. The present authors should thoroughly check these papers, and make it very clear how their study is different (if at all) from these previous studies of which some were carried out already in the 1970's, i.e. about 40 years ago, and in a substantially revised version of their manuscript (MS) clarify what new knowledge (if any) their study has generated in this regard.

The authors are aware of this body of literature listed by the reviewer. They were not included in the manuscript primarily because almost all indicated the same evolution of geochemical conditions within the chamber as Stachowitsch and co-workers experiments already realized in the Adriatic with the same system used here as a reference. Kristiansen's study was helpful in that it added manganese and iron behavior under different oxic conditions in a sandy sediment which is comparable to the sediment of our study site. We have now extended our bibliographic corpus when we claim that DET (Mn, Fe, SO₄²⁻ and Alkalinity) results confirm what is well established in the literature. See end of section 4.2.

Only few of these studies followed porewater evolution during the experiment. Even if some of them evidenced the role of decaying faun on sulfide production, to our knowledge there are no studies that documented an opposite gradient of sulfide and the role of the sediment as a sink during anoxia under certain conditions. It was rather the opposite. To emphasize our new findings, we have now created a section in the discussion about the uncommon sulfide features (section 4.3.).

In addition, as we have specified more precisely in the new version of the manuscript, the main goal of this geochemical study was to give – to ecologists studying meiofauna survival after long-term anoxia – the chemical context of microhabitats in which they lived to interpret survival strategies, alternative metabolisms, etc... (see special issue accompanying papers)

Third, even if our study has in some cases merely confirmed earlier observations elsewhere, the fact that we combined different sampling and analytical techniques at different temporal and spatial scales is a useful step forward in confirming established paradigms. Beyond this, however, we have clearly added new insights into the understanding of biogeochemical processes under transient anoxia.

Second, if there was a downward flux of sulfide towards the sediment where sulfides were quickly oxidized by metallic oxides, then it needs to be shown that metallic oxides were present below a zone of sulfide production. I could not see that this was made clear in the MS.

We added to the section discussing sulfur residence time (section 4.3.) a sentence explaining that the sediment from our study site has a high amount of reducible iron: "It seems that sandy sediment behaves as an auto depurative system limiting the residence time of S(-II) within the sediment and in overlying waters. Indeed, iron concentration within the sediment is about 350 µmol g⁻¹ at the surface and few decimeters below (Hines et al., 1997) and this stock of iron is mainly coated onto the surface of silicates as Fe₂O (Arčon et al., 1999) and constitutes a large reservoir of reducible iron."

Thirdly, the authors claimed that sulfide enrichment in the water column in coastal systems is strongly controlled by the biomass of benthic macrofauna and its decay

during hypoxia. Two of the most well known anoxic and sulfidic marine basins in the world are the Black Sea and the Baltic Sea, of which at least the latter is a coastal system. These basins contain no benthic macrofauna below the oxycline, but still there is active sulfide production in these anoxic sediments, which significantly contribute to the sulfide enrichment in the water column of these basins.

Of course our statement stands only in the context of transitional hypoxic systems, which are generally eutrophic and bear a high density of benthic organisms. We modified the abstract to specify the type of environments for which our statements are valid: "our results suggest that sulfide enrichment in the water column of coastal systems which are episodically anoxic is strongly controlled by the biomass of benthic..."

I can thus not find that the claim the present authors did is justified at all; at least it cannot be generalized in the way the authors did. If this claim is to be trustworthy, the experiments should have been made in sediment with and without benthic fauna, and the sulfide production (and possible accumulation in the water of the chambers) be compared between zoic and azoic experiments.

In situ experiments in azoic sediments cannot be made without prior asphyxiation of the zone before. This would alter the organic carbon distribution, the redox front positioning... We tried to study areas with no apparent macroepifauna, but our imaging dataset showed that some (in)fauna was present. Still, the comparison between this set of experiments and those realized previously by Stachowitsch and coworkers shows that with visible epibenthic macrofaunal clumps, the sulfide production starts less than 3 days after closure of the chambers (e.g. Blasnig et al., 2013; Riedel et al., 2008; Stachowitsch et al., 2007). From those experiments that lasted for 1 week we cannot say how long sulfide remained free in the water within the chamber. We agree with the referee that this study opens many perspectives, a classical situation in almost every scientific study.

Fourthly, the authors claimed that the residence time of sulfide in the water column is controlled by iron content (as solid oxides or as dissolved reduced cation) within the sediment. I would like to see (in the revised version of the MS) a calculation or a budget in which the authors show how much sedimentary iron is needed stoichiometrically in their system to control the residence time of sulfide (with regard to oxidation or precipitation), and compare that with the iron content actually being present.

Iron content within the sediment in this area is about $400 \mu\text{mol g}^{-1}$. This concentration is rather constant within the 10 first centimeters of the sedimentary column (Hines et al., ECSS, 1997). Minimal values are observed at the surface, which are about $350 \mu\text{mol g}^{-1}$. Most of it is present as Fe_2O_3 coated onto silicates (Arçan et al, JSR, 2000). Indeed the sediment is whitish/yellowish, indicating not much FeS or organic matter in its lattice (see study site and the plate, last figure). If we consider a density of 2.6

for silicates and a concentration of iron about $350 \mu\text{mol g}^{-1}$, we can calculate within the first centimeter of sediment an iron concentration of about 9 mol/m^2 .

Considering the density of foraminifera and copepods from Langlet et al. and Grego et al (this issue), we have about 2000 individual per 10 cm^2 , which means 2 million/ m^2 . Considering an average biomass for meiofauna of $2 \mu\text{gC/ind}$ (Movellan et all, BG, 2012; Shimanaga and Shirayama, OA, 2000), this corresponds to about 4 gC/m^2 , i.e. 0.33 molC/m^2 .

If we consider a ratio between C and S for the sulfate reduction reaction of 2, this means that we can release 0.16 mol of sulfur, which corresponds to a concentration of 0.16 mol/125L , in extensor 1.28 mmol/L of sulfide.

The residence time of sulfide within the chamber will depend on these values and on the inward flux of sulfide. This influx cannot be determined easily from our data. Nonetheless, if we consider that the concentration of reduced sulfur within the chamber is about 1.28 mmol/L and its penetration is about 2 mm , then the flux is about $1.28/0.2 \cdot D_{HS}$. This represents a flux of about $3 \text{ mol HS}^-/\text{m}^2/\text{day}$ and a residence time of a few hours. However, we considered only meiofauna because macrofauna was not quantified. If the biomass increases by 1 or 2 orders of magnitude considering the macrofauna, then the residence time will increase as well. In addition, the bigger the organism, the slower the degradation and the longer the source of sulfide will be active. Moreover, transport of sulfide from the overlying water into the sediment will be less exclusively dominated by diffusion when a layer of decaying material separates metallic oxides from the sediment and the sulfidic waters.

In conclusion, we can say that the biomass of dead organisms and the decay rate will control the duration of the efficiency of the sulfidic source. The quantity of metallic oxides controls the sulfur trapping capacity (sink efficiency): if the sediment is muddy and already rich in iron sulfide, it will be ineffective as a sink for additional sulfide. Then, transport processes in the water column (mixing) will control the residence time of sulfide (and other reduced compounds), as observed in lagoons such as Thau in the Mediterranean (Souchu et al., 1998; Metzger et al., 2007). In the Adriatic, iron is present in the first decimeters of sediment, constituting a very important reservoir and giving the sediment a large sink efficiency. The observation of such process is clearly worthy of publication.

It is difficult to add such rough calculations to the MS. As mentioned above, we have now specified the iron content of the sediment more clearly to support the hypothesis of the sandy sediment as an efficient sink of sulfur during anoxic conditions.

There are a number of grammatical and/or linguistics errors in the MS (too many to list here). The MS should therefore be language corrected by a person with English as her/his mother tongue.

The manuscript has been gone through again by a professional scientific English proofreader"

My recommendation is that the MS undergoes a major revision and then is resubmitted for a new review.