

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), SO₄(-II) and alkalinity. 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), SO₄(-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. 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. 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 effluxes. 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

p1,L20. associated with

p1,L26. Is alkalinity (why capital A?) a redox-sensitive species?

p1,L28. anoxia was established

p1,L29. Specifically mention the oxidation mechanism to explain the rusty color formation.

p1,L30. Decomposition of macro-organisms at the sediment-water interface

p1,L31. What is “important” production?

p1,L32. downward flux of sulfide into the sediment

p2,L1. sulfide was below detection

p2,L4. residence time in the water column

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.

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”

p2,L12. associated with (mass) mortality

p2,L13. In most cases

p2, L14. water circulation is restricted

p2, L14. residence times of what?

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

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.

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

p2,L20. Explain “progression of anoxia”, please be more specific.

p2, L21. the evolution of hypoxic events in the North Sea (and where in the North Sea?)

p2, L24. a decrease in anoxic events has been reported since the 1990s

p2, L26. phosphorus

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

p2, L28. Again, what is “important”? Significant, large, appreciable...?

p2, L28. In what form is it available in the sediment?

p2, L29. the Thau Lagoon

p2, L29. What does “summer conditions” mean?

p2, L30. phosphorus

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?

p3, L11. delete “this issueb”

p3, L14. favoring vertical separation between redox sensitive elements

p3, L15. iron (Fe) and manganese (Mn) (oxyhydr)oxides (surface sediments often contain fresh hydrous ferric oxide rather than ferric oxides such as goethite and hematite), and use element abbreviations from here on.

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

p3, L19. elements that are not redox-sensitive. 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).

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. Also, is the succession changed by changing redox conditions, or just the vertical extent of redox zones?

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? 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.

p3, L26. When do seasonal hypoxic conditions occur? I assume summer, but it’s good to be explicit.

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?

p3, L31. at 24 m water depth

p3, L33. during a series

p4, L5. for the studies [...] that were conducted within the larger collaboration

2. Materials and Methods

p4, L11. check spaces in notation geographic location

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

p4, L14. How can a shoal be “deep”? Please explain?

p4, L14. longer residence time, and of what?

p4, L19. the benthic macrofaunal community

p4, L23. mostly diatoms

p5, L2. What does the acronym EAGU stand for?

p5, L3. guarantee optimal isolation

p5, L4. the sidewalls were pushed

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?

p5, L24. 1.5 % w/w

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

p6, L17. 0.01 mol L⁻¹ (personal preference, I guess)

p6, L31. Can the authors provide quantitative information on the accuracy and precision, or relative standard deviation or something similar?

p7, L1. 0.01 mol L⁻¹ (personal preference, I guess)

p7, L15. sodium hydrogen carbonate

3. Results

p7, L17. No mention of the probe sulfide data? 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.

p7, L21. Fig. 1

p7, L27. The lines are mixed up in the caption of Fig. 1.

p8, L4. Remove extra space between “experiments.” and “Results”

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.

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

p8, L12. Probe numbers are A7-10 and A7-5, I believe (from Figure 2).

p8, L22. concentrations of about 179 and 108

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?

p8, L31. There seems to be a step in the SO₄(-II) data at ~ -5 cm (N-46), any idea what caused this?

p8, L32. “basically shows the same pattern”. Well, the onset of the SO₄(-II) decrease has shifted upwards substantially (6 to 1 cm depth) for A7-22.

p9, L7. What happened to the data from probe AY-46?

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

p9, L21. Below the SWI up to what depth?

p9, L24. contrasting patterns

p9, L26. With a relatively high amount of scatter, ideas about the source of this scatter?

p9, L28. Maybe notable that 3.5 mM is actually a decrease compared to 1 month?

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

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 (oxyhydr)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 O₂ is zero) offers a strong suggestion that it is indeed sulfide, but I am interested in how possible interferences were dealt with.

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 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.

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?

p11, L28. I do not follow how the fact that the 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?

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).

p12, L5-6. I believe some caution is advised here, as the SO₄(-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).

p12. L17-18. Repetitive, p11 L30

p12, L30-32. “This indicates” in L32 links back to sulfide production in L30, but is now separated by rates. Restructure.

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?

p13, L19-20. Again, link sentences: a typical pattern [...]; after closure oxygen was quickly depleted [...]

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

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

p13, L28. What is meant by “use of metallic oxides”?

p13, L28. under hypoxic conditions

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

p13, L32. Following this conceptual model

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.

p14, L25. Sulfate reduction is not “visible”, it is suggested by the normalized SO₄(-II) profiles (or are you referring to the black layer formed at the surface of the sediment cores in Fig. 6G?).

p14, L28-30. In my opinion, these closing statements deserve a more prominent place in your discussion, also because the intro clearly mentions that this study was designed to provide constraints for the interpretation of faunal data.

p15, L2. Why does the direct link between SO₄ and alkalinity (as sulfate reduction generates bicarbonate) necessarily reflect the “dominant” role of OM mineralization?

p15, L9. concentrations of free sulfide

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?

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

p15, L23. outside the chamber

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.

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

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

p15, L33. Can the authors explain how a straight OC profile (not shown) automatically indicates that OM is supplied due to macrofaunal mortality?

p16, L1-2. I doubt the relevance and necessity of this sentence.

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 (D_{50}) could be provided to end all uncertainty?

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.

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

p16, L1. macroepifauna

p17, L9. seems to mimic (no need to toot your own horn with a term like “admirably”, right?)

p17, L21. I would prefer consistent terminology, referring to the upward migration of redox zones in the sediment.

p17, L24. What is “important sulfide production”?

Table 2. Capitalization of names

Fig. 1. Incorrect legend in caption (switched).

Figures in general: Capitalization first words in captions.