

Interactive comment on “The control of hydrogen sulfide on benthic iron and cadmium fluxes in the oxygen minimum zone off Peru” by Anna Plass et al.

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Dear editor,

This is my contribution to help Biogeosciences and the authors of this manuscript to improve the diffusion of this very valuable work. I did the best according to my knowledge and understanding to be fair in my criticism and hope that this piece of work will be published. However I think that there is still some work to be done.

Sincerely

Dr. Edouard Metzger

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General comments The main concern of this study is the precision of flux modeling from chemical profiles as for porewaters as for near-bottom waters. Since mass balance calculations and main conclusions are made out of these data, I would suggest a more extended presentation of methods, results to allow reader to better evaluate the quality of discussion and conclusions made.

Some reorganization could be made in the introduction to show better how what is known about metals and OMZ functioning and what can be added from the study. It would also help to better specify hypotheses made and features predicted on benthic fluxes of trace elements.

The importance of TM benthic fluxes is stated in the abstract and the conclusion as important for surface marine ecology. Without suggesting any intention from the authors, I believe that from the present study to such statement the shot is really too long and this may mislead the less careful reader towards rapid conclusions appealing a bit to its emotion instead of its reason

Specific comments

Abstract L41-42 I am not sure to follow the causality between metal relative metal solubility and spatial-temporal heterogeneity L45-47 the last sentence of the abstract tends to suggest that decrease of cadmium solubility due to sulfide increase consequently to oxygen declining may affect marine ecosystems. The sentence appears to me overstated, out of the scope of what your data can say, overall, as a general sentence that would appeal to emotion. I would suggest to find another sentence to take perspective. Maybe adding another metal that you must have analyzed using a ICPMS to the study showing different sulfide affinities would have helped to strengthen such a statement.

Introduction All along the introduction, it is stated that little is known about TM benthic fluxes in hypoxic environments. I would disagree with that. The authors cite themselves several of them and I think of studies done by Faganeli and coworkers in the Adriatics, work done during the Microbent project in Thau lagoon including by myself. Work in

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hypoxic estuaries such as the Gironde or the Scheldt among others. I have the feeling that if authors had detailed more about TM behavior in different environments during occurrence of hypoxia/anoxia and sulfide release into the water column they could have made a series of predictive hypotheses on what would be Cd behavior in the Peruvian OMZ. Overall, I am not a fan of the outline of the introduction because the rationale is at the beginning and the state of the art shown after is too far to make the reader quite sur about what are really the hypotheses made here and what is really new.

Methods Incubation time was of 32h, how oxygen evolved within chambers that were not anoxic in the beginning?

How the benthic boundary layer's thickness is established and what is its dynamics? That should be mentioned in the introduction as how it may affect benthic fluxes What was the detection and quantification limit for Cd measurements

I am aware that there is plenty of literature with diffusive flux calculations from overlying water and the first porewater concentrations. I think this is wrong as soon as a 2-point calculation is subject to the precision of those points and overlying water concentration is an average of 10 to 30 cm of water column according to the fullness of the core. If any author took the entire porewater profile to make an averaged concentration for gradient calculation nobody would take the calculation seriously. I would at least be skeptical about calculations taking only two points to model a line from which, one is an average of something it is impossible to fully describe with such sampling method. I would say that this can be overtaken adding a supplementary point for the gradient determination. Unfortunately, only one of your profiles can apply. This aspect must be clearly discussed in the manuscript and conclusions made from such calculations carefully done. High resolution methods exist.

Linear regressions with standard deviation of the slope are not shown in the document, this should appear in the graphics with also error bars for each point

Particulate flux calculations and CdS water column uptake calculations should also be

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detailed here, especially the last one.

Results

I think that section 3.1. appeals a lot to literature to be part of the result section. Only bottom oxygen data is described from figure 2. I would suggest authors to discard the figure 2, table 2 is sufficient, and put that description in the methods sections. For a result section I would avoid naming sections using processes such as “biogeochemical cycling”. I would suggest to simply call it: “Porewater and benthic fluxes” then “iron, then “cadmium”

I would also suggest to avoid citations. Why citations are provided for iron and not for cadmium? Some symmetry should be maintained between these elements at least here to underline differences in results

In the methods section I made a comment about the thickness of the benthic boundary layer. According to the 4 metres profile from the bottom, it appears that the benthic boundary layer is clearly thinner than 0.5 m as concentrations are stable in your data for almost all profiles. I believe from in situ data of oxygen profiles that this boundary layer is within the range of few micrometers to few centimeters. I am not sure those data are really relevant here and could be discarded or remain as supplementary data. Line 351 authors say that initial incubation concentrations were higher than “bottom samples”. This pleads to the fact that those bottom samples did not describe the benthic boundary layer. This should be said somehow. Did the authors thought of showing modelled gradients in the porewater profiles instead of showing modelled incubation points from diffusive fluxes?

Discussion

4.1.1. Talking about incubations 1, 9 and 10 you mention bioturbation as a potential artefact, what about oxygen consumption and sulfide precipitation during incubation? Actually a combination of all that could happen as oxygen depletion could bring endo-

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bionts to surface (see riedel et al experiments in the adriatics) or enhance bioirrigation (Duport et al, 2007) favoring sulfide efflux or iron precipitation. Did you consider leaks in the chamber or dysfunctional homogenization? This is a current issue with in situ incubation. Oxygen and sulphide data from incubations are really missing here to state about ventilation processes or leaking

4.1.2. I am not convinced about the half-life calculations since there is little change in iron concentrations and they do not fit with a reaction transport model to me. What about these data being colloidal fractions that pass the $0.2 \mu\text{m}$ poresize of the filter that would have little reactivity as shown by the slight slopes that look mostly within error bars? I agree that 1 point from station 8 and two from station 1 are clearly above error bar range but only station 8 seems to indicate that you caught the BBL. However, station 1 profile points to 2 homogeneous layers that suggest diffusion is not dominant there Silica data should appear somewhere

4.2.1. Line 632 is it possible to detail how CdS precipitation in the near bottom water column was calculated? Show linear regressions, statistical significance and determination coefficients. What are the ranges in table 3? This section is very interesting but I feel uncomfortable with the lack of details about calculations and numbers out of it. It is a pity because it is I guess the most important part of the study

Conclusions Station 1 seems to weaken the first statement of the conclusion The order of TM affinity towards sulfide is shown for the first time in the conclusion. It should be said more explicitly in the introduction

The expansion of OMZ is evocated to draw a future scenario of TM burial/recycling within the OMZ but what about seasonality and other cyclic controls such as el nino/la nina conditions? Conclusions seem a bit too bold in that way. I am not sur that a putative enhancement or decrease of TM upward flux to surface waters (that is by the way not shown here with the Cd example) would affect marine ecology. At least nothing in the paper discusses it. If I read only the conclusion and the abstract, this will be the

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take-home message of the paper I would guess and the paper does not address such important question.

Technical corrections

Line 189 “compared” Line 191 “covered” Line 207 “weighted” Line 317 what are op-topodes? Line 563 “can take”

Figures 5 and 7 should show linear regressions and equations as well as error bars for the data points. Then, equations and quality of regressions should be quickly described to prepare the discussion section about iron being oxidized by nitrogen compounds

Details from saturation indices shown in the caption of figure 10 should maybe appear within the text of the manuscript in the methods or the discussion

Table 3 what is within brackets for station 1 flux from chambers. This calculation would show what evolution of Cd concentration within the chamber? Is that coherent with your data?

Figure 9 reminds me a figure from my paper about cadmium fluxes in a seasonal hypoxic lagoon (Metzger et al., 2007) with a kind of threshold. You could put in the x-axis oxygen concentration and or sulfide and or nitrate. Why did you do only a figure for iron?

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