Dear Michael Staubwasser, we would like to thank you for reviewing our manuscript and your constructive comments.

In this response letter referee comments are listed in italic font, followed by the authors responses to each individual comment. Changes that will be made to the manuscript are underlined.

Referee comment 1:

The input data required to verify the authors' flux calculations from concentration gradients between the uppermost pore water sample and the water column sample is absent from the manuscript’s figures and tables. That includes the porosity used in equation 3 and the tortuosity calculated therefrom in eq. 2. Nor are the input concentration values given. I cannot glean them from fig. 4, as the scale is too small and most pore water profiles appear to show an enormous spread in the uppermost two data points. What values were used for the calculation? Which one is the true surface in fig. 4? What is the reason for this spread in pore water concentrations so close to the surface — e.g. St1_M136 (Fe: ~ 100 nM and >1 nM) and St4_M136 (Fe: low nM range? and > 6 µM). Comparing bottom water column data (fig. 3) does not suggest one of these plotted pore water values could actually be the bottom water concentration. I think it would be better, to calculate concentration gradients from more than just two data points for Fe and Cd. Perhaps the authors would also consider to show the 0-500 nM range in high resolution, and the few numbers above at lower resolution with a break in the axis between?

Response to referee comment 1:

We fully agree that the input data for the diffusive flux calculations need to be listed in the manuscript. The input data (i.e., porosity, concentration values, in-situ temperature, pressure and salinity) will be listed in a table in the appendix.

For the diffusive flux calculations we deliberately decided to use the two point concentration gradient between the uppermost pore water sample and the overlying bottom water. We know that this method has its limitations, but need to stay with this approach for the following reasons.

1. This is a commonly used approach which allows us to compare our diffusive fluxes to fluxes from other publications (e.g. Sundby et al., 1986; Wamken et al., 2001; Turetta et al., 2005; Pakhomova et al., 2007; Noffke et al., 2012; Lenstra et al., 2019).

2. The strong gradients between the uppermost pore water and bottom water sample is typically observed within open-marine oxygen minimum zones (e.g. Noffke et al., 2012; Scholz et al., 2019). Since H2S accumulates close to the surface in these settings, the dissolved Fe peak in pore water is very narrow (1 – 2 cm) and located close to the sediment-water interface. Applying more advanced methods for the determination of diffusive fluxes, e.g. curve fitting, would fail to capture the sharp
gradients at the sediment surface and, thus, lead to erroneous flux estimates (see also Shibamoto and Harada, 2010; Dale et al., in prep.)

3. Bottom water concentrations are very small (maximum a few hundreds of nM) compared to the concentrations in the uppermost pore water sample (several µM). Therefore, the gradient between pore water and the bottom water is mostly dependent on the pore water concentration. For the same reason, varying the bottom water concentration over the range observed in our data set has a negligible effect on the benthic flux.

We will explicitly include the above explanation in section 2.3 Flux calculations.

Referee comment 2:

I also don’t like the way these gradient-based diffusive flux calculations (lines) are shown over the flux chamber time series data in fig. 5. Better use the water column data as a starting point - since chambers were flushed with ambient bottom water - than the first chamber time series value. There often is quite a difference between the ambient bottom water and the first chamber value that the authors do not explain. Sometimes that difference is hard to understand. In Sta 1 ambient water is higher than the starting value of the chamber (flushed with ambient water). At Sta 9, chamber values (~ 80 nM) are much higher throughout than ambient water (~ 5 nM), but apparently there is no diffusive flux of Fe. That discrepancy does not agree with the authors’ general statement in the abstract that the two flux estimates agree with each other.

Response to referee comment 2:

Different Fe concentrations inside and outside of the chamber are to be expected because of diffusive Fe release from the sediment and an accumulation in the enclosed water volume inside the benthic chamber. Furthermore, the bottom water enclosed in the benthic chamber is much closer to the seafloor compared to the bottom water samples collected closest to the seafloor (at 0.5 m). We assume that the concentrations in the bottom water enclosed in the chamber represents the average concentration over the first 30 cm above the seafloor. Outside of the chamber, a concentration gradient between the seafloor and the bottom-near water column is likely to establish because of diffusive release of Fe from the sediment and removal in the bottom water. Therefore, it is not surprising that different concentrations are observed in the chamber and in the bottom water 50 cm above the seafloor.

Furthermore, the water sample at 0.5 m away from the seafloor was collected in sampling bags with peristaltic pumps over a time span of 32 hours. This means that, in contrast to the benthic chamber, where samples were taken within minutes at discrete points in time, short-term concentration changes cannot be seen.

For the reasons given above, we cannot expect to see the same concentration value in different sample types and cannot use bottom water values as a starting point for the incubations.
The above explanations will be added to the discussion in section 4.1.1 Comparison of diffusive and in-situ benthic chamber iron fluxes.

We will add linear regressions for the concentration change over time during the benthic chamber incubation (figures 5 and 7). We prefer to also present the slopes calculated from pore water profiles to facilitate the comparison of benthic fluxes derived by these two different approaches.

Referee comment 3:

Generally, I see an unaddressed problem in that the Fe concentration data for the near-bottom water column and the flux chambers were filtered at 0.2 µm and acidified for later analysis. That would dissolve all colloidal Fe, which I would expect to be quite abundant near the bottom (see e.g. Fitzsimmons et al. 2015, Mar Chem 173 pp 125 for a similar problem in ocean water underneath dust plumes, and Heller et al. 2017, GCA 211, pp 174 for a discussion of particulate - and colloidal - removal of dFe in the Peruvian OMZ). I am aware of the authors citing the latter manuscript, but they do not cite it in the context of colloidal/particulate removal of dFe. I realize, that the necessary ultra-filtration to quantify colloidal Fe was not implemented, and of course, cannot be provided in hindsight. However, I would like to ask the authors to deal with this problem in the discussion. There is so much scatter in the Fe concentration time series from the flux chambers, that I am certain the dFe data suffer from colloids. Colloidal Fe would not count for flux calculations based on pore water - bottom water concentration gradients, and would very much complicate flux estimates based on the linear trend calculation from the flux chamber time series. My quick suggestion would be to provide two estimated for fluxes based on minimum and maximum estimates, but perhaps the authors can come up with a better way to deal with this issue. A discussion of this aspect would really benefit the manuscript. I suggest to discuss this aspect at the end of paragraph 4.1.1. In addition, bioirrigation should contribute considerably to resuspension of particles and colloids as well - a process which the authors briefly mention in lines 441-446 in general terms but do not seem to connect to their scattered flux chamber data.

Response to referee comment 3:

We agree that colloidal or nanoparticulate Fe are likely to play a role in Fe cycling on the Peruvian margin, especially close to seafloor, where particles are quite abundant. Unfortunately, we did not differentiate colloidal and truly dissolved fractions during our sampling, which is why we cannot discuss this aspect based on our data.

The transfer of Fe between dissolved, colloidal and particulate pools is likely to affect the balance between dissolved Fe transport away from the seafloor or re-precipitation and deposition to some extent. To outline the role of suspended particles in modulating benthic Fe fluxes we already refer to the work of Homoky et al., 2012. In addition, we will take the following steps to address the reviewer’s comment:

We will make it clearer in section 4.1.1 that colloidal Fe could modify Fe concentrations within our samples, as colloids are quite reactive. They are much more soluble than larger particles and can be rapidly reduced and dissolved in anoxic environments, but
they can also be an intermediate step in dissolved Fe removal through aggregation of larger particles (Raiswell and Canfield, 2012). On the other hand, Fitzsimmons and Boyle, 2014 observed that soluble (< 0.02 µm) rather than colloidal Fe was the dominant fraction within the oxygen minimum zone in the tropical north Atlantic.

We will refer to the processes mentioned above to explain the scatter in Fe concentrations observed during benthic chamber incubations.

We don’t understand the reference to Heller et al., 2017 in the context of colloids as this publication does not discuss the role of colloidal Fe.

Finally, we fully agree with the reviewer’s comment that further research on particle dissolved interactions is needed and we will explicitly mention this in the revised version (section 4.1.1. Comparison of diffusive and in-situ benthic chamber iron fluxes, starting from line 488).

We do connect our scattered flux chamber data at stations 1, 9 and 10 to bioturbation and bioirrigation in lines 433 – 436, we will add to this statement, that bioturbation and bioirrigation could also lead to particle or colloid resuspension.

Referee comment 4:
In the abstract, lines 20-23, I would suggest the authors phrase the suggested “agreement” of different flux calculations somewhat more careful. This is not a very convincing statement even without considering the colloid problem. At best, there is agreement for some of the stations.

Response to referee comment 4:
Following the reviewer’s recommendation, we will rephrase lines 20 – 23 to make clear that we distinguish between Fe fluxes within the permanent oxygen minimum zone and outside of the permanent oxygen minimum zone. The benthic diffusive Fe fluxes and Fe fluxes from benthic chamber incubations do mostly agree well within the permanent oxygen minimum zone, whereas outside of the oxygen minimum zone there is a larger discrepancy between the two estimates.

Referee comment 5:
In the conclusion, I don’t think it is appropriate to claim that Fe just diffuses out of the sediment column. The authors themselves have made the case for bioturbation and bioturbation as a significant process for Fe enrichment in the flux chambers.

Response to referee comment 5:
We will rephrase this part of the conclusions and only refer to diffusion as being the dominant process for Fe fluxes within the permanent oxygen minimum zone, where bottom-dwelling macrofauna is absent. We are aware that additional processes could
play a role within the permanent oxygen minimum zone. However, we feel it is appropriate to only refer to the main process in the conclusions.

Technical referee comments:

*Technical aspects that should be corrected: a) Please show cruise AND station number in figures 1 and 2. b) I believe it would be useful to show the H2S data along with the Cd data in fig. 6, since they are discussed together.*

Response to technical referee comments:

We will implement both your suggestions a) and b). Station numbers will be added to the map in fig. 1 and to the caption of fig. 2. We will display the profiles of H2S concentrations in pore waters not only in figure 4 but also in figure 6.

References


Raiswell, R. and Canfield, D. E.: The Iron Biogeochemical Cycle Past and Present,


