We would like to thank Edouard Metzger and Michael Staubwasser for their constructive reviews.

In this response, *referee comments are listed in italic font*, followed by the authors responses to each individual comment. Changes that were made to the manuscript are underlined. The revised manuscript including track changes is listed below.

Referee 1 comment 1:

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 usinc a ICPMS to the study showing different sulfide affinities would have helped to strengthen such a statement.

Response to referee 1 comment 1:

We are using the elements Fe and Cd as prototypes, as they have a contrasting sulfide solubility, and interpolate their behavior to trace metals which have an intermediate sulfide solubility (lines 86 – 92, 686 – 689, 699 - 701). The concentration/reservoir of a trace metal in the ocean is dependent on the respective input and output fluxes of this element. Consequently, benthic recycling and burial processes are an important aspect of the oceanic mass balance. As especially Fe and also other trace metals can often be the limiting factor for primary productivity, the availability of trace metals has a direct impact on phytoplankton growth. Where bottom water is upwelled to the surface ocean, the benthic burial or release of a trace metal can limit or fuel primary productivity.

We added an explanation to make this causality clearer in the revised version in lines 88 – 103 “Because of their contrasting tendency to form sulfide minerals and different supply pathways to the sediment, Fe and Cd can serve as prototypes to provide information about how sedimentary fluxes of different TMs may respond to declining oxygen concentrations. Under more reducing conditions the mobility of TMs can either be enhanced or diminished, e.g., through precipitation of sulfide minerals that are buried in the sediments (e.g. Westerlund et al., 1986; Rigaud et al., 2013; Olson et al., 2017). Increased burial or release of TMs at the seafloor can have an impact on the amplitude of primary productivity, especially at the eastern ocean boundaries where the near-bottom water column is connected to the surface ocean via upwelling. Moreover, since the inventories of TMs in the ocean are generally dependent on the respective input and output fluxes, changes in the balance between trace metal recycling and burial can have an impact on oceanic TM reservoirs on longer timescales. By comparing the benthic biogeochemical cycling of Fe and Cd across spatial and temporal redox gradients, we aim to provide general constraints on how the stoichiometry of bio-essential TMs in seawater may be affected by ocean deoxygenation.”.

We are currently working on a second paper where we will present aspects on sedimentary cycling and benthic fluxes of other trace metals off Peru including Zn, which has a low sulfide solubility and Co which has a high sulfide solubility, that are in agreement with the conclusions of the present manuscript.

Referee 1 comment 2:

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 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.

Response to referee 1 comment 2:

It was not our purpose to disregard earlier work on sedimentary trace metal dynamics in inner-shore and coastal environments like lagoons and estuaries. In sections 1.2 and 1.3 we refer to earlier studies on benthic trace metal biogeochemistry. We note, however, that except for Fe, little work has been done in open marine systems where the redox- and sediment-dynamics are different compared to estuaries and lagoons. The expansion of our knowledge on trace metal cycling and fluxes in these open-marine environments is the goal of our study.

In the revised manuscript we included further citations to studies in inner-shore environments such as Metzger et al., 2007 and Point et al., 2007 and rephrased lines 155 – 160 “Most previous studies have focused on the benthic cycling of Cd in near- and in-shore environments such as estuaries and lagoons (e.g. Westerlund et al., 1986; Colbert et al., 2001; Audry et al., 2006b; Metzger et al., 2007; Point et al., 2007; Scholz and Neumann, 2007). By contrast, little is known about Cd cycling in open-marine sedimentary environments, where the redox- and sediment-dynamics are different.”.

In the general section on trace metal behavior (1.1 Scientific rationale) we refer now more explicitly to the knowledge gained in studies on estuaries and lagoons that trace metals can precipitate as sulfides when redox conditions change and H_2S concentrations increase in the revised version in lines 91 -94 “ Under more reducing conditions the mobility of TMs can either be enhanced or diminished, e.g., through precipitation of sulfide minerals that are buried in the sediments (e.g. Westerlund et al., 1986; Rigaud et al., 2013; Olson et al., 2017).”.

Referee 1 comment 3:
Methods Incubation time was of 32h, how oxygen evolved within chambers that were not anoxic in the beginning?

Response to referee 1 comment 3:
The evolution of oxygen concentrations during the benthic lander incubations will be published by Clemens et al. (in preparation).

The incubated bottom water in chambers below the oxygen minimum zone (station 9 and 10) did not become anoxic. At station 9 (750 m) the oxygen concentrations decreased from around 3 µmol at the beginning of the incubation to around 2 µmol at the end of the incubation. At the station 10 (950 m) oxygen remained above 10 µmol throughout the incubation time. For the incubation at station 1 (75 m) we cannot exclude that traces of oxygen were present during the first 5 hours of the incubation (some air bubbles may have been trapped inside the chamber during the lowering through the water column, that then dissolved during the beginning of the incubation). This may have reduced dissolved Fe concentrations in the first sample of this incubation through oxidative removal, however excluding this first value would not affect the overall flux magnitude derived from this incubation.

Referee 1 comment 4:
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

Response to referee 1 comment 4:
It was our goal to sample and to capture the cycling of trace metal cycling in the highly dynamic layer overlying the seafloor. The common definition of the benthic boundary layer is "a discrete layer of flowing sea water above a benthic substrate, delimited vertically by its contact with free stream flow" (D.J. Wildish, in Encyclopedia of Ocean Sciences (Second Edition), 2001). We acknowledge that, strictly speaking, our sampling interval does not correspond to the benthic boundary layer in the proper sense. We therefore decided to refer to "near-bottom water column" in the revised version.

For Cd measurements we applied the method by Rapp et al., 2017, where the detection limit for Cd is 0.8 pmol L^{-1}, which is well below the lowest concentrations of our samples (40 pmol L-1). The detection limit of Cd is listed now in lines 293 - 294 in the revised version "The detection limits were 28.8 pM for Fe and 0.8 pM for Cd (Rapp et al., 2017).".

Referee 1 comment 5:
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.

Response to referee 1 comment 5:
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; Warnken 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 H_2S accumulates close to the surface in these settings, the dissolved Fe peak in pore water is very narrow (order of 1 - 2 cm) and located close to the sediment-water interface. More advanced curve fitting methods would fail to capture sharp gradients at the sediment surface and would, therefore, yield erroneous flux estimates (see also Shibamoto and Harada, 2010; Dale et al., in prep.)

We included an explanation for choosing the two point concentration gradient for diffusive flux calculations in lines 321 – 328 in the revised version “We chose to use the commonly applied approach of a two point concentration gradient for the determination of diffusive fluxes, as more advanced curve fitting methods would fail to capture sharp concentration gradients at the sediment surface and, thus, lead to erroneous flux estimates (Shibamoto and Harada, 2010).”.

Referee 1 comment 6:
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

Response to referee 1 comment 6:
We plotted linear regressions for the concentration change over time during the benthic chamber incubation for Fe and Cd (Fig. 5 and 7). We also listed the equations and the coefficient of determination for each linear regression in the supplement in Table S4.

In figures where error bars are not shown, the analytical error is smaller than the symbol size, which is stated in the figure captions.

Referee 1 comment 7:

Particulate flux calculations and CdS water column uptake calculations should also be detailed here, especially the last one

Response to referee comment 7:
The calculations used for the quantification of the sedimentary Cd sink and the different delivery pathways to the sediment are explained in section 4.2.2 Quantification of the sedimentary Cd sink. How we determine the particulate delivery of Cd to the sediment via CdS precipitation in the near-bottom water column is explained below Table 3 (Cd enrichment in the sediment after subtraction of diffusive and organic Cd sources). We explain this better in lines 676 – 679 in the revised version “The Cd delivery via precipitation in the water column was determined as the remainder of Cdxs * MAR after subtraction of the two other sources (i.e., diffusive flux and minimum/maximum delivery by organic material).”.

Referee 1 comment 8:
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 woud 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 a “biogeochemical cycling”. I would suggest to simply call it: “Porewater and benthic fluxes” then “iron, then “cadmium”

Response to referee 1 comment 8:
In section 3.1 we present our measured data of oxygen, nitrate and nitrite during both cruises. The prevailing biogeochemical conditions are important for the trace metal cycling- That is why it is crucial to leave this data in the manuscript.

Regarding the very special oceanic condition, the occurrence of a coastal El Niño during our cruise in 2017, we refer to literature instead of our own data as this includes atmospheric and oceanographic observations that we could not conduct ourselves. We moved this part to the introduction to section 1.4 Study area.

We fully agree and changed the titles of the results sections as suggested in 3.2 Bottom water, pore water and benthic flux data and then in subsections 3.2.1 Iron and 3.2.2 Cadmium.

Referee 1 comment 9:
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

Response to referee 1 comment 9:
We removed the first part of the sentence starting in line 354 including the citations in line 355 -356.

Referee 1 comment 10:

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 date 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?

Response to referee 1 comment 10:

As mentioned in response to referee comment 4 we will replace the term 'benthic boundary layer' by the 'near-bottom water column'.

Regarding our statement in line 351 (comparing Fe concentrations in the bottom waters collected inside and outside of the benthic chambers): 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.

We added an explanation in lines 432 – 435 in the revised version explaining the different concentrations between bottom water outside and within the benthic chamber "Concentrations of Fe in bottom waters from benthic chamber incubations are mostly higher than in ambient bottom waters because of Fe release from the sediment and an accumulation in the enclosed water volume inside the benthic chamber.".

As mentioned in response to referee comment 6 we plotted linear regressions for the concentration change over time during the benthic chamber incubation for Fe and Cd (figures 5 and 7) together with the slopes calculated from pore water profiles to facilitate the comparison of benthic fluxes derived by these two different approaches.

However, applying a transport-reaction model, which would need to involve carbon, sulfur, nitrogen and iron turnover to generate accurate pore water profiles of dissolved Fe, is beyond the scope of the present paper.

Referee 1 comment 11:
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 endobionts 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

Response to referee 1 comment 11:
Hydrogen sulfide could not be detected within bottom waters from benthic chamber incubations with our method, which has a detection limit of 1 µmol L^{-1}. For Fe to precipitate as sulfide several hundred µmol L^{-1} of H_2S are required. Therefore, we exclude Fe sulfide precipitation within the benthic chambers.

As mentioned in our response to referee comment 3, we cannot exclude a slight oxygen contamination within the benthic chamber at station 1 during the very beginning of the incubation (some air bubbles may have been trapped inside the chamber during the lowering trough the water column, that then dissolved during the beginning of the incubation). This may have reduced dissolved Fe concentrations in the first sample of this incubation through oxidative removal. However, excluding this first value would not affect the overall flux magnitude derived from this incubation.

At stations below the permanent oxygen minimum zone (station 9 and 10) the oxygen was not consumed during the incubations, which is why it is unlikely that endobionts came to the sediment surface.

Referee 1 comment 12:
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 _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

Response to referee 1 comment 12:
The determination of the removal rates of Fe in near bottom waters are based on the assumption that silica is transported vertically by eddy diffusion and the modelled eddy diffusion coefficient from our data determines the half-life of Fe in the first 4 m above the seafloor. It is possible that our assumption of solute transport by eddy diffusion is not correct. Alternatively, decreasing Fe and Silica concentration above the seafloor could be due to super-imposed water layers with different Fe and silica concentrations but little vertical exchange. In this case our calculated half-life would be an underestimation. We are very aware of these limitations and expanded section 4.1.2

to explicitly discuss the uncertainties of this method in line 533 – 540 in the revised version "The approach assumes that $Si(OH)_4$ is transported vertically by eddy diffusion and eddy diffusion and oxidation control the half-life of Fe in the first 4 m above the seafloor. It is possible that our assumption of solute transport by eddy diffusion is not correct. Alternatively, decreasing Fe and $Si(OH)_4$ concentration above the seafloor could be due to super-imposed water layers with different Fe and $Si(OH)_4$ concentrations but little vertical exchange. In this case our calculated half-life would be an underestimation.".

We only applied the half-life calculations at stations with a discernable gradient within the first 4 m above the seafloor. This is clearly the case at station 4, but even though the gradient at station 3 falls within error we decided to also use this station because it still shows a clear gradient when compared to silica.

The silica concentrations measured in near bottom waters are listed now in Table S3 in the supplement.

Referee 1 comment 13:
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 post important part of the study

Response to referee 1 comment 13:
The determination of the particulate delivery of Cd to the sediment via CdS precipitation in the water column is explained below Table 3. We also explained this better in lines 676 – 679 in the revised version "The Cd delivery via precipitation in the water column was determined as the remainder of Cd_{xs} * MAR after subtraction of the two other sources (i.e., diffusive flux and minimum/maximum delivery by organic material).".

We plotted the linear regressions for the concentration change over time during the benthic chamber incubation for Fe and Cd (figures 5 and 7). We mention now the coefficient of determination for each linear regression in Table S4 in the supplement.

The ranges in Table 3 listed in column "Cd from organic matter" result from the minimum and maximum estimate of Cd that is delivered to the sediment via organic material (see below Table 3 and explanation in section 4.2.2). These values were determined by multiplying the average concentration ratio of Cd to C in phytoplankton (Moore et al., 2013) with published particulate organic carbon rain rates (maximum estimate) or burial rates (minimum estimate) for each individual site (Dale et al., 2015). The ranges in Table 3 in the column "CdS precipitation in water column" result from the subtraction of the minimum and maximum of Cd that is delivered by organic matter, we explain this better now below Table 3.

Referee 1 comment 14:

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

Response to referee 1 comment 14:
We added to the introduction the order of decreasing sulfide solubility for several mono-sulfide forming trace metals in the revised version in lines 60 – 61 "(e.g. Fe, Zn, Cd; listed in the order of decreasing sulfide solubility).".

Referee 1 comment 15:
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 take-home message of the paper I would guess and the paper does not address such important question.

Response to referee 1 comment 15:
In our manuscript we want to focus on long-term environmental changes, even though we are aware that seasonality or non-cyclic oceanographic and meteorological features as ENSO are important to consider. There are other publications dealing with these short term changes e.g. by Scholz et al., 2011, who discussed the impact of ENSO-related oxygen fluctuations on the early diagenesis of redox-sensitive trace metals.

The concentration/reservoir of a trace metal in the ocean is dependent on the respective input and output of this element. Consequently, benthic recycling and burial processes are an important aspect of oceanic mass balance. As especially Fe and also other trace metals can be often the limiting factor for primary productivity the availability of TMs has a direct impact on phytoplankton growth. As bottom water can be upwelled to the surface ocean, the benthic burial or release of a trace metal can have an impact on the amplitude or fuel/limit primary productivity. We refer to this last statement in the introduction in the revised version in lines 94 – 97 "Increased burial or release of TMs at the seafloor can have an impact on the amplitude of primary productivity, especially at the eastern ocean boundaries where the near-bottom water column is connected to the surface ocean via upwelling.".

Technical comment 1 referee 1:
Line 189 "compared" Line 191 "covered" Line 207 "weighted" Line 317 what are optopodes? Line 563 "can take"

Response to technical comment referee 1:
These mistakes were corrected.

Technical comment 2 referee 1:
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

Response to technical comment 2 referee 1:
We implemented these suggestions. We plotted linear regressions for the concentration change over time during the benthic chamber incubation for Fe and Cd (Fig. 5 and 7). We also mention the coefficient of determination for each linear regression in the supplement in Table S4. R^2 values are briefly described in the revised version in lines 392 - 395 “At these stations also the highest R2 for the linear regressions of the concentration change over the incubation time were calculated (Station 4: R2 = 0.7, Station 6: R2 = 0.5) (Table S4). “ and in lines 421 - 423 “At sites within the OMZ, Cd removal within the chamber was near-linear (Stations 4, 5 and 6: R^2 = ≥ 0.9) (Table S4), which translates to a removal flux of 13 – 23 µmol m^{-2} y^{-1}. “.

Technical comment 3 referee1:
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

Response to technical comment 3 referee 1:
We noticed that the equilibrium constants that were applied were missing and added them to the caption of Fig. 10 in the revised version in lines 1215 – 1218 “Equilibrium constants (log K under standard conditions) for Fe (FeS ppt: -3.92), Ni (millerite: -8.04), Zn (sphalerite: -11.62) and Cd (greenokite: -15.93) were taken from the PHREEQC WATEQ4F database (Ball and Nordstrom, 1991)”.

We mention how we calculated the saturation indices in lines 690 -694 “This notion is illustrated in Fig. 10, showing saturation indices calculated based on the range of TM concentrations observed in the ocean and typical H_2S concentrations observed in anoxic marine environments (nM – µM concentrations represent sulfidic events in the water column; µM – mM concentrations are typical for pore waters).”.

Technical comment 4 referee 1:
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?

Response to technical comment 4 referee:
In Table 3 the numbers in brackets represent the flux calculated from the Cd concentration difference between the bottom water (0.5 m) and the first sample from the benthic chamber (taken after 0.25 h) which was characterized by near-complete Cd depletion. This is explained below Table 3.

The flux is coherent with our data in the sense that it would be high enough to explain the Cd enrichment in the sediment. We added this statement in the revised version in lines 703 – 707 “ At Station 1, where the surface sediment below the benthic chamber was highly sulfidic, the particulate Cd removal calculated from the concentration difference between the bottom water (0.5 m) and the first sample from the benthic chamber incubation (taken after 0.25 h) was high enough to explain the total Cd enrichment in the sediment.”.

Technical comment 5 referee 1:
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?

Response to technical comment 5 referee 1:
In figure 9 the spatial extension of biogeochemical conditions are indicated by bars above the figure (oxygenated, nitrogenous, sulfidic).

Indeed, it would be very interesting to compare also the variability of Cd fluxes between different seasons or years under changing biogeochemical conditions. Unfortunately, however, no benthic Cd fluxes were determined or published prior to our 2017 cruise.

Referee 2 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 2 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) is listed now in the revised version in Tables S1 and S2 in the supplement.

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; Warnken 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 H_2S 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 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 included an explanation for choosing the two point concentration gradient for diffusive flux calculations in lines 321 – 328 in the revised version "We chose to use the commonly applied approach of a two point concentration gradient for the determination of diffusive fluxes, as more advanced curve fitting methods would fail to capture sharp concentration gradients at the sediment surface and, thus, lead to erroneous flux estimates (Shibamoto and Harada, 2010).".

Referee 2 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 2 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.

We added an explanation in lines 432 – 435 in the revised version explaining the different concentrations between bottom water outside and within the benthic chamber “Concentrations of Fe in bottom waters from benthic chamber incubations are mostly higher than in ambient bottom waters because of Fe release from the sediment and an accumulation in the enclosed water volume inside the benthic chamber.”.

In the revised version linear regressions for the concentration change over time during the benthic chamber incubation are shown now in Fig. 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 2 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 2 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 made it clearer in section 4.1.1 that colloidal Fe could modify Fe concentrations within our samples in lines 485 – 493 “Furthermore, colloidal Fe could modify Fe concentrations within our samples and explain some of the fluctuations observed during the incubations. 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 aggregate into larger particles (Raiswell and Canfield, 2012). The transfer of Fe between dissolved, colloidal and particulate pools is likely to affect the balance between Fe transport and re-precipitation and -deposition to some extent. However, since did not differentiate between colloidal and truly dissolved fractions during our sampling, we cannot discuss this aspect further based on our data.”.

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 mention this in lines 544 – 546 in the revised version “Further research on dissolved-particulate interactions, including the role of colloidal Fe, in bottom waters is needed to better constrain how sedimentary Fe fluxes are modified in the near-bottom water column.”.

We do connect our scattered flux chamber data at stations 1, 9 and 10 to bioturbation and bioirrigation in lines 433 – 436. We added that bioturbation and bioirrigation could also lead to particle or colloid resuspension in lines 483 – 484 in the revised version “Bioturbation and bioirrigation could also contribute to particle resuspension at oxic stations, thus leading to removal of dissolved Fe.“.

Referee 2 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 2 comment 4:

Following the reviewer's recommendation, we rephrased lines 20 – 23 in the revised version "Diffusive Fe fluxes and Fe fluxes from benthic chamber incubations (-0.3 – -17.5 mmol m-2 y-1) are broadly consistent at most stations, indicating that diffusion is the main transport mechanism of dissolved Fe across the sediment-water interface. ".

Referee 2 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 biorrigation and bioturbation as a significant process for Fe enrichment in the flux chambers.

Response to referee 2 comment 5:

We rephrased 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 in lines 742 – 743 in the revised version "Within the OMZ, where bottom dwelling macrofauna is absent, diffusion is the main process that transports Fe from the sediment pore water into the bottom water".

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 comments referee 2:

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 comments referee 2:

We implemented your suggestions. Station numbers were added to the map in Fig. 1 and to the caption of Fig. 2. Hydrogen sulfide concentrations in pore waters are also plotted in Fig. 6 now.

The control of hydrogen sulfide on benthic iron and cadmium fluxes in the oxygen minimum zone off Peru

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Abstract

Sediments in oxygen-depleted marine environments can be an important sink or source of bio-essential trace metals in the ocean. However, the key mechanisms controlling the release from or burial of trace metals in sediments are not exactly understood. Here, we investigate the benthic biogeochemical cycling of Fe and Cd in the oxygen minimum zone off Peru. We combine bottom water ~~profiles,~~and pore water ~~profiles~~concentrations, as well as benthic fluxes determined from pore water profiles and in-situ from benthic chamber incubations, along a depth transect at 12° S. In agreement with previous studies, both concentration-depth profiles and in-situ benthic fluxes indicate a ~~Fe~~ release of Fe from sediments ~~into~~to the bottom ~~waters~~water. Diffusive Fe fluxes and Fe fluxes from benthic chamber incubations ~~are roughly consistent (~~(-0.3 – -17.~~1~~5 mmol m^{-2} y^{-1}~~),~~) are broadly consistent at most stations, indicating that diffusion is the main transport mechanism of dissolved Fe across the sediment-water interface. The occurrence of mats of sulfur oxidizing bacteria on the seafloor represents an important control on the spatial distribution of Fe fluxes by regulating hydrogen sulfide (H_2S) concentrations and, potentially, Fe sulfide precipitation within the surface sediment. ~~Removal~~ Rapid removal of dissolved Fe after its release to anoxic bottom waters ~~is rapid in the first 4 m away from the seafloor (half-life < 3 min) which~~ hints to oxidative removal by nitrite ~~or interaction~~and interactions with particles in the ~~benthic boundary layer.~~near-bottom water column. Benthic flux estimates of Cd ~~are indicative of~~suggest a flux into the sediment within the oxygen minimum zone. Fluxes from benthic chamber incubations (up to 22.6 µmol m^{-2} y^{-1}) exceed ~~the~~ diffusive fluxes (< 1 µmol m^{-2} y^{-1}) by a factor > 25, indicating that downward diffusion of Cd across the sediment-water interface is of subordinate importance for Cd removal from benthic chambers. As Cd removal in benthic chambers co-varies with H_2S concentrations in the pore water of surface sediments, we argue that Cd removal is mediated by precipitation of CdS within the chamber~~.~~ water or directly at the sediment-water interface. A mass balance approach, taking into account the contributions of diffusive and chamber fluxes ~~and fluxes measured in benthic chambers~~ as well as Cd delivery with organic material, suggests that CdS precipitation in the near-bottom water could make an important contribution to the overall Cd mass accumulation in the sediment solid phase. According to our results, the solubility of trace metal sulfide minerals (Cd << Fe) is a key-factor controlling trace metal removal and consequently the magnitude as well as the temporal and spatial heterogeneity of

sedimentary fluxes. We argue that depending on their sulfide solubility, sedimentary source or sink fluxes of trace metals will change differentially as a result of declining oxygen concentrations and an associated expansion of sulfidic surface sediments. Such a trend could cause a change in the trace metal stoichiometry of upwelling water masses with potential consequences for marine ecosystems in the surface ocean.

1. Introduction

1.1 Scientific rationale

The world´s oceans are losing oxygen (e.g. Keeling et al. 2010; Stramma et al. 2010; Helm et al. 2011). In total around 2 % of ~~oceanic~~ oxygen has been lost over the past five decades (Schmidtko et al., 2017) and an expansion of oxygen minimum zones (OMZs) in the tropical oceans has been documented over the same timespan (Stramma et al., 2008). The biogeochemical cycling of several nutrient~~-~~-type trace metals (TMs) is likely to be particularly susceptible to changing oxygen concentrations as they occur in different oxidation states (e.g. Fe, Mn, Co) and/or are precipitated as sulfide mineral in anoxic-sulfidic environments (e.g. ~~Zn, Cd).~~Fe, Zn, Cd; listed in the order of decreasing sulfide solubility). However, with the exception of Fe ~~(Dale et al., 2015a; Lohan and Bruland, 2008; Rapp et al., 2018; Schlosser et al., 2018; Scholz et al., 2014a)~~(Dale et al., 2015a; Lohan and Bruland, 2008; Rapp et al., 2018; Schlosser et al., 2018; Scholz et al., 2014a), little information is available on how other TM fluxes will respond to ocean deoxygenation. As certain TMs are essential for the growth of marine organisms (e.g. Fe, Mn, Co, Ni, Zn, Cd), TM availability~~ in the oceans~~ can (co-)limit primary productivity and therefore affect oceanic carbon sequestration through the biological pump (Saito et al., 2008; Moore et al., 2013; Morel et al., 2014). As a consequence, a better understanding of how TMs respond to low oxygen conditions is essential for predicting how marine ecosystems and the carbon cycle will evolve in the future ocean, with modelling scenarios predicting a continuation of ocean deoxygenation (Bopp et al., 2002; Oschlies et al., 2008; Keeling et al., 2010)

Marine sediments are an important source or sink of TMs to the ocean under low oxygen conditions (Böning et al., 2004; Brumsack, 2006; Scor Working Group, 2007; Severmann et al., 2010; Noble et al., 2012; Biller and Bruland, 2013; Conway and John, 2015b; Klar et al., 2018). In the OMZ off the coast of Peru, substantial fluxes of reduced Fe and other TMs across the sediment-bottom water interface have been documented (Noffke et al., 2012; Scholz et al., 2016) or inferred (Hawco et al., 2016). While a number of studies have addressed biogeochemical processes that lead to benthic Fe release, the key biogeochemical processes and conditions that control the sedimentary release or burial of other TMs in open marine systems are still poorly constrained. Moreover, a detailed picture of removal or stabilization processes and rates that take place in the highly dynamic ~~benthic boundary~~water layer overlying the seafloor is lacking.

In this article, we compare the benthic biogeochemical cycling of Fe and Cd. It has been established that the Peruvian OMZ represents a source of dissolved Fe to the ocean (Noffke et al., 2012; Fitzsimmons et al., 2016; John et al., 2018). In contrast, earlier studies have demonstrated that OMZs represent a sink for Cd (Janssen et al., 2014; Böning et al., 2004). ~~Because of their contrasting tendency to form sulfide minerals and different supply pathways to the sediment, Fe and Cd can provide information about how sedimentary fluxes of different TMs may respond to declining oxygen concentrations.~~Because of their contrasting tendency to form sulfide minerals and different supply pathways to the sediment, Fe and Cd can serve as prototypes to provide information about how sedimentary fluxes of different TMs may respond to declining oxygen concentrations. Under more reducing conditions the mobility of TMs can either be enhanced or diminished, e.g., through precipitation of sulfide minerals that are buried in the sediments (e.g. Westerlund et al., 1986; Rigaud et al., 2013; Olson et al., 2017). Increased burial or release of TMs at the seafloor can have an impact on the amplitude of primary productivity, especially at the eastern ocean boundaries where the near-bottom water column is connected to the surface ocean via upwelling. Moreover, since the inventories of TMs in the ocean are generally dependent on the respective input and output fluxes, changes in the balance between trace metal recycling and burial can have an impact on oceanic TM reservoirs on longer timescales. By comparing the benthic biogeochemical cycling of Fe and Cd across spatial and temporal redox gradients, we aim to provide general constraints on how the stoichiometry of bio-essential TMs in seawater may be affected by ocean deoxygenation.

1.2. Marine biogeochemistry of iron

Iron is the most abundant TM in phytoplankton and part of a range of metalloenzymes that are involved in important biological functions, such as photosynthesis or nitrogen fixation (Twining and Baines, 2013). Despite Fe being ~~the fourth most~~highly abundant~~ element~~ in the continental crust, its low availability limits primary productivity in up to 30 % of the surface ocean area (Moore et al., 2013). This limitation arises from the low solubility of ~~Fe(III), the~~its thermodynamically stable form in ~~oxygenated~~oxic waters~~.~~, Fe(III). Concentrations can reach up to ~ 1 nM when Fe(III) is kept in solution through complexation with organic ligands (Rue and Bruland, 1997; Liu and Millero, 2002; Boyd and Ellwood, 2010; Raiswell and Canfield, 2012). The thermodynamically stable form of Fe under anoxic conditions, Fe(II), is more soluble and therefore anoxic waters are typically characterized by higher dissolved Fe concentrations (up to tens of nM) (Conway and John, 2014; Vedamati et al., 2014; Fitzsimmons et al., 2016; Schlosser et al., 2018).

Sediments within OMZs are considered an important source of dissolved Fe and some of the highest sedimentary Fe fluxes have been observed in these regions (Severmann et al., 2010; Noffke et al., 2012). Under anoxic conditions, Fe(II) can be liberated from the sediments into pore waters from Fe-(oxyhydr)oxides through reductive dissolution by microbes or abiotic reduction with H_2S (Canfield, 1989). In the absence of oxygen, dissolved Fe(II) escapes the rapid re-oxidation and subsequent (oxyhydr)oxide precipitation and can, therefore, diffuse from pore waters into bottom waters. However, in anoxic OMZs, where denitrification takes place, Fe(II) can also be re-oxidized with nitrate as a terminal electron acceptor, either mediated by nitrate-reducing microbes or abiotically ~~by~~through reaction with nitrite (Straub et al., 1996; Carlson et al., 2013; Scholz et al., 2016; Heller et al., 2017). The solubility of Fe in sulfidic (i.e. NO_3^- and NO_2^- depleted) water is relatively high (Rickard et al., 2006) and ~~it has been observed, that~~ during sulfidic events dissolved Fe can accumulate in the water column (up to hundreds of nM) because of decreased Fe oxidation (Scholz et al., 2016) and stabilization as aqueous Fe sulfide complexes and clusters (Schlosser et al., 2018). ~~However, Fe fluxes across the benthic boundary have been hypothesized~~

~~to decrease as H$_2$S accumulation in the surface sediment impedes Fe escape through precipitation of Fe sulfide minerals (Scholz et al., 2014b).~~ However, Fe fluxes across the benthic boundary have also been hypothesized to decrease under strongly sulfidic conditions in the surface sediments, when pore waters become oversaturated with respect to Fe monosulfide (Scholz et al., 2014), which is the precursor for pyrite (FeS$_2$) (Raiswell and Canfield, 2012).

1.3. Marine biogeochemistry of cadmium

~~Even though its~~Cd is abundant in phytoplankton despite concentrations that are one order of magnitude lower ~~compared to~~than Fe~~, Cd is abundant in phytoplankton (Twining and Baines, 2013).~~(Moore et al., 2013; Twining and Baines, 2013). A function for Cd as a catalytic metal atom in the carbonic anhydrase protein has been found in diatoms (Lane and Morel, 2000) and it can also substitute Zn and enhance phytoplankton growth under Zn limitation in different phytoplankton species (Price and Morel, 1990; Lee and Morel, 1995; Sunda and Huntsman, 2000; Xu et al., 2008). ~~Inside the~~In marine sediments Cd can be released from the solid phase ~~into~~to the pore waters through the remineralization of organic matter (Klinkhammer et al., 1982; Collier and Edmond, 1984; Gendron et al., 1986; Gerringa, 1990; Audry et al., 2006; Scholz and Neumann, 2007). After its release to the pore water, Cd can ~~either~~ diffuse across the sediment-water interface~~, or under~~. Under anoxic and sulfidic conditions, Cd is thought to be precipitated as CdS (Greenockite) and retained in the sediment (Westerlund et al., 1986; Gobeil et al., 1987; Rosenthal et al., 1995; Audry et al., 2006). Due to its low sulfide solubility, CdS can precipitate at much lower H$_2$S concentrations than FeS (~~Mackinawite), which is the precursor for pyrite (FeS$_2$~~mackinawite) (Morse and Luther, 1999).

~~The few studies on pore water concentration and benthic fluxes of Cd, mostly carried out in estuaries or coastal settings,~~ Most previous studies have focused on the benthic cycling of Cd in near- and in-shore environments such as estuaries and lagoons (e.g. Westerlund et al., 1986; Colbert et al., 2001; Audry et al., 2006b; Metzger et al., 2007; Point et al., 2007; Scholz and Neumann, 2007). By contrast, little is known about Cd cycling in open-marine sedimentary environments, where the redox- and sediment-dynamics are different. Previous studies on sedimentary Cd cycling generally concluded that the flux of organic material and the presence of H$_2$S are the most important factors controlling the balance between Cd recycling versus precipitation and burial ~~(e.g. Westerlund et al. 1986; Colbert et al. 2001; Audry et al. 2006; Scholz and Neumann 2007).~~(e.g. Westerlund et al., 1986; Colbert et al., 2001; Audry et al., 2006; Metzger et al., 2007; Scholz and Neumann, 2007). Low oxygen regions in the ocean are considered an important sink for Cd (Janssen et al., 2014; Conway and John, 2015a; Xie et al., 2019) and sediments below OMZs are highly enriched in Cd (Ragueneau et al., 2000; Böning et al., 2004; Borchers et al., 2005; Muñoz et al., 2012; Little et al., 2015)~~, however~~. However, the respective contributions of different Cd removal ~~mechanism~~mechanisms to Cd accumulation in the sediment have not been quantified.

1.4. Study area

Seasonal upwelling of nutrient-rich waters off the Peruvian coast in austral winter leads to ~~a~~ high rates of primary productivity in the ~~euphotic~~photic zone (~ 300 mmol C m^{-3} d^{-1}) (Pennington et al., 2006). The combination of oxygen consumption through the respiration of this organic matter and low oxygen concentrations in water masses that supply upwelling regions, leads to the formation of one of the world's most intense OMZs, with complete oxygen consumption in the OMZ core~~ of the OMZ~~ between ~ 100 m – 300 m water depth (Karstensen et al., 2008; Thamdrup et al., 2012). Upon oxygen depletion, NO_3^- can serve as an electron acceptor for respiration~~, therefore~~. Therefore, denitrification, dissimilatory ~~nitrate~~ reduction of NO_3^- to ammonium (DNRA) and anaerobic ammonium oxidation (anammox) with NO_2^- are important biogeochemical processes within the anoxic and nitrogenous water column (Lam et al., 2009; Lam and Kuypers, 2011; Dalsgaard et al., 2012). The OMZ overlying the Peruvian shelf is a temporally and spatially dynamic system where biogeochemical conditions can range from fully oxic to anoxic and sulfidic. Occasional shelf oxygenation events occur mostly during El Niño events and are linked to the propagation of coastal trapped waves~~, which mostly occur during El Niño events~~ (Gutiérrez et al., 2008)~~, but could be also observed during a coastal El Niño event (Lüdke et al., 2019). During such events oxygen can reach down~~. During such events, oxygenated water can be found on the upper slope to 200 m – 300 m water depth (Levin et al., 2002). By contrast, sulfidic events can occur during periods of stagnation, when ~~not only~~ oxygen~~ but also~~, NO_3^- and NO_2^- become depleted in the water column due to ~~low water mass exchange.~~sluggish ventilation. Once NO_3^- and NO_2^- are depleted, chemolithoautotrophic H_2S oxidation is impeded. ~~Under such conditions, H_2S~~Hydrogen sulfide produced by bacterial sulfate reduction in sediments can then be released ~~into~~to the water column (Schunck et al., 2013)~~, with the amount of H_2S being released on the Peruvian shelf~~ at rates reaching several mmol m^{-2} d^{-1} (Sommer et al., 2016).

Our sampling campaign (cruises M136 and M137) took place in April and May 2017, during the decline of a coastal El Niño event. A coastal El Niño is a local phenomenon that refers to reduced upwelling and increased sea surface temperatures off the coasts of Peru and Ecuador, with typically heavy rainfall on land. During this event in austral summer, coastal waters off Peru showed a strong positive sea surface temperature anomaly of up to 2 to 4 °C (Echevin et al., 2018; Garreaud, 2018). The warming is proposed to be a result of strong local alongshore wind anomalies and equatorial Kelvin waves propagating towards the Peruvian coast (Echevin et al., 2018; Peng et al., 2019).

2. Methods

2.1 Sampling and sample handling

In this study, data from three different types of samples were combined: (1) pore waters for the determination of benthic diffusive fluxes and to study TM cycling in sediments; (2) Benthic chamber incubations, to determine in-situ fluxes across the sediment-water interface; (3) ~~Near bottom~~Bottom water concentration-depth profiles to determine the fate of TMs in the particle-rich and ~~reactive benthic boundary layer~~dynamic near-bottom water column.

~~Our~~The sampling took place during RV Meteor cruises M136 and M137 in austral autumn between April and May 2017. We also ~~compare~~compared our ~~recent~~ data ~~set~~ to benthic diffusive Fe(II) ~~flux data~~fluxes from RV Meteor cruise M92~~, which~~ that took place in austral summer during January 2013. Our sampling stations ~~cover~~covered the entire Peruvian shelf and slope across a transect at 12°S (Fig. ~~1).~~

~~This transect covered~~ 1) with water depths from 75 ~~m~~ – to 950 m ~~and includes~~, thus including stations above, inside and below the permanent OMZ. Our sampling of pore waters and sample collection from benthic chamber incubations generally followed the methodology described in Noffke et al. (2012).

Short sediment cores of 30 ~~cm to~~ – 40 cm length were retrieved with a multiple corer (MUC). Upon recovery, the cores were directly transferred into the ship's cool room (4°C). The supernatant bottom water was instantly sampled ~~immediately~~ and filtered through 0.2 µm cellulose acetate filters (Sartorius) and acidified to pH < 1 with subboiled distilled HNO_3. The sediment cores were subsequently sampled in vertical sections in a glove bag under Ar atmosphere to prevent any contact with oxygen. The sediment samples were centrifuged to separate the pore waters from the sediment solid phase. Pore waters were then filtered in another Ar-filled glove bag through 0.2 µm cellulose acetate filters (Sartorius). An 8 ml aliquot ~~of 8 ml~~ was acidified to pH < 1 with subboiled distilled HNO_3 and stored in acid cleaned low-density polyethylene (LDPE) bottles for TM analysis. Another aliquot was taken for analysis of H_2S concentrations. Additional sediment subsamples were collected in pre-~~weight~~weighed cups for ~~the determination of~~ water content and porosity ~~and~~determination as well as for ~~the determination of~~ Cd and organic C concentrations measurements in the solid phase.

Benthic landers ~~that consist of~~, constructed from titanium frames ~~and contain~~, containing two circular benthic chambers ~~to conduct~~for in-situ incubations, were deployed on the seafloor (see Sommer et al. (2009) for details). After placement of the lander on the seafloor, ~~two circular~~the benthic chambers ~~with an~~ (internal diameter of 28.8 cm) were partially driven into the sediment, covering a sediment area of 651.4 cm^2. ~~The seawater~~A volume ~~that~~between 12 – 18 l, overlying the first 20 – 30 cm of the seafloor, was enclosed in the chamber ~~varied between 12 l and 18 l,~~ , depending on the insertion depth of the chamber into the sediment. Prior to the incubation, the seawater contained in the chamber was repeatedly replaced with ambient seawater to replace solutes and flush out particles~~, which were~~ that might have been mobilized during the insertion of the chamber into the sediment. Over the incubation time of around 32 hours, 8 consecutive samples of 12 ml were filtered in-situ through 0.2 µm cellulose acetate filters (Sartorius) via peristaltic pumps and collected in quartz glass tubes. All sampling tubes were acid cleaned prior to use to guarantee a TM clean sampling. After recovery of the lander, the quartz glass tubes were transferred to the laboratory and ~~the obtained sample amount of 12 ml for each incubation time was~~samples were stored in acid cleaned LDPE bottles and acidified to pH < 2 with subboiled distilled HNO_3. Other samples were collected simultaneously for analysis of nitrogen species. The incubated sediments within the benthic chamber were sampled after recovery of the lander and pore waters were extracted to analyze H_2S concentrations for comparison with pore water profiles from parallel MUCs.

To determine TM concentrations across the ~~benthic boundary layer, we used the lander to collect~~near-bottom water column, water samples were collected at ~~a distance of~~ 0.5, 1.0, 2.0, 3.0 and 4.0 m ~~from~~above the seafloor using sampling apparatus attached to the landers. Filter holders with 0.2 µm polyether sulfone filters (Supor) were attached at the various depths and connected to sampling tubes that went through peristaltic pumps into gas sampling bags (Tedlar). ~~The sampling at distances of~~Sampling at 3.0 m and 4.0 m above the seafloor was realized by attaching the filter holders and tubing to an arm that was automatically unfolded upon placement of the lander at the seafloor. The peristaltic pumps transferred the seawater from ~~their~~the sampling ~~depth~~depths into the sampling bags over the same time period ~~of~~as the lander incubations of around 32 hours. This resulted in an average sample volume of 1.5 l per depth. All filters, tubing and sampling bags were acid cleaned prior to deployment to guarantee a TM clean sampling. Directly after sample retrieval, an 60 ml aliquot ~~of 60 ml~~ was stored in acid cleaned LDPE bottles and acidified to pH < 2 for TM analysis. Another aliquot was taken for analysis of silicic acid ($Si(OH)_4$).

2.2 Analytical methods

Concentrations of Fe(II) in pore waters were measured on board directly after sample retrieval by photometry using the ferrozine method (Stookey, 1970). Other geochemical parameters in our different samples were also determined photometrical (U-2001 Hitachi spectrometer) using standard techniques (Grasshoff et al., 1999). Hydrogen sulfide concentrations were determined using the methylene blue method and ~~silicic acid~~$Si(OH)_4$ concentrations were determined using a heptamolybdate solution as reagent. Concentrations of nitrogen species were determined by an auto-analyzer (QuAAtro, SEAL Analytical) using sulfanilamide as reagent (Hydes et al., 2010).

For TM analysis of bottom water samples we followed the procedure described by Rapp et al. (2017), ~~where~~whereby the TMs ~~are~~were pre-concentrated by a fully automated device (SeaFAST). After raising the sample pH to 6.4 with an ammonium acetate buffer (1.5 M), ~~a~~15 ml of sample~~ amount of 15 ml~~ was loaded onto a chelating resin column, where the seawater matrix was rinsed off, before the TMs were collected into 1ml elution acid (1 M subboiled HNO_3). Due to the smaller size of pore water samples and samples from benthic lander incubations, a half-automated device (Preblab) with a smaller sample loop and thus dead volume was ~~applied for these sample types.~~used. On this device, sample loading and collection as well as the addition of buffer was done manually. For samples from benthic lander incubations and pore waters, an amount of 3 ml and ~~for pore waters~~ 1 ml, respectively, was needed for pre-concentration. The samples were diluted with de-ionised water (MilliQ, Millipore) to increase the sample volume to 5 ml for samples from benthic chamber incubations and to 3 ml for pore waters. The pre-concentrated samples were measured by ICP-MS (HR-ICP-MS; Thermo Fisher Element XR) and TM concentrations were quantified by isotope dilution. The detection limits were 28.8 pM for Fe and 0.8 pM for Cd (Rapp et al., 2017). Accuracies for replicate measurements of ~~certified~~ reference seawater certified for TMs are listed in Table 1.

~~Cadmium and Al concentrations in sediments for~~For the calculation of sedimentary Cd enrichments (Cd_{xs}~~)~~), Cd and Al contents in sediments were determined following total digestions~~. Freeze~~ of freeze dried and ground sediment samples. The sediment was digested in 40 % HF (suprapure), 65 % HNO3 (suprapure) and 60 % $HClO_4$ (suprapure). Concentrations were measured by ICP-OES (VARIAN 720-ES). The reference standard MESS was used to check the digestion procedure~~, the~~. The accuracy was ± 0.3 % for Cd and ± 1.3 % for Al (MESS-3 Cd: 0.24 ± 0.01 µg g^{-1}, recommended value 0.24 ± 0.01 µg g^{-1}, MESS-3 Al: 8.59 ± 0.11 µg g^{-1}, recommended value 8.59 ± 0.23 µg g^{-1}).

Organic carbon content in the ~~sediments~~sediment was determined~~,~~ using an Elemental Analyzer (Euro EA) after removal of inorganic carbon with 0.25 mM HCl~~, using an Elemental Analyzer (Euro EA).~~. Precision of the measurement was ± 1 %.

2.3 ~~Flux~~Diffusive flux calculations

Benthic diffusive fluxes (F_D) were determined using Fick's first law of diffusion using concentration gradients between the uppermost pore water sample (0 – 1 cm) and the overlying bottom water (dC/dx) (Boudreau, 1997):

$$F_D = -\Phi D_{sed}(\mathrm{dC/dx}) \quad (1)$$

The effective molecular diffusion coefficients of Fe and Cd for sediments (D_{sed}) were calculated from the molecular diffusion coefficient in seawater (D_{sw}) under standard conditions (Li and Gregory, 1974) by adjusting it to in-situ temperature, pressure and salinity ~~using~~applying the Stokes-Einstein Equation. ~~Diffusion~~We determined the diffusion coefficients for sediments ~~were calculated~~ as follows:

$$D_{sed} = D_{sw}/\theta^2 \quad (2)$$

Tortuosity (θ) was calculated from porosity (Φ) as follows (Boudreau, 1997):

$$\theta^2 = 1 - \ln(\phi^2) \quad (3)$$

~~Positive fluxes are directed into the sediment.~~

Positive values represent a flux from the bottom water into the sediment pore water, negative values a flux from the sediment pore water into the bottom water. All input values for the diffusive flux calculations are listed in Tables S1 and S2 in the supplement.

We chose to use the commonly applied approach of a two point concentration gradient for the determination of diffusive fluxes, as more advanced curve fitting methods would fail to capture sharp concentration gradients at the sediment surface and, thus, lead to erroneous flux estimates (Shibamoto and Harada, 2010).

The fluxes from benthic lander incubations were calculated from the slopes of linear regressions~~, resulting from concentration changes over the incubation times.~~ from the concentration-time data. The relevant equations are listed together with the coefficients of determination (R^2) in Table S4 in the supplement. Fluxes were ~~corrected for~~ determined using the water volume enclosed in the benthic chamber, ~~which was determined~~estimated for each deployment from the insertion depth of the benthic chamber into the sediment.

3. Results

3.1 Biogeochemical conditions in the water column

Due to the particular atmospheric and oceanographic conditions, the decline of a coastal El Niño during our sampling campaign (cruises M136 and M137), the water column overlying the Peruvian shelf was oxygenated. Oxygen concentrations were > 20 µM in the water column down to around 100 m water depth. ~~Cruise M136 and M137 took place in April and May 2017, during the declining phase of a coastal El Niño event.~~However, bottom water oxygen concentrations directly above the seafloor, measured using optodes attached to lander, were below the detection limit (> 1 µM) at the shallowest station (Station 1).~~ A coastal El Niño is a local phenomenon that refers to reduced upwelling and increased sea surface temperatures off the coasts of Peru and Ecuador, with typically heavy rainfall on land. During this event in austral summer, coastal waters off Peru showed a strong positive sea surface temperature anomaly of up to 2 to 4 °C (Echevin et al., 2018; Garreaud, 2018). The warming is proposed to be a result of strong local alongshore wind anomalies and equatorial Kelvin waves propagating towards the Peruvian coast (Echevin et al., 2018; Peng et al., 2019). Due to the particular atmospheric and oceanographic conditions, the water column overlying the Peruvian shelf was oxygenated during our sampling campaign. Oxygen concentrations were > 20 µM in the water column down to around 100 m water depth. However oxygen concentrations in bottom waters directly above the seafloor on the shallowest station (station 1) were below the detection limit (> 1 µM) measured through optopodes attached to lander.~~ The OMZ, with O_2 concentrations < 5 µM, extended from around 120 to 400 m water depth. The water column within the OMZ was nitrogenous (i.e. NO_3^- reducing) as indicated by the presence of NO_2^- (≥ 4 µM), an intermediate product of denitrification (Zumft, 1997). Oxygen gradually increased to > 50 µM~~ from~~ below 400 m towards 950 m water depth (Fig. 2). As we will compare some of our data to those of an earlier cruise (M92), the corresponding oxygen distribution across the Peruvian continental margin is shown for comparison (Fig. 2).

~~3.2 Benthic iron cycling~~

3.2 Bottom water, pore water and benthic flux data

3.2.1 Iron

Iron concentrations in near~~-~~-bottom waters decreased from near~~-~~-shore to off~~-~~-shore stations, from > 100 nM at the shallowest shelf station at 75 m water depth (~~station~~Station 1) to 6 nM at 750 m water depth (~~station~~Station 9) (Fig. 3). At a number of stations within the OMZ (~~stations~~Stations 3 and 4), vertical concentration gradients were observed. Here Fe concentrations decreased by 15 ~~-~~– 20 nM from 0.5 to 4 m above the seafloor. Multiple sampling at the shallowest shelf station (~~station~~Station 1) revealed that Fe concentrations were temporally variable and ranged from ~ 100 nM at the end of April to < 60 nM at the end of May 2017.

Concentrations of Fe(II) in pore waters were highest (up to a few µM) in the upper 5 – 10 cm of the sediment cores. ~~Downcore~~Deeper in the sediment cores, concentrations decreased to > 0.2 µM (Fig. 4). At all stations, sharp concentration gradients between the uppermost pore water and bottom water sample were observed, with higher concentrations in pore waters at the sediment surface ~~were higher~~(µM) than in the overlying bottom water~~, which~~ (nM). This observation implies a diffusive flux from pore waters into bottom waters. The steepest concentration gradients across the sediment-water interface were observed within the OMZ. The highest Fe(II) concentrations at the sediment surface (> 6 µM) ~~occurred~~were observed at ~~station~~Station 4 (145 m water depth). At this station, the benthic diffusive flux into the bottom waters was also highest ~~with~~ at -17.~~1~~5 mmol m^{-2} y^{-1}. The lowest diffusive fluxes of 0.0 (due to concentrations below the detection limit) and -0.~~4~~3 mmol m^{-2} y^{-1} were observed on the upper slope below the OMZ at ~~stations~~Stations 9 and 10 respectively (Table 2). An accumulation of H_2S in pore waters coincided with a depletion of Fe(II) concentrations (Fig. 4). At ~~station~~Station 1, we observed the highest H_2S concentrations throughout the core and in particular at the sediment surface, with maximum concentrations reaching > 4 mM. At ~~stations~~Stations below the OMZ (~~stations~~Stations 9 and 10), no H_2S was detected within pore waters (Fig. 4).

Iron concentrations inside the benthic chambers ~~were generally higher than in ambient bottom waters, and reached maximum values > 300 nM. At stations 4 and 6, located inside the OMZ, concentrations in the chambers increased in a linear way during the incubation. At stations above and below the OMZ, we did not observe a linearly increasing concentration trend over the incubation time. Following previous~~

~~studies (Turetta et al., 2005; Severmann et al., 2010; Noffke et al., 2012; Lenstra et al., 2019) and for comparison with diffusive fluxes, we estimated benthic Fe fluxes from linear regressions from the change in Fe concentrations in the benthic chamber against incubation time (Table 2). To test the plausibility of the flux magnitude within the chamber, we also calculated theoretical concentration gradients over time based on our diffusive flux estimates (Fig. 5). Our incubation data were largely consistent in direction and slope with the diffusive benthic fluxes. Especially at stations inside the OMZ (station 4 and 6), where the highest diffusive fluxes of 17.1 and 8.3 mmol m^{-2} y^{-1} were observed, the projected and observed concentration gradients were in good agreement. At stations below the OMZ, diffusive fluxes of < 1 mmol m^{-2} y^{-1} were too low to be detected over our~~reached maximum values > 300 nM. At Stations 4 and 6, located inside the OMZ, concentrations in the chambers increased in a linear way during the incubation. At stations above and below the OMZ, we did not observe a similar trend over time. For comparison with diffusive fluxes, we estimated benthic Fe fluxes from linear regressions of Fe concentrations versus time (Table 2). We also calculated the theoretical concentration gradients over time in the benthic chambers based on our diffusive flux estimates (Fig. 5). The incubation data were largely consistent in direction and slope with the diffusive fluxes. In particular, the projected and observed concentration gradients were in good agreement at stations inside the OMZ (Station 4 and 6), where the highest diffusive fluxes of -17.5 and -8.0 mmol m^{-2} y^{-1} were observed. At these stations also the highest R^2 for the linear regressions of the concentration change over the incubation time were calculated (Station 4: $R^2 = 0.7$, Station 6: $R^2 = 0.5$) (Table S4). At stations below the OMZ, diffusive fluxes of < 1 mmol m^{-2} y^{-1} were too low to be detected over the incubation time of 32 hours.

~~3.3 Benthic cadmium cycling~~

3.2.2 Cadmium

In near-bottom waters Cd concentrations increased with distance from the coast, from 0.4 nM at the shallowest station at 75 m water depth (~~station~~Station 1) to 1.1 nM below the OMZ at 750 m water depth (~~station~~Station 9). ~~Cd~~Cadmium concentrations were constant at each station between 0.5 and 4 m above the seafloor (Fig. 3).

Cadmium concentrations in pore waters ranged between 0.1 – 2 nM (Fig. 6). Within the OMZ, bottom water concentrations were higher than concentrations in pore water ~~within~~at the sediment surface ~~sediments~~ (0 - 1 cm~~)~~), indicating a downward diffusive flux into the sediments. The benthic diffusive fluxes inside the OMZ were ~~of~~on the order of 0.~~5~~6 – 0.8 µmol m^{-2} y^{-1} (Table 3). In contrast, at ~~station1~~Stations 1 and 9 an upward-directed concentration gradient was observed, indicating a diffusive flux from the sediments into bottom waters. The upward diffusive flux ~~ranged from~~ was -1.9 µmol m^{-2} y^{-1} above the permanent OMZ~~, to~~ and -0.2 µmol m^{-2} y^{-1} below the OMZ (Table 3). Pore water Cd concentrations at greater sediment depths were mostly higher than bottom water concentrations. In some cases (~~station~~Stations 3 and 4), elevated pore water Cd concentrations (up to 2 nM) coincided with elevated H$_2$S concentrations (few hundred µM).

In the benthic chambers three different Cd ~~patterns~~trends were observed (Fig. 7). Above the permanent OMZ (~~station~~Station 1), Cd concentrations in the chambers were low (< 0.2 nM) throughout the incubation period, indicating ~~that there was~~ no Cd flux. At sites within the OMZ (~~station~~Stations 4, 5 and 6), concentrations decreased from ~ 0.6 ~~nM to~~ – 0.3 nM over the course of the incubation. Below the OMZ (~~stations~~Stations 9 and 10), Cd ~~concentration~~concentrations in the chamber were high (~ 1 nM) and remained constant or increased slightly during the incubation. At sites within the OMZ, Cd removal within the chamber was ~~nearly~~ near-linear~~,~~ (Stations 4, 5 and 6: R^2 = ≥ 0.9) (Table S4), which translates to a removal flux of 13 ~~-~~– 23 µmol m^{-2} y^{-1}. The Cd removal fluxes in benthic chambers were more than one order of magnitude higher than diffusive benthic fluxes (0.~~5~~6 – 0.~~7~~8 µmol m^{-2} y^{-1}) (Table 3).

4. Discussion

4.1 Benthic iron cycling

4.1.1 Comparison of diffusive and in-situ benthic chamber iron fluxes

Concentrations of Fe in bottom waters from benthic chamber incubations are mostly higher than in ambient bottom waters because of Fe release from the sediment and an accumulation in the enclosed water volume inside the benthic chamber. In the absence of oxygen and, thus, bottom-dwelling macrofauna at stations within the OMZ, bioturbation and bioirrigation are unlikely to exert an important control on sedimentary Fe release. Consistent with this notion, the slope calculated from benthic diffusive fluxes is largely consistent with the concentration gradients observed within the benthic chambers (Fig. 5). Moreover, our fluxes from benthic chamber incubations and diffusive fluxes are generally of the same order of magnitude (~~few mmol m^{-2} y^{-1}) (~~Table 2). Therefore, diffusive transport of dissolved Fe from the sediment into the bottom water seems to be the main control on the concentration evolution observed within the benthic chamber.

Some of the concentration gradients in benthic chambers are non-linear, indicating that the Fe flux was not constant during the incubations. ~~This observation~~This is a common observation in Fe flux data from benthic chamber incubations and higher Fe fluxes generally have higher R^2 values for the linear regressions (Friedrich et al., 2002; Turetta et al., 2005; Severmann et al., 2010; Lenstra et al., 2019). However, the non-linearity can be used to identify additional processes affecting Fe concentrations and fluxes within the benthic chamber, which may also affect fluxes under natural conditions. One possible process that can remove dissolved Fe(II) under anoxic conditions is Fe oxidation with NO_3^- as the terminal electron acceptor or oxidation with NO_2^- (Straub et al., 1996; Carlson et al., 2013; Klueglein and Kappler, 2013). The oxidation of reduced Fe in the absence of oxygen, either ~~biologically~~microbially mediated ~~by~~with NO_3^- or abiotically ~~by~~with NO_2^-, has been hypothesized to be important in the water column of the Peruvian OMZ (Scholz et al., 2016; Heller et al., 2017). During our incubation at ~~station~~Station 4 (Fig. 8), we observed a decline in Fe concentrations during the first ten hours of the incubation time. Concurrently, NO_3^- concentrations were decreasing, while NO_2^- accumulated, presumably due to progressive denitrification and release from the sediments. Once NO_3^- and NO_2^- were ~~quantitatively reduced~~depleted, Fe concentrations started to rise again~~ and the following concentration increase resulted~~, resulting in the highest in-situ Fe flux observed throughout our sampling campaign (Table 2). The coincidence in timing of Fe accumulation and NO_2^- decrease suggest that depletion of Fe at the beginning of the incubation was most likely caused by Fe oxidation with NO_2^-. The incubation at ~~station~~Station 4 was the only one where NO_3^- and NO_2^- were ~~quantitatively~~substantially removed during the incubation. However, the high Fe flux cannot be interpreted as a natural flux estimate at steady state. In general, we argue that bottom water NO_2^- concentrations exert a first order control on the intensity of Fe efflux at the absence of oxygen and, therefore, need to be considered in the evaluation of sedimentary Fe mobility in anoxic-nitrogenous OMZs.

During the incubations at ~~the stations~~Stations 1, 9 and 10, Fe concentrations did not continuously increase but ~~varied~~fluctuated between high and low values. This observation could be explained by a combination of bioirrigation and bioturbation at stations where oxygen was present (stations 9 and 10), as well as rapid Fe oxidation and precipitation processes. Under oxic conditions, bottom-dwelling macrofauna is likely to increase the transfer of dissolved Fe from the sediments into the bottom water (Elrod et al., 2004; Lenstra et al., 2019). During episodes of oxygenation a population of macrofauna that can enhance bioturbation and bioirrigation was observed on the Peruvian shelf (Gutiérrez et al., 2008). However, under oxic conditions, any Fe delivered to the chamber is prone to rapid oxidative removal. Moreover, ex-situ experiments have demonstrated a fast and efficient removal of up to 90% of dissolved Fe in incubated bottom waters due to particle resuspension (Homoky et al., 2012). ~~Interactions~~Bioturbation and bioirrigation could also contribute to particle resuspension at oxic stations, thus leading to removal of dissolved Fe.

Furthermore, colloidal Fe could modify Fe concentrations within our samples and explain some of the fluctuations observed during the incubations. 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 aggregate into larger particles (Raiswell and Canfield, 2012). The transfer of Fe between dissolved, colloidal and particulate pools is likely to affect the balance between Fe transport and re-precipitation and -deposition to some extent. However, since did not differentiate between colloidal and truly dissolved fractions during our sampling, we cannot discuss this aspect further based on our data.

Oxidation processes and interactions with particles ~~and oxidation processes~~ can efficiently remove Fe shortly after its transfer to bottom waters and this process is likely to be most intense close to the seafloor where the highest particle concentrations prevail. We argue that the same processes are reflected by declining Fe concentrations away from the seafloor in some of the bottom water profiles (at ~~station~~Stations 3 and 4) (Fig. 3).

4.1.2 Removal rates of dissolved iron in the ~~benthic boundary layer~~near-bottom water column

We observed declining Fe concentrations in the first 4 m away from the seafloor at ~~station~~Stations 3 and 4, which hints at removal of dissolved Fe in the near bottom waters~~,~~ after its release from the sediments. To differentiate between dilution with ambient bottom water (by currents) from Fe removal from the dissolved phase, Fe concentrations were normalized by ~~silicic acid (~~$Si(OH)_4$~~)~~ measured in the same samples (Fig. 3). Due to opal dissolution within Peru margin sediments, ~~silicic acid~~$Si(OH)_4$ is released into bottom waters (Ehlert et al., 2016). In contrast to Fe, we assume that ~~silicic acid~~$Si(OH)_4$ behaves conservatively and precipitation reactions within the bottom waters are of subordinate importance. The decreasing Fe to $Si(OH)_4$ ratios at ~~station~~Station 3 and 4 with distance from the seafloor indicate that there is Fe removal within the ~~benthic boundary layer~~near-bottom water column that must be related to precipitation processes or scavenging.

We further constrained rates of dissolved Fe removal at stations with a discernable Fe to $Si(OH)_4$ gradient within the first 4 m distance from the seafloor. To this end, we first determined an eddy diffusion coefficient (K_y) using ~~silicic acid~~$Si(OH)_4$ fluxes from benthic chamber incubations (F_{Si}) (see chapter 2.3 for methodology) and the known concentration gradient of dissolved ~~silicic acid~~$Si(OH)_4$ within the bottom water (d_{Si}/d_x), where x is the height above the seafloor. At the seafloor, the flux of ~~silicic acid~~$Si(OH)_4$ from the sediment is equal to the flux in the water column.

$$F_{Si} = -K_y(\cancel{d_{si}}d_{Si}/d_x) \qquad (4)$$

This equation can be ~~rearranged to find~~solved for the eddy diffusion coefficient.

Dissolved Fe in the bottom water (DFe) can be described by the ~~following~~ solving the diffusion-reaction~~-transport~~ equation for DFe (ignoring advection and assuming a steady-state first-order consumption of dissolved Fe):

$$DFe = C_{BW} * exp.(-\cancel{\sqrt{KFeox}/\sqrt{Ky})}\sqrt{k_{Feox}}/\sqrt{K_y}) \qquad (5)$$

The equation can be fitted to the measured DFe concentrations in the bottom water by adjusting the Fe concentration directly above the seafloor (C_{BW}) and the Fe oxidation constant (~~K_{feox}~~k_{Feox}). From the fitted first-order rate constant ~~K_{Feox}, we can determine~~k_{Feox}, the half-~~lives~~life for dissolved Fe in bottom waters can be calculated.

The half-~~lives~~lifes of dissolved Fe in the first 4 m away from the seafloor are 2.5 min and 0.3 min at ~~station~~Stations 3 and 4, respectively (Table 4). Another study reported a dissolved Fe half-life of 17 hours under nitrogenous conditions in the first 10 ~~to~~– 20 m above the seafloor in the Peruvian OMZ (Scholz et al., 2016). Our calculations suggest that Fe removal in near-bottom waters is much faster. The approach assumes that $Si(OH)_4$ is transported vertically by eddy diffusion and eddy diffusion and oxidation control the half-life of Fe in the first 4 m above the seafloor. It is possible that our assumption of solute transport by eddy diffusion is not correct. Alternatively, decreasing Fe and $Si(OH)_4$ concentration above the seafloor could be due to super-imposed water layers with different Fe and $Si(OH)_4$ concentrations but little vertical exchange. In this case our calculated half-life would be an underestimation.

As mentioned above~~,~~ (chapter 4.1.1), in the absence of oxygen, removal processes of dissolved Fe could be related to oxidation of dissolved Fe with NO_2^- or to interactions with suspended particles, which are likely to be most abundant directly above the seafloor. Further research on dissolved-particulate interactions, including the role of colloidal Fe, in bottom waters is needed to better constrain how sedimentary Fe fluxes are modified in the ~~benthic boundary layer~~near-bottom water column.

4.1.3 Controls on the temporal variability of benthic iron fluxes

The Peruvian OMZ is known to experience high-amplitude fluctuations in upwelling intensity as well as variability in bottom water oxygen, NO_3^-, NO_2^- and H_2S concentrations (Pennington et al., 2006; Gutiérrez et al., 2008; Graco et al., 2017; Ohde, 2018). To get an insight into how different biogeochemical conditions control benthic diffusive Fe(II) fluxes, we ~~compare~~compared the fluxes from our recent cruise with fluxes from our earlier cruise M92 (Fig. 9). Cruise M92 took place in austral autumn 2013 following the main upwelling season and during a period of intense primary productivity. Due to reduced upwelling and stable density stratification, the water column on the shallow shelf was not only depleted in oxygen but also in NO_3^- and NO_2^- during cruise M92 (Sommer et al., 2016). Under such conditions, chemolithoautotrophic H_2S oxidation with NO_3^- or NO_2^- was impeded so that pore water H_2S could be released from the sediment into the water column. As a result, the water column during M92 was sulfidic between around 50 ~~and~~– 150 m water depth with the highest H_2S concentration of 13 µM observed at 50 m depth (Fig. 2). While the biogeochemical conditions on the shallow shelf were fundamentally different to those during M136 and M137, below 150 m water depth the conditions were largely comparable (oxygen-depleted, NO_3^-: 20 – 30 µM, NO_2^- up to 9 µM between 150 – 300 m). At the stations with similar biogeochemical water column conditions, the Fe(II) fluxes during both ~~our~~ sampling campaigns were remarkably similar (Fig. 9). However, similar to the temporal variability of Fe concentrations in bottom waters at ~~station~~Station 1 (Fig. 3), we observed a pronounced difference in the diffusive flux magnitude on the shallow shelf~~,~~ where the biogeochemical conditions differed between both cruises. The highest diffusive flux during M92 in 2013 of -22.7 mmol m^{-2} y^{-1} was measured at ~~station~~Station 1. By contrast, during M136/137 in 2017 we ~~observed~~determined a much lower flux of -2.6 mmol m^{-2} y^{-1} at this station. During M136 and M137 the highest flux of -17.~~1~~5 mmol m^{-2} y^{-1} was measured at ~~station~~Station 4~~,~~ ~~located~~ at 145 m water depth.

Diffusive fluxes are a function of the concentration gradient between pore water and bottom water (Eq. (1)). As dissolved Fe concentrations in bottom waters are generally much lower (nM) compared to those observed in pore waters~~,~~ (µM), the flux magnitude is chiefly determined by differences in pore water Fe concentrations. During M92, pore waters at the sediment surface were characterized by high dissolved Fe concentrations (4.8 µM in the upper pore water sample), which resulted in a steep gradient and a comparably high Fe flux. Under the slightly sulfidic conditions that prevailed in the water column during M92, oxidative removal of dissolved Fe(II) with NO_3^- or NO_2^- was impeded (Scholz et al., 2016) and dissolved Fe(II) could be stabilized as aqueous iron sulfide (Schlosser et al., 2018). Therefore, the bottom water was characterized by high dissolved Fe concentrations (up to 0.7 µM in ~~MUCs overlying~~the supernatant bottom water of MUCs).

Despite oxic conditions in the water column during M136 and M137, we observed much higher H_2S concentrations in surface sediments at ~~station~~Station 1 compared to M92 (4100 µM during M136 and M137 versus 1800 µM during M92 within the first 8 cm of the core) (Fig. 4). Because of higher H_2S concentrations, Fe concentrations were controlled by the solubility of Fe monosulfide minerals (FeS). It may seem counterintuitive that the surface sediment was highly sulfidic, while the overlying water column was oxygenated. In order to explain this observation, we need to consider the role of mats of filamentous sulfur oxidizing bacteria in controlling H_2S concentrations in surface sediments. (Gutiérrez et al., 2008; Noffke et al., 2012; Yücel et al., 2017). During M92 these mats were generally abundant on the shelf and upper slope~~, thus limiting the extent of H_2S accumulation within surface sediments~~ (Sommer et al., 2016)~~.~~, thus limiting the extent of H_2S accumulation within surface sediments. Previous studies demonstrated that mats of sulfur oxidizing bacteria can disappear during periods of oxygenation (Gutiérrez et al., 2008). Consistent with this previous finding, visual inspection of the seafloor using the video-guided MUC revealed that the abundance of bacterial mats on the seafloor seemed greatly reduced, which is most probably related to oxic bottom water conditions on the shallow shelf during the coastal El Niño event. As these microaerophilic organisms tend to avoid high oxygen concentrations they probably started to ~~withdraw into the sediment once oxygen levels raised. Furthermore, an abundance of red squat lobster (*Pleuroncodes monodon*), which are known to feed on bacterial mats (Gallardo et al., 1994), was observed at the seafloor on the shallow shelf. We suggest that the retreat~~die off or withdraw into the sediment once oxygen levels raised. We suggest that the disappearance of sulfide-oxidizing bacteria under oxic conditions created a situation where H_2S accumulation in the surface sediment and FeS precipitation limited the extent of Fe release into the bottom water.

4.2 Benthic cadmium cycling

4.2.1 Comparison of diffusive and in-situ benthic chamber cadmium fluxes

At stations above ~~the permanent~~ and below the permanent OMZ (~~stations~~Stations 1, 9 and 10), diffusive Cd fluxes and fluxes in benthic chambers were largely consistent (Table 3). In contrast, the fluxes determined with benthic chambers at stations within the OMZ (~~station~~Station 4, 5 and 6) were 25 to 40 times higher than the diffusive flux (Table 3). This discrepancy demonstrates that diffusion cannot be the dominant process leading to the continuous decrease of dissolved Cd during benthic chamber incubations. Alternatively, Cd could be precipitated within the benthic chamber and removed through downward sinking of Cd-rich particles. Cadmium sulfide (greenockite) has a relatively low solubility compared to sulfide minerals of other TMs (~~solubility product of~~ CdS ~~= -16.4~~ << FeS ~~= -3.9~~). It is generally agreed that CdS precipitation can ~~takes~~take place at trace amounts of H_2S (H_2S < 1 µM, i.e., below the detection limit of the method applied in this study) (Davies-Colley et al., 1985; Rosenthal et al., 1995). Previous studies using in-situ benthic flux chambers have concluded that production of H_2S in the sediment or the accumulation of H_2S in benthic chambers during incubations can switch the direction of the Cd flux or intensify Cd removal through CdS precipitation (Westerlund et al., 1986; Colbert et al., 2001). Precipitation of CdS during the incubation is, therefore, a viable explanation for the discrepancy between diffusive Cd flux and Cd fluxes in benthic chambers observed in our study. Furthermore, the three different ~~pattern of Cd concentration~~ trends of Cd concentrations observed in benthic chamber incubations can be related to H_2S concentrations in the surface sediment below the benthic chambers (Table 3). At stations within the OMZ~~,~~ (Stations 4,5 and 6), pore water H_2S concentrations in surface sediments were moderate (few µM). It is likely that there was a continuous leakage of trace amounts ~~if~~of H_2S from the pore water into the ~~incubated~~ bottom waters during the incubation, thus leading to CdS precipitation and declining Cd concentrations. On the shallowest shelf station~~,~~ (Station 1), where pore water H_2S concentrations in the surface sediment were high (hundreds of µM), a potentially large amount could have been released at the beginning of the incubation, thus explaining pronounced Cd depletion in the chamber compared to the surrounding bottom water (0.1 nM within the chamber compared to 0.4 nM outside the chamber). Below the OMZ~~,~~ (Stations 9 and 10), where there was no H_2S present in surface sediments, there was no Cd depletion in the chamber during the incubation and, consistent with previous studies in oxic settings (Westerlund et al., 1986; Ciceri et al., 1992; Zago et al., 2000; Turetta et al., 2005), both diffusive and benthic chamber flux data were indicative of an upward-directed flux out of the sediment. Due to the absence of H_2S, dissolved Cd released from biogenic particles in the surface sediment could accumulate in the pore water thus driving a diffusive flux out of the sediment.

4.2.2 Quantification of the sedimentary cadmium sink

Consistent with our Cd flux data there is general consent that OMZs are a sink for Cd. Several water column studies have observed Cd depletion in water masses within the Peruvian and other OMZs, which was mostly attributed to Cd removal via CdS precipitation in sulfidic micro-niches within particles in the water column ~~(Janssen et al., 2014; Conway and John, 2015b; Xie et al., 2019).~~(Janssen et al., 2014; Conway and John, 2015b). Sedimentary studies showed that Cd is highly enriched in OMZ sediments, which has mostly been attributed to the delivery of Cd with organic material and subsequent fixation as CdS within sulfidic sediments (Ragueneau et al., 2000; Böning et al., 2004; Borchers et al., 2005; Muñoz et al., 2012; Little et al., 2015). Based on our data, we can quantify the delivery of Cd to the sediments via three different pathways: (1) diffusion across the sediment-water interface and CdS precipitation within the sediment; (2) Cd incorporation by phytoplankton and delivery to the sediment with organic matter; (3) CdS precipitation in the water column and particulate delivery to the sediment (Table 3).

The enrichment of Cd in the sediment relative to the lithogenic background (expressed as excess Cd concentration~~,~~; Cd$_{xs}$) was calculated using the following equation (Brumsack, 2006):

$$Cd_{xs} = Cd_{sample} - Al_{sample} * (Cd/Al)_{crust} \quad (6)$$

The Cd/Al ratio of the upper continental crust ($1.22*10^{-6}$) was used as lithogenic background reference (Taylor and McLennan, 2009). To ~~get a~~calculate the flux of Cd to the sediment, Cd$_{xs}$ was multiplied with the mass accumulation rate (MAR) from published data for each individual site (Dale et al., 2015b). To approximate the amount of Cd delivered to the sediment with organic material, the average concentration ratio of Cd to C in phytoplankton (Moore et al., 2013) was multiplied by published particulate organic carbon rain rates (maximum estimate) or burial rates (minimum estimate) for each individual site (Dale et al., 2015b). The Cd delivery via precipitation in the water column was determined as the remainder of Cd$_{xs}$ * MAR after subtraction of the two other sources (i.e., diffusive flux and minimum/maximum delivery by organic material).

Sediments at all stations on the Peruvian shelf and slope are enriched in Cd relative to the lithogenic background. The accumulation rate of ~~Cd$_{xs}$~~Cd decreases with distance from the coast from 250 µmol m^{-2} y^{-1} at ~~the station~~Station 1 ~~at 75 m~~ to 4 µmol m^{-2} y^{-1} at ~~station~~Station 9 ~~at 750 m water depth~~ (Table 3). These fluxes generally exceed the amount of Cd delivered to the sediments via diffusion and associated with organic material. Together these mechanisms of Cd delivery can only account for ~ 20 % of the ~~Cd$_{xs}$~~Cd enrichment at stations above and inside the permanent OMZ, with the delivery with organic material being of greater importance. The remaining ~~water column Cd removal (~~~Cd enrichment in the sediment (~ 80 ~~%)~~%), after subtraction of diffusive and minimum/maximum organic Cd sources, must be related to CdS precipitation in the water column and delivery of Cd-rich particles to the sediment. This removal process can be a combination of CdS precipitation in sulfidic micro-niches around sinking particles (Janssen et al., 2014; Bianchi et al., 2018), CdS precipitation in sulfide plumes (Xie et al., 2019) when sedimentary H_2S can spread throughout the water column (Schunck et al., 2013; Ohde, 2018), and precipitation of CdS in the near-bottom water (this study). Our estimated CdS precipitation in the water column within the OMZ ~~agree~~agrees with the Cd fluxes ~~we~~ determined from benthic chamber incubations, where dissolved Cd removal takes place in the ~~first~~ 20 ~~cm~~ – 30 cm ~~away from~~ of overlying water above the ~~sediment surface.~~seafloor. These Cd removal fluxes from benthic chambers alone are sufficient to account for 41 % – 68 % of the estimated particulate Cd removal from the water column and 38~~% -~~ % – 60 % of total ~~Cd$_{xs}$~~Cd enrichment in the sediment within the OMZ (Table 3). Considering that Cd precipitation in near-bottom water is unlikely to be restricted to the 20 – 30 cm above the seafloor, covered by our benthic chambers, the removal flux associated with this process is likely to be even higher. At Station 1, where the surface sediment below the benthic chamber was highly sulfidic, the particulate Cd removal calculated from the concentration difference between the bottom water (0.5 m) and the first sample from the benthic chamber incubation (taken after 0.25 h) was high enough to explain the total Cd enrichment in the sediment.

Below the OMZ, at ~~750 m~~Station 9, where the smallest Cd enrichment ~~is~~was observed, the relative contribution of Cd delivery with organic material increases. About half of the ~~Cd$_{xs}$~~Cd enrichment can ~~derive from~~be attributed to organic material at this station.

Once Cd is delivered to the sediment, it can either stay fixed in the solid phase or ~~it can~~ be released ~~into~~to the pore waters. Cadmium concentrations in pore waters of subsurface sediments (> 10 cm sediment depth) were mostly higher than bottom water concentrations (Fig. 6), indicating a transfer of Cd from the solid phase into pore waters during early diagenesis. Cadmium sulfides are considered highly insoluble and stable within sediments (Elderfield et al., 1981), even~~–~~ upon re-oxygenation (Rosenthal et al., 1995). Therefore, Cd release through re-dissolution of CdS is ruled out as a potential source of dissolved Cd. Alternatively, Cd liberation upon remineralization of organic material could explain elevated Cd concentrations in the pore water. Elevated Cd concentrations in sulfidic pore waters have been observed in previous studies and attributed to Cd stabilization through formation of organic and inorganic complexes~~–~~ (Gobeil et al., 1987; Sundby et al., 2004). Experimental data gave evidence for the presence of dissolved Cd bisulfide and polysulfide complexes in pore waters. An increase of electrochemically active Cd after UV irradiation, was explained by the destruction of electrochemically inactive bisulfide and polysulfide complexes (Gobeil et al., 1987). At very high H_2S concentrations (> 10^{-3} M) the solubility of Cd may increase due to an increase in these bisulfide and polysulfide complexes. Under such highly sulfidic conditions, Cd solubility may even exceed the solubility in oxygenated waters and highly sulfidic sediment can eventually ~~turn into~~lead to a diffusive source of Cd to the bottom water (Davies-Colley et al., 1985). Such a scenario ~~can~~may explain the negative (i.e., upward-directed) diffusive Cd flux at ~~station~~Station 1, where the pore waters of surface sediments are highly sulfidic.

5. Conclusions and implications for trace metal sources and sinks in the future ocean

Consistent with earlier work, our results demonstrate that that OMZ sediments are a source for Fe and a sink for Cd. Moreover, based on our findings~~ allow to further constrain the different~~, biogeochemical conditions and processes that control the benthic fluxes of these TM across the Peruvian OMZ can be further constrained.

~~Iron~~Within the OMZ, where bottom dwelling macrofauna is ~~transported via~~absent, diffusion is the main process that transports Fe from the sediment pore water into the bottom water. The accumulation of high levels of H_2S in pore waters, modulated by the abundance of sulfur oxidizing bacteria, can reduce diffusive Fe release through sulfide precipitation within pore waters. In anoxic bottom waters Fe can be rapidly removed, likely via oxidation ~~by~~with NO_2^- and/or interaction with particles. Benthic Cd fluxes are directed from the bottom water into the sediment within the OMZ. Diffusive fluxes and delivery of Cd via organic material cannot account for the sedimentary Cd enrichment. Instead CdS precipitation in near~~-~~-bottom waters could be the most important pathway that delivers Cd to the sediments.

According to our results, H_2S concentrations in surface sediments exert a first order control on the magnitude and direction of Fe and Cd fluxes across the sediment-water interface. With generally decreasing oxygen concentrations in the ocean and an expansion of OMZs (Stramma et al., 2008; Schmidtko et al., 2017), sulfidic surface sediments will likely also expand. With regard to the solubility of their sulfide minerals, Fe and Cd represent two opposite end members. The solubility of sulfide minerals of other important nutrient-type TMs, such as Ni and Zn, is intermediate between those of Fe and Cd (Fe > Ni > Zn > Cd). An expansion of sulfidic surface sediments is thus likely to affect sedimentary TM fluxes in a differing manner. This notion is illustrated in Fig. 10, showing saturation indices calculated based on the range of TM concentrations observed in the ocean and typical H_2S concentrations observed in anoxic marine environments (nM ~~-~~– µM concentrations represent sulfidic events in the water column~~, pore water conditions are represented by up~~; µM ~~-~~– mM concentrations~~).~~ are typical for pore waters). Cadmium sulfide minerals become oversaturated at nM to µM H_2S concentrations, which ~~is~~explains why Cd removal can take place in the bottom water in OMZs. By contrast, FeS is highly undersaturated under the typical biogeochemical conditions in the water column. Therefore, FeS precipitation is unlikely to take place in the water column, even under somewhat more reducing conditions. Other sulfide-forming TMs have an intermediate sulfide solubility~~,~~ (e.g. Zn, Ni), which could imply that the direction and magnitude of their sedimentary fluxes is susceptible to expanding ocean anoxia. The differing response of TMs to an expansion of sulfidic conditions may cause a change in the TM stoichiometry of upwelling water masses with potential consequences for TM-dependent marine ecosystems in surface waters.

Data availability

The data will be made available at Pangaea upon publication of the article.

Author contribution

AP and FS conceived the study. AP, FS, AD, SS conducted the sampling at sea. AP analyzed the trace metal concentrations. AP and FS prepared the manuscript with contributions from all co-authors.

Competing Interests

The authors declare that they have no conflict of interest.

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Figure captions

Fig. 1: ~~Bathymetrical map of~~Sampling stations on the Peruvian continental margin ~~and sampling stations~~ during cruises M136 & M137 along ~~the~~a latitudinal depth transect at 12° S. The sampling stations for pore ~~water profiles~~waters are depicted by white stars, for bottom ~~water profiles~~waters by yellow dots and for benthic chamber incubations by red dots.

Fig. 2: Oxygen, nitrate, nitrite and hydrogen sulfide ~~profiles~~concentrations on the Peruvian slope (Station 10, 1000 m depth), crossing the oxygen minimum zone (upper panel), and the upper shelf (Station 1, 75 m depth) (lower panel) during cruises M136 & M137 and M92 along the 12° S transect.

Fig. 3: Near~~-~~-bottom water ~~profiles~~ concentrations of dissolved Fe and Cd ~~concentrations~~ and dissolved Fe to silicic acid ratios ~~in the benthic boundary layer~~ 0.5 m to 4 m above the seafloor across the 12° S transect. ~~Depicted by the~~The red ~~diamond is~~ diamonds show results from a second sampling ~~with a time difference of~~ at Station 1 one month ~~at station 1~~later. Concentrations of silicic acid are listed in Table S3 in the supplement.

Fig. 4: Pore water ~~profiles of~~ dissolved Fe(II) and hydrogen sulfide concentrations. ~~For station 7 (300 m water depth) and station 10 (950 m water depth) pore water profiles are not shown to save space, but the diffusive fluxes are listed in table 2.~~ ~~The profile of~~ Data from an earlier cruise, M92, at ~~station~~Station 1 (75 m water depth) ~~is~~are displayed for comparison. The uppermost sample ~~of each profile~~ represents the bottom water concentration. ~~All symbols are within error~~The analytical error is smaller than the symbol size.

Fig. 5: Dissolved Fe concentrations in incubated bottom waters from benthic chamber incubations. ~~The~~The grey dashed line represents the linear regressions of the concentration change over the incubation time. The equations for these linear regressions are listed together with the coefficients of determination (R^2) in Table S4 in the supplement. The black dashed line represents theoretical concentration gradients over the incubation time based on our benthic diffusive fluxes (Table 2). ~~All symbols are within~~The analytical error~~.~~ is smaller than the symbol size.

Fig. 6: Pore water ~~profiles of~~ dissolved Cd and hydrogen sulfide concentrations. The uppermost sample ~~of each profile~~ represents the bottom water concentrations. ~~All symbols are within~~The analytical error is smaller than the symbol size.

Fig. 7: Dissolved Cd concentrations in incubated bottom waters from benthic chamber incubations. ~~The~~The grey dashed line represents the linear regressions of the concentration change over the incubation time. The equations for these linear regressions are listed together with the coefficients of determination (R2) in Table S4 in the supplement. The black dashed line represents theoretical concentration gradients over the incubation time based on our benthic diffusive fluxes (Table 3). ~~All symbols are within error~~The analytical error is smaller than the symbol size.

Fig. 8: Dissolved Fe, nitrate and nitrite concentrations in incubated bottom waters from the benthic chamber incubation at ~~station~~Station 4 (145 m water depth).

Fig. 9: Comparison of benthic diffusive Fe(II) fluxes between cruises M136 & M137 and M92 on the Peruvian shelf. Negative values represent fluxes from the sediment pore water into the bottom waters. Shaded bars on the upper panel display the geochemical conditions in the water column during the time of sampling.

Fig. 10: Schematic overview of ~~how~~ the possible mobility of different trace metal ~~may respond~~ to an expansion of sulfidic conditions. Saturation indices (SI) were calculated for different H_2S concentrations and reported minimum and maximum concentrations of trace metals in the water column (data from Bruland and Lohan 2003). ~~Solubility products for Fe (FeS ppt), Ni (Millerite), Zn (Wurtzite), Zn (Greenokite) were taken from the Pitzer database (Plummer et al., 1988)~~Equilibrium constants (log K under standard conditions) for Fe (FeS ppt: -3.92), Ni (millerite: -8.04), Zn (sphalerite: -11.62) and Cd (greenokite: -15.93) were taken from the PHREEQC WATEQ$_4$F database (Ball and Nordstrom, 1991).The results are approximate since concentrations instead of activities were used for calculations. A positive SI is indicative of oversaturation whereas a negative SI is indicative of undersaturation.

Table 1: Accuracy ~~values for~~of replicate concentration measurements (n = 7) of certified reference seawater for trace metals NASS-7 and CASS-6 by ICP-MS.

	NASS-7 certified value	NASS-7 measured value	CASS-6 certified value	CASS-6 measured value
Fe (µg/L)	0.351 ± 0.026	0.352 ± 0.017	1.56 ± 0.12	1.56 ± 0.03
Cd (µg/L)	0.0161 ± 0.0016	0.0162 ± 0,0024	0.0217 ± 0.0018	0.0216 ± 0.0016

Table 2: Comparison of benthic diffusive Fe(II) fluxes out of the sediment and geochemical bottom water conditions between ~~M92 and~~ M136 & M137 and M92 on the Peruvian shelf. Fluxes during M92 correspond to similar depth (see Fig. 9).

station	M136 & M137	M136 & M137	M136 & M137	M136 & M137	M136 & M137	M136 & M137	M92	M92
	water depth	latitude	longitude	~~bottom~~ water column condition	Fe(II) flux diffusive	Fe flux benthic chamber	~~bottom~~ water column condition	Fe(II) flux diffusive
	(m)	(S)	(W)		(mmol m^{-2} y^{-1})	(mmol m^{-2} y^{-1})		(mmol m^{-2} y^{-1})
1	75	12°13.52	77°10.93	$O_2 < 5$ µM	-2.56	-1.74	slightly sulfidic	-22.69
3	130	12°16.68	77°14.95	nitrogenous	-0.81	-	slightly sulfidic	-3.16
4	145	12°18.71	77°17.80	nitrogenous	-17.~~08~~45	-8,57	nitrogenous	-5.77
5	195	12°21.50	77°21.70	nitrogenous	-2.~~72~~49	2.01	nitrogenous	-1.51
6	245	12°23.30	77°24.82	nitrogenous	-~~8.31~~7.96	-5,43	nitrogenous	-10.20
~~7~~	~~300~~	~~-~~	~~-~~	~~nitrogenous~~	~~-3.02~~	~~-~~	~~nitrogenous~~	~~-3.12~~
9	750	12°31.35	77°35.01	$O_2 > 5$ µM	0.00	-6.11	$O_2 > 5$ µM	0.400
~~9~~10	970	12°34.90	77°40.32	$O_2 > 5$ µM	-0.~~25~~26	-1.68	$O_2 > 5$ µM	-0.12

Table 3: Comparison of sedimentary Cd excess compared to the lithogenic background and the contribution of Cd delivery to the sediment via different pathways: (1) diffusion across the sediment-water interface and Cd sulfide precipitation within the sediment; (2) Cd incorporation by phytoplankton and delivery to the sediment with organic matter; (3) Cd sulfide precipitation in the water column and particulate delivery to the sediment.

station	water depth	Cd excess sediment[1]	(1) Cd flux diffusive	Cd flux benthic chamber	H_2S in surface ~~in~~ sediment below benthic chamber	(2) Cd from organic matter[2]	(3) CdS precipitation in water column[3]
	(m)	(µmol m^{-2} y^{-1})	(µmol m^{-2} y^{-1})	(µmol m^{-2} y^{-1})	(µM)	(µmol m^{-2} y^{-1})	(µmol m^{-2} y^{-1})
1	75	248.87	-1.85	-1.6 (3109.5~~)*~~)[4]	641.02	8.34 ~~-~~– 49.04	199.83 – 240.53
3	130	153.41	0.83	-	-	4.87 – 17.40	135.19 – 147.72
4	145	35.07	0.~~52~~54	13.4	1.30	1.55 – 6.48	28.07 – 32.99
5	195	44.76	0.~~72~~63	22.6	9.52	5.71 – 7.71	36.36 – 38.36
6	245	35.15	0.55	21.2	0.40	3.60 – 6.54	28.06 – 31.00
9	750	4.44	-0.~~24?~~30	0	0	1.48 – 3.21	1.23 – 2.96

[1] Calculated after Brumsack (2006) and multiplied ~~with~~by the mass accumulation rate for each site (Dale et al., 2015b).

[2] Determined by multiplication of Cd ~~to~~ /C ratio in average phytoplankton (Moore et al., 2013)~~. For maximum values organic carbon rain rates and for minimum values organic carbon accumulation rates (Dale et al., 2015b) were used.~~

with particulate organic carbon rain rates (maximum values) and organic carbon accumulation rates (minimum values) for each individual site (data from Dale et al., 2015b).

[3] Remainder of Cd excess in sediment after subtraction of diffusive and minimum and maximum organic Cd sources.

[*4] Flux calculated from ~~gradient of Cd~~the concentration difference between the bottom water ~~concentration~~ (0.5 m) and ~~concentration in~~the first sample from the benthic chamber incubation ~~sample (~~(taken after 0.25 h).

Table 4: Modelled half-~~lives~~lifes ($t_{1/2}$) of dissolved Fe within the first 4 m distance from the seafloor at ~~station~~Stations 3 ~~(130 m water depth) and station 4 (145 m water depth)~~and 4 and data used for determination of $t_{1/2}$ using Eq. (4) and Eq. (5).

station	water depth	$Si(OH)_4$ flux benthic chamber (F_{Si})	$Si(OH)_4$ concentration gradient (d_{Si})	~~Eddy~~eddy diffusion coefficient (K_y)	~~Modelled~~modelled Fe at sediment surface (C_{BW})	Fe oxidation constant (~~K_{Feox}~~k_{Feox})	~~Half-live~~half-life in ~~benthic boundary layer~~near-bottom water column ($t_{1/2}$)
	(m)	(µmol cm^{-2} d^{-1})	(µmol cm^{-3} cm^{-1})	(m^2 s^{-1})	(nM)	(d^{-1})	(min)
3	130	0.73	-4.05*10^{-6}	1.~~5510^{-6}~~55*10^{6}	70	400	2.5
4	145	0.33	-1.~~4410~~44*10^{-6}	1.~~9610^{-6}~~96*10^{6}	81	3500	0.3

Supplement

Table S1: Input data from M136 & M137 for diffusive flux calculations.

station	Fe(II) concentration bottom water (µM)	Fe(II) concentration in pore water at sediment surface (µM)	Cd concentration bottom water (nM)	Cd concentration in pore water at sediment surface (nM)	porosity	temperature (C°)	pressure (bar)	salinity
1	0.10	1.06	0.22	0.90	0.93	16.17	8.77	35.06
3	0.17	0.47	0.81	0.65	0.95	13.96	13.90	34.97
4	0.00	6.34	0.66	0.47	0.96	13.96	15.40	34.97
5	0.00	0.59	0.68	0.44	0.96	13.21	20.40	34.92
6	0.06	3.14	0.76	0.55	0.95	13.33	25.60	34.94
9	0.00	0.00	0.99	1.25	0.74	6.28	75.00	34.55
10	0.01	0.37	-	-	0.61	4.36	98.20	34.55

Table S2: Input data from M92 for diffusive flux calculations.

station	Fe(II) concentration in bottom water (µM)	Fe(II) concentration in pore water sediment surface (µM)	porosity	temperature (C°)	pressure (bar)	salinity
1	0.70	4.83	0.96	13.99	8.1	34.98
3	0.21	0.77	0.98	13.84	13.90	34.98
4	1.15	1.80	0.96	13.77	15.50	34.96
5	0.03	0.31	0.96	13.16	20.50	34.94
6	0.20	2.13	0.96	13.16	25.40	34.94
9	0.03	0.03	0.84	5.17	78.30	34.54
10	0.00	0.06	0.74	4.62	103.4	34.55

Table S3: Silicic acid ($Si(OH)_4$) concentrations in the near-bottom water column.

	Station 1	Station 3	Station 4	Station 5	Station 6	Station 9
distance from seafloor	$Si(OH)_4$ concentration	$Si(OH)_4$ concentration	$Si(OH)_4$ concentration	$Si(OH)_4$ concentration	$Si(OH)_4$ concentration	$Si(OH)_4$ concentration
(m)	(µM)	(µM)	(µM)	(µM)	(µM)	(µM)
0.5	31.28	29.74	24.86	24.32	27.28	-
1	31.63	29.22	24.51	24.20	27.14	56.22
2	-	29.2	23.61	24.35	27.02	56.04
3	31.38	28.66	24.36	-	-	55.96
4	31.27	28.17	24.20	24.00	27.04	55.44

Table S4: Equations for linear regressions from benthic chamber incubation data (Y = concentration, X = incubation time) and coefficients of determination (R^2).

station	Fe	Fe	Cd	Cd
	linear regression	R^2	linear regression	R^2
1	Y = 0.88 * X + 186.18	0.01	Y= 0.00 * X + 0.068	0.06
4	Y = 4.78 * X + 7.07	0.72	Y = -0.01 * X + 0.55	0.96
5	Y = -0.89 * X + 89.28	0.1	Y = -0.01 * X + 0.53	0.89
6	Y = 2.32 * X + 57.34	0.47	Y = -0.01 * X + 0.58	0.87
9	Y = 2.95 * X + 76.38	0.49	Y = 0.00 * X + 1.01	0.36
10	Y = 0.67 * X + 28.20	0.12	Y = 0.00 * X + 0.99	0.07