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Biogeosciences Discussions

Interactive comment on "Interaction between hydrocarbon seepage, chemosynthetic communities and bottom water redox at cold seeps of the Makran accretionary prism: insights from habitat-specific pore water sampling and modeling" *by* D. Fischer et al.

D. Fischer et al.

dfischer@marum.de

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Author response to comments by two anonymous referees

We appreciate and acknowledge the very helpful comments and corrections of the two anonymous referees which significantly improved the original version of the manuscript. The detailed responses to the reviewer's comments, questions and suggestions can be found on the next pages.

Response to anonymous referee #1

General comments:

. . .Along these lines, it also appears logical that the escaping gas is methane but if available, the authors should show data on this or explain their assumption.

Response: The composition of the escaping gas is discussed in great detail in another manuscript (Römer et al. (in review with Journal of Geophysical Research - Oceans): "Gas bubble emission from submarine hydrocarbon seeps at the Makran continental margin (offshore Pakistan))". These authors clearly show that the gas is dominated by microbial methane, which makes our assumption of sulfate reduction coupled to anaerobic oxidation of methane reasonable. To avoid overlap of the two studies, we decided to keep the discussion of gas composition as part of the study by Römer et al.

. . .Unfortunately, these are not so much on the scientific level, i.e., there is (almost) nothing really wrong, but rather related to style and grammar.

Response: Orthography and punctuation of the entire manuscript has been re-assessed and corrected in the revised version.

While reading, I lost several times the connection between “Flare” and “GeoB-site”. As the authors targeted a variety of different seep sites, it is absolutely crucial that an easy-to-follow coding is applied. One possibility would be to drop GeoB and the 6 digits used for each core and to give the sites trivial names. The original core numbering can than be listed with these trivia in a table to provide further information on the core (that would be one more column in Tab 1).

Response: The site-coding is simplified in the revised manuscript, in order to ease readability. We gave the sites trivial names, as suggested by the referee, and added these in an additional column in Table 1.

Specific comments: P9766, L20ff: This is a weak argument. Many seep biota use sulfide as an electron donor, they don’t detoxify their environment from it.

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It has been pointed out earlier that seep-fauna need hydrogen sulfide for their symbionts, but that sulfide is at the same time toxic for metazoans. This was the reason why we stated this ambivalent relationship in the introduction and cite the work by Wallmann et al. (1997). We changed this aspect in later sections of the manuscript to focus more on the sulfide-dependence, as criticized by the referee.

P9767, L2-3: the sentence is crippled here

We rephrased this sentence to clarify our statement.

P9767, L19: Fig. 1 shows the bathymetry of the area but not the tectonics. I would also cut the lower part of the figure or include enlargements of the flare areas.

The reference to Fig. 1 in this sentence was deleted. Furthermore, we significantly modified Fig. 1 in order to highlight and enlarge the local bathymetry of the different seep-sites, as requested by the referee.

P9768, Section 3. I would suggest describing the sampling scheme with the different habitats etc. in greater detail and simplify as much as possible (see my comments above). It would be unfortunate if the reader gets lost here (as I did), because the rest of the paper will not be understandable anymore.

We rearranged and shortened section 3 to ease readability.

P9768, L24: give reference to Fig. 1, here it really fits.

Changed accordingly.

P9768, L24: add a comma after “these four seep sites”. Orthography of the entire manuscript, particularly punctuation needs a polish.

Changed accordingly.

P9770 first paragraph: now the reader gets the first time an idea about the logic of your sampling scheme and habitat coding... (this is one example where the text is a bit

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chaotic). I would move this information upwards to the beginning of section 3.

Changed accordingly.

P9770, L7: this sentence is odd. I'd change to something like: After ROV and MUC retrieval...

Sentence rephrased

P9770, L17: also this sentence is odd. I suggest to change it to: The reproducibility of the above methods was verified by analyzing replicated standards.

Sentence rephrased

P9770, L22: erase "according to Eq. (1)

Changed accordingly.

P9771, L4: exchange "derived" with "determined"

Changed accordingly.

P9771, L5: explain why you used the modeled and not the measured gradient.

The sentence is redundant here. We deleted it. The idea was in the first place to use the modeled fluxes, because the sulfate profiles may be disturbed by in situ or ex situ degassing, as discussed in detail in the manuscript.

P9771, L13: specify how far away your sampling was from Bohrmann's site(s).

We added the information in the revised manuscript.

P9771, L18-20: this sentence is not well connected to the previous paragraph.

The sentence is redundant here. We deleted it.

P9771, L26ff: the referencing reads oddly. Firstly, it's only one other seep that is mentioned here; secondly, it would read better if the sentence would be rephrased to something like this: Notably, CoTReM has already been applied successfully for modeling transport processes and geochemical reactions in other seep systems, namely AOM-, advection- and bioirrigation rates at several (?) mud volcanoes in the Eastern Mediterranean (Haese et al., 2003, 2006).

We changed the sentence according to the suggestion.

P9772, L3ff: If you couldn't determine porosity (core dried after PW extraction?), then explain it here.

We added a sentence stating that porosity was not determined, because pore water extraction with rhizons removed much of the interstitial water, which would lead to wrong porosity data.

P9772, L8-10: I'd rephrase the sentence to something like this: Instrumental values for bottom water concentrations of sulfate, sulfide and methane (?) define the upper boundary conditions. Did you measure these in cores? from niskin bottles? If the first, then I would be careful with these values because you'll undoubtedly find leaking of PW into overlying bottom water if you retrieve a gassy core from such depth.

Bottom water concentrations were determined from supernatant water in retrieved push cores, as is stated in the methods section. In the discussion section we discuss ex situ and in situ degassing as one possible error source.

P9773, section 4.1: With respect to the lack of porosity data, how realistic is a decrease from 31 to 29 mM? Could this be in the range of error/noise?

We exclude this magnitude ($\sim$2 mM) of error/noise for these cores. The profiles are almost linear and gently approach lowest sulfate concentrations with depth.

P9774, L18-19: did you measure sulfide in the bottom water, or is it just the gradient?

In fact, we did measure sulfide in the supernatant water of retrieved cores. However, we do not show the data because – as we have stated in the manuscript – the cores

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from the central Habitat a are most likely affected by ex situ degassing or in situ bubble-irrigation.

P9776, L10ff where you describe data: Try grouping your results: i.e, habitats X at Flare Y and Z showed similar PW data, while habitat A at these flares where characterized by... Right now, it appears to me - after reading the text twice - that you just pile up facts/data without a recognizable order. I'm sure you had something in mid, but it is not apparent for the reader.

We have grouped our results as suggested by the referee (habitat a at site x shows these features, while habitat b at site y is different). We considered this very precise and detailed description of the concentration profiles in the respective habitats of different seeps to be crucial to understand the discussion of different pore water transport processes in section 5.

P9778, L1ff: I think the most obvious feature is that the central habitats are characterized by much higher gradients and that sediment surface sulfide concentrations are higher (thus indicating higher AOM rates). If fluid flow is the controlling factor limiting sulfate penetration into the sediment (as e.g at Mud Vulcanoes), then sulfide levels stay low (because AOM is hampered by not having access to sulfate).

Yes, but we wanted to point out that the uppermost measured samples (supernatant water of retrieved cores, see "methods" section) are depleted in sulfate in Habitat a cores, compared to other habitats.

P9778, L13ff. I don't understand the discussion about shifting OMZ depth resurrecting (?)macro fauna: you noticed alive macro fauna, correct? So, apparently, these organisms are active despite the low oxygen levels. I doubt that polychaetes and bivalves can "keep their breath" for extended time periods such as eg a monsoon cycle).

We do not expect that the fauna can "keep their breath" for as long as monsoonal cycles. Indeed, we measured extremely low bottom water oxygen concentrations at sites below the core-OMZ, where we as well found vast colonies of fauna. At first glance, this is a contradiction. We just wish to point out that apparently these oxygen levels are still high enough to support faunal life. Nevertheless, the general supply with oxygen in this critical depth-interval may be governed by the periodically shrinking and expanding OMZ as stated in the manuscript and in the literature.

P9779, L18ff: this part about lateral flow fits to the Haeckel reference above. I'd either move it there or move the first part of this particular discussion from above to here.

In this paragraph we discuss possible scenarios that may explain the occurrence of sulfate below the SMT. We discuss the concepts by Haeckel et al. (2007, in situ gas ebullition) and by O′Hara et al. (1995, convection) and conclude that increasing sulfate concentrations below the assumed depths of the SMT at Habitat a-sites are likely affected by convection of interstitial and bottom water. The gas ebullition theory by Haeckel and colleagues appears to play only a minor role in this context and we would thus like to keep this paragraph as it is.

P9780, L5: I'd not call 5 mM change "minor"

We deleted "minor".

P9780, L27ff: You can not make this statement about sulfide tolerance: As it is now, you suggest that high H2S levels are toxic for the white mats whereas the orange mats tolerate this. However, as both are thiotrophs, it could also be that the distribution of orange and white types is controlled by competition FOR sulfide.

It is true that the thiotrophs rely on the supply with hydrogen sulfide. We do, however, not say that high hydrogen sulfide levels were toxic for white mats, but not for orange mats. We only refer to chemotactic behavior of different mat-types towards sulfide concentrations and fluxes, which is well in accordance with the findings by e.g. Lichtschlag et al. (2010) cited earlier in this paragraph. To avoid the apparent misunderstanding and to clarify our statement, we deleted the term "concentration" from this sentence.

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P9781, L5-6: I guess the tubes were still sticking in the sediments, thus the worms would still have access to sulfide.

Yes, the polychaetes must have access to the sulfide-pool at depth. Here we discuss the filamentous bacteria that are attached to the tubes or to carbonate pieces, but not to the sediment, and that are thus disconnected from the interstitial sulfide-pool. We rearranged this sentence to clarify our statement.

P9783, L11: add de Beer et al., 2006 and Kaul et al., 2006

We added de Beer et al. (2006) and Kaul et al. (2006).

P9783, L27: again, be careful here. Many organisms responsible for bioirrigation at cold seeps live on H_2S! and actively mine for it.

The statement in the manuscript was redundant and we therefore deleted this sentence.

P9784, section 5.4. I really liked this section

Thank you.

P9784, L3: I am not a modeling expert but logically, I would think that it is a problem if the H_2S sink is not included. Often, all H_2S is consumed in a cold seep Habitat by thiotrophs.

The model produces slightly higher hydrogen sulfide concentrations than those measured, which is likely to be due to authigenesis of iron sulfides – a process that has not been the focus of the study and does not affect the conclusions drawn from our investigations. However, the different degree of overestimated sulfide release in the different modeled habitats supports our interpretations later in this paragraph. Furthermore, we assessed in our study the evolution of the depth of sulfide release (SMT) determined by varying transport processes, rather than the depth of the sulfide sink (e.g. uptake by thiotrophs, mineral authigenesis).

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P9784, L21: Add Niemann et al., 2006 here (bioirrigation at HMMV)

OK.

Response to anonymous referee #2

General comments:

During recovery of the cores from highly gaseous sediments severe disturbance will occur due to outgassing of methane. The sediments may contain 85 mM of methane, thus ca 80 mmol/L porewater will gas out (3-4 L gas/L sediment), during which significant exchange between seawater and sediment, and vertical mixing inside the cores will occur. This should really be discussed. The resulting spreading of the porewater profiles will lead to an underestimation of the advective flow. It also can explain the presence of sulphide in the watercolumn of some of the cores.

Response: We added a sentence to discuss ex situ mixing as a possible error-source in section 5.1 in the revised manuscript. We further added a sentence in section 5.3, where we report our modeling results, stating that fluid flow modeled from pore water profiles affected by ex situ degassing may be underestimated. However, we did not observe any major visual indicators for this process (e.g. gassy voids or pockets in the retrieved sediment, turbid supernatant bottom water, ex situ gas ebullition) in the examined cores. It is thus assumed that the cores and associated pore water profiles discussed in the manuscript represent more or less the in situ situation at the quantified sites. In section 5.2, we discuss the occurrence of hydrogen sulfide in the bottom water of some of the cores. Due to the observation of many thiotroph filaments that are attached to carbonate chunks at the sediment surface, we conclude that hydrogen sulfide must be present in the bottom water in situ, in order to nourish the observed microbes, which apparently do not have access to the interstitial sulfide-pool.

It would be good to explain the model better. It is a 1-D model, yet bioirrigation is 3-D. The total flux at each depth will be the sum of the advection, diffusion and bioventilation.

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Diffusion and advection can be approached as 1-D, upwards or down wards directed. Bioventilation is not. The same amount of water that is pumped downward will move up. The net areal velocity is thus 0. Yet, the depth integrated irrigation rates are expressed in velocity, m/year. The direction is not given. To include the bioirrigation in a budget we need an expression like Jtotal = J(diffusion)+J(advection)+J(bioirrigation). On p 9772 a mixing coefficient was mentioned. This will have a unit of m2/year? How does this translate to velocity? A spatial dimension seems to be lost. The authors should explain how this inconsistancy is solved.

Response: We used the modeling software CoTReM which uses a bioirrigation term as it is described in Haese et al. (2006) and in Wallman et al. (1997). In the revised version of the manuscript we added the differential equation used by CoTReM and explain the three considered transport terms diffusion, advection and bioirrigation. The model is 1D and simulates bioirrigation to be a vertically downward flow and advection to be a vertically upward flow. The interplay of the counter-directed transport mechanisms is explored in section 5.4, where the rates of both processes are directly compared to each other (Fig. 8). The mixing coefficient for bioirrigation mentioned on p 9772 is given as x*yr-1 and does thus not have a unit of m2*yr-1, as stated by the reviewer. The depth-integrated bioirrigation then results in a downward flow (cm*yr-1), as stated in the manuscript (cf. Haese et al., 2006).

It was argued that bioventilating fauna will eventually outcompete more simple sulphide oxidising organisms, such as bactaria. This because they can mine deeper for reduced substances. This is a plausible hypothesis. Thus mats are seen as first colonizers, followed by fauna, that deepen the SMTZ, and make the reduced matter unavailable for bacteria that rely on an overlapping zone of oxygen and sulphide. However, clams can move rapidly, and thus would quickly invade the mat areas. Would there be an upper limit of upflow velocity, where fauna cannot sustain?

Response: Yes, clams can migrate rapidly. However, they would only do so if they would be forced to by environmental changes (e.g. decreasing supply with hydrogen sulfide). The upper threshold flow-velocity for fauna to thrive in advective systems is not known but must be at least one order of magnitude higher than those reported in our study.

Specific comments:

On p9773 mats are described in the OMZ, where DO<1_M. This is based on older data. I do not believe that this low oxygen concentration is still there as the mats need electron acceptor. Are these really mats or precipitates? Such mistakes have been made, caution is needed.

In fact, the oxygen levels were measured during our expedition (data not shown in this manuscript, but see Bogus et al. (Biogeosciences Discuss., 8, 11359-11403, 2011) "The effect of meter-scale lateral oxygen gradients at the sediment-water interface on selected organic matter based alteration, productivity and temperature proxies") and are thus not older data, as stated by the reviewer. The oxygen data discussed in our manuscript were obtained from CTD-casts that were conducted at slightly different locations, than the coring sites. Thus, subtle changes or fluctuations in the bottom water oxygen contents could be masked by the rather coarse CTD sampling grid. Thiotrophic mats need only small amounts of oxygen to perform respiration. The mats are there, hence there must be an electron acceptor available for the microbes to oxidize hydrogen sulfide. From high-definition video sequences we identified the white/rose- and orange-stained patches at the respective seep-centers as microbial mats that are typical of sites of active gas discharge. Based on these observations we address the question, whether the observed patches consist of the filamentous thiotrophic bacteria Beggiatoa or Marithioploca. At sites of extremely vigorous discharge, we sometimes found thin films or aggregates of bluish-white mm-scale nodules of a rigid substance on the sediment surface, which was easily to be distinguished from the microbial mats comprising very soft and long filaments that gently swayed in turbulent water.

P9784 The too low sulphide levels found are also due to loss during recovery, H2S will

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be subjected to outgassing.

We added a sentence on this issue in the revised version of the manuscript.

P9785 Scenario A, so the total absence of upflow, is impossible, as then no supply of methane would occur. Same remark for L 8-9, P 9786.

We do not agree with this statement. In our model, the absence of any advective flow of pore water does not hamper diffusion to proceed. Even if advection approaches zero velocity, diffusion, which is considered in all simulated scenarios, allows dissolved methane to migrate upward.

P9787 An unlogical sentence: L8 'which induces' should be 'by inducing', L9 'intense sulphide release' should be 'increasing AOM'.

We have rearranged the sentence to clarify our statement.

P9787 I like L18-22. The authors should explain where and when these massive pavements are formed. Also why it is striking that they are observed (P9788, L 6).

In this section we argue that the mentioned chemosynthetic communities at water depth below 1850 m ("Flare 6") represent more mature seep-ecosystems, than those examined in our study. The occurrence of massive pavements of authigenic carbonates at this site supports our argument, because these may indicate a prolonged period of seepage and carbon sequestration in authigenic carbonates. At sites investigated in our study, seep-ecosystems comprised several other communities including small clams and polychaetes. Furthermore, our study sites were characterized by a distinctly less degree of carbonate authigenesis, compared to site "Flare 6".

Interactive comment on Biogeosciences Discuss., 8, 9763, 2011.

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