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Biogeosciences Discussions

Interactive comment on "Kinetic bottlenecks to chemical exchange rates for deep-sea animals II: Carbon dioxide" *by* A. F. Hofmann et al.

A. F. Hofmann et al.

ahofmann.mbari@gmail.com

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Reply to reviewer #1

Hoffmann et al. present an elegant theoretical paper concerning the ability of marine organisms to rid themselves of excess CO_2. Specifically they look at the problem as a diffusive boundary layer problem, in which the rate limiting step occurs in that d.b.l. They show that since CO_2 is subject to chemistry in the d.b.l. (unlike O_2) that the transfer of CO_2 is significantly enhanced. They also contrast their CO_2 results with results of O_2 transfer (presented in a companion paper) and show that O_2 dominates the (potential) negative impacts to orgamisms given current and predicted oceanic

conditions. However if pCO_2 throughout the ocean is tripled the negative impact of CO_2 (through d.b.l. flux) may become important in some locations.

We thank the reviewer for this comment. The details of CO_2 chemistry and rate processes are notoriously complex and it is good to see this succinct and correct analysis of our manuscript.

General comments

This paper is for the most part well-written and clear. Section 3 is less pleasant to read than the rest of the document, but it is still clear.

We thank the reviewer for these compliments - and acknowledge the criticism. Section 3 will be improved in a revised version of the paper.

There are numerous references in the text to the O_2 companion paper. For the reader interested in the details of the derivations, I strongly suggest that the reader be directed more exactly to the material of interest - e.g. "Equation X, Hofmann et al. 2012 companion paper" or "Section X, Hofmann et al...".

Agreed. We will do that.

A Table that simply lists each symbol used and its meaning and units would be exceptionally useful for the reader. Not only are these symbols used in the equations, but they also appear frequently in the text. Quickly glancing at a table is much less cumbersome than finding the text in which the symbol was first defined.

Agreed also on this point. A respective table will be added to the revised version of the manuscript.

Regarding choice of figures and presentation, since $E_{max}^{CO_2}$ and RP_{CO_2} plots tell similar stories (at least to this reader, they are linearly related..). I would suggest focussing on only one of those parameters - E... if it were me, since that one includes the b.l. thickness, which is a critical feature, in the main text and relegate a suite of plots of the other param (say R) to an appendix. Section 3 may be less cumbersome and more focused.

Again, we fully agree. Section 3 will be restructured and some plots and some text will be moved to an appendix.

In detail, we will:

- *Keep figure 1 (in the BGD version) in paper proper (since we received a compliment on it - see below), and retain a short paragraph in Section 3, explaining the general purpose of Fig 1 (Fig. 2 in the revised version).*
- *However, move the detailed description of fig 1 to an appendix - which tremendously improves the flow of Section 3.*
- *This detailed description of Fig 1 (now Fig 2) in the appendix will also be structured into sub-sections to improve the reading-flow and thus to make it more*

understandable.

- *also add subtle textual changes to better string the story to be told to this new appendix section.*
- *remove the discussion of RP_{CO_2}, and discuss $E_{max}^{CO_2}$ instead - in a more streamlined fashion.*
- *of Fig 2 in the BGD version, we will retain only the EF plots in the paper proper, as advised, RP_{CO_2} plots will be moved to the appendix (for comparison with SP_{O_2} from the companion paper). The EF=1 case plots will be completely removed.*
- *move Fig 3 (in the BGD paper: example oceanographic data) up to the Materials and Methods section.*
- *move the RP_{CO_2} panel of Fig 7 (of the BGD version) with its accompanying text in section 3.4 to an appendix*

Many of the things noted here, can also serve as replies to the request to restructure Section 3 (see below).

Figure 1 is an excellent figure and gives the reader a quick sense of what matters in these equations.

Thank you very much. Figure 1 will be retained in the manuscript proper.

Specific comments (scientific questions issues)

There are two places in which the text could benefit from a little more explanation in the technical development of the theory, at least for this reader. In general I think that the paper could be made accessible to a wider variety of readers by adding this detail. (That said, most of Section 2 is clear and well explained.)

(1) First, preceding equation 5, the equation makes perfect sense if $E\_tissue \gg E\_dbl$, however E-tissue is not discussed (at least in this paper) and this point (I think) is quite important to the article. Why are the rates in tissue so much greater? A non-biologist simply does not have a sense of these aspects even if they are perfectly obvious to a biologist.

We thank the reviewer for this remark, as it uncovered that we indeed did not explain the steps leading up to Eq. 5 (of the BGD version of the manuscript) clear enough. What we calculate is an upper limit for gas transport as posed by boundary layer transport. The true flux might indeed be limited by tissue transport, which, however, heavily depends on the organism in question, therefore hinders a true organism-independent comparison of various oceanic regions to one another (which is the intention for metrics presented in this paper), and is thus not treated here.

We will change Section 2.1.1. of the revised version of the paper to better reflect this.

(2) The concept of "enhancement factor" is also central to this paper. The paper would benefit from a brief justification of its use (in addition to the supplied references). Specifically the kinetics of these reactions.. convince me that the residence time of

CO2 in the d.b.l. is long enough for it to reach eqm with biocarbonate.

First of all, it needs to be noted that equilibrium does not have to be reached for the EF concept to be valid. EF is defined based on the kinetic reaction constants (lower case k's), not the equilibrium constants (upper case K's), effectively representing a relation between the kinetics of diffusion and CO_2 reactivity. This fact makes EF an ideal concept to also treat cases where CO_2 does not reach equilibrium with the seawater carbonate system, yet CO_2 reactivity significantly enhances diffusive transport.

To make this clearer, we will add a paragraph after the initial definition of EF in Section 2.1.2. that

- *notes that EF and similar concepts of treating CO_2 reactivity in the DBL have a long history*
- *stresses the fact that EF is defined to also describe cases that are not in (reaction) equilibrium*
- *gives typical values of quantities involved to illustrate the orders of magnitude for typical cases*

And a small point - isn't “Quinn and Otto, 1971“ the original ref?

Thank you very much for pointing out this oversight on our part, which will, of course, be corrected in the revised version of the manuscript. Actually, Quinn and Otto (1971) cite an even older reference (Bolin, 1960), which we will also include in the revised *version of the manuscript.*

In section 2.1.3 (p10 para 1) the authors point out that a planar EF description is appropriate in this study (makes perfect sense), and state that the boundary layer property is "meant for large scale oceanic comparison only and appropriate values... can be substituted." It is unclear to this reader what other systems the authors might be referring to and what the critical aspects may be. A little more text to flesh this aspect out after curiousity is peaked would be welcome.

This passage of the text is actually a result of many a discussion with biologists who work on particular animals with particular shapes, sizes and properties. Here, we wanted to "please everyone" and point out, that model descriptions incorporating specific shapes and properties can of course be used with treatments similar to ours, which would yield results more specific to a given organism. Particularly, when organisms are very small, a spherical model description might be appropriate. We also wanted to make sure, however, that what we aim at here, is a generic comparison of various oceanic regions to one another, and that to this end, a planar description is most appropriate.

In general, one can say that, most likely, we were trying to be too detailed with the statement in the BGD version of the paper. The bottom line is that the planar description is generic, works well and is appropriate for all but the very smallest (i.e. microbial) scales which are not considered here. We will change the respective paragraph in the revised version of the paper accordingly.

Also, suggest point to the section in which sensitivity to fluid flow is explored.

Agreed, will be done in the revised version.

Bulk flow velocities are an important feature in determining the b.l. thickness. I assume that this flow velocity is the "relative velocity", i.e. if a fish is swimming the velocity of the flow that it is experiencing.

Correct. We mean the 'relative' velocity. This will be made clearer in the revised version of the manuscript in several locations:

- *Concerning this issue, there are a few words in the accompanying O_2 paper, we will incorporate something along the same lines in Section 3 of the revised paper: "Oxygen transport across the respiratory surface diffusive boundary layer is such a critical property that animals typically work to control flow and thus manage the supply of their respiratory rate needs. However there clearly are cases where the physically driven external flow field is controlling (Patterson and Sebens, 1989; Shashar* et al.*, 1993) and is reflected in the physical distribution of organisms. And if O_2 transport is insufficient then either physical work to increase flow and thin the boundary layer is required, or organisms must resort to a temporary draw down of their finite store of alternative internal chemical energy supply."*
- *Basically, fluid flow velocity and changes therein can be seen as a measure of energy required to maintain respiratory needs. Whether this required energy will be supplied by the energy contained in ambient flow or is a result of animal activity like pumping or swimming is deliberately not distinguished here. We will add according lines to Section 3 of the revised version of the paper.*

- *Both in the Materials and Methods section and in the Appendix discussing the sensitivity of RP_{CO_2} and $E_{max}^{CO_2}$ to u_{100}, we will add "relative" velocity.*

Some discussion of the range of u_{100} chosen would be most useful. For example, what are typical currents over the SC shelf? (or a range of these currents..) and what organisms are the authors focusing on? Benthic dwellers will experience much smaller currents in the bottom b.l. (of the flow) than pelagics, or at least I assume so. Since vertical profiles of the derived parameters are shown and discussed I assume that pelagics are of interest here, but is there a limit in size or capability?

Let me answer twofold to this comment:

- *For pelagics, swimming and or pumping might be more important than ambient flow. Therefore (and due to lack of suitable ambient current flow data for our stations) our depth profiles are calculated with one single constant flow velocity (so what is shown in the profiles is mainly the influence of temperature and pressure). If flow data are available for given locations, those, of course can be incorporated in calculations using our definitions. We will add a paragraph in Section 3 of the revised paper to make this clearer.*
- *For benthics, ambient flow velocity matters more, and we will include a few representative flow values for Santa Monica Bay and Basin in the respective paragraph of Section 3 of the revised version of the manuscript.*

Generally, Pinder and Feder (1990) nicely sum up the role of animal activity and/or ambient flow for thinning the boundary layer around gas exchange surfaces:

"The diffusional boundary layer ought to pose a significant resistance to cutaneous oxygen uptake in still or slowly moving water. Animals should be able to minimize this boundary layer resistance by moving, ventilating the skin, or choosing aquatic microhabitats with moving water (Feder and Burggren, 1985; Feder and Pinder, 1988). Several investigators have reported findings that are consistent with these expectations. For example, Telmatobius culeus (the Lake Titicaca frog), an aquatic skin-breather, bobs its body up and down in hypoxic water (Hutchison et al. 1976). Cryptobranchus alleganiensis (the hellbender) rocks or sways from side to side more frequently in hypoxic water (Guimond and Hutchison, 1973; Boutilier et al. 1980; Boutilier and Toews, 1981). Experimental ventilation of the skin and locomotor movement both increase cutaneous oxygen uptake in ranid frogs (Burggren and Feder, 1986; Pinder and Burggren, 1986)."

In our treatment, we consider flow velocity as a measure for energy required to sustain respiratory needs. This energy can be contained in ambient flow or can be supplied by animal activity. To not have to delve into energy budget calculations inside the animal, we deliberately do not distinguish between the two (see also comment above).

At what speeds (u_{100}) do the diffusive flux b.l. equations break down?

Again, concerning this issue we wrote some general words in the O_2 companion paper, a variant of which will be added in Section 2.1.3 of revised version of this manuscript:

"While being simplified, the description for the DBL thickness implemented here reproduces the general non-linear dependency of L on the fluid flow velocity u_{100}, and the dependency of this relation on temperature. Although for real animals,

considerable fine structure of gas exchange tissues may exist, and the animal will maintain a boundary layer typical for its respiratory needs, the physical forcing required to change the thickness of this layer will follow the same physical laws.“

More specifically, for large values of u_{100}, resulting boundary layer thicknesses will be small, however, the relations still make sense. For low values of u_{100}, however, there are limits. Again, we write in the O_2 paper and we will write in Section 2.1.3 of the revised version of this manuscript:

”The limit case of $u_{100} \rightarrow 0$ would yield $L \rightarrow \infty$. This example formulation for L (or better K) as a function of u_{100} is thus not defined in a physically meaningful way for zero flow velocity and should not be used for the stagnant water case. Here we plot L with a minimum of $u_{100} = 0.5\ cm\ s^{-1}$, which can be seen as an operational lower limit.“

In Section 3.1 - Fig 1 E.H. goes to 1. Do the equations reduce to the exactly to the simple diffusive flux equation (with no enhancement) when E.H. approaches one? In other words are there any approximations made in order to solve the more involved case in which the residence time of CO_2 is a similar order to the diffusive flux time? If there are no caveats then the authors simply need to reassure this reviewer. If there are - then some mention needs to be made, when assumptions for equations are being violated etc.

Assuming that EF is meant here, we can say that, yes, for large values of u_{100}, EF approaches 1. This is, simply put, due to the fact that the boundary layer becomes so small, that there is virtually no time anymore for CO_2 to react within the boundary

layer. No assumptions are violated here, as the boundary layer thickness, the diffusion coefficient and the kinetic reaction coefficients for the prominent carbonate system reactions are explicitly incorporated in the definition of EF (see also comment above), exactly to express also cases where there is virtually no enhancement of diffusive transport due to CO_2 reactivity. In those cases, indeed, the equations effectively reduce to the diffusion equations, as now diffusion alone, virtually not influenced by reactivity becomes rate determining for CO_2 export. We believe that, especially when a few more sentences on EF will be added in the revised version of the manuscript (see above), this question should be satisfactorily answered.

Technical corrections

Abstract line 15 - sentence starting ”For organisms...” is too long making it difficult to follow.

Agreed. We will rephrase.

Abstract - in general - the last half, which pertains to the detail in this paper is not as well written and would benefit from some focused editing.

Agreed. We will rework the abstract.

Introduction - pg 4,line 15 - reference to Shaffer. Shaffer et al. aren't the only modellers to publish oxygen results. The authors list a host of carbon dioxide related papers at the end of the same paragraph - suggest that they expand their literature a little on the oxygen side as well.

Agreed. We have cited many papers about oxygen and hypoxia in the O_2 *companion paper, the appropriate ones we will cite in a revised version of this manuscript as well. Especially, we will make clear that Shaffer et al. is merely one example paper on* O_2 *and not the only one.*

Section 2.1.3, line 5 "this results" "this" what? approximation?

*What is meant here is that the mathematical operation of **multiplying** (we wrote "dividing" which is a typo and which will be corrected) both sides of the oxygen equation equivalent to Eq. 13 by the boundary layer thickness L results in a right-hand side of the equation that does not contain L anymore - and thus is free of organism species specific variables and parameters. If we then introduce a quantity that is defined by the right-hand side of the equation, we obtain a purely non-organism specific quantity (the oceanic "oxygen supply potential"* SP_{O_2}*). In the* CO_2 *case, this same operation of multiplying both sides of Eq. 13 by L does NOT lead to a right-hand side free of L, since EF is also a function of L. We nevertheless define the oceanic "*CO_2 *removal potential" (*RP_{CO_2}*) to be the right hand side of Eq. 13 divided by L, to obtain an equivalent quantity to the* O_2 *quantity, albeit one that does depend on L for the* CO_2 *case. However,* SP_{O_2} *and* RP_{CO_2} *can be directly compared, which is our reason for introducing* RP_{CO_2} *in the explained way.*

We will rephrase this paragraph in the revised version of the paper to make our reasoning clearer.

Section 2.6, line 9 "Bulk fluid free stream" isn't this desriptor redundant? I thought that "bulk ocean" was "free stream" here.

Agreed. We will fix this.

line 10 - does it matter to the reader that the chemical solutions were obtained using "R"?

Well, it does indeed not matter for the results with which tools they have been obtained. However similar to an experimental paper, (where the whole experimental setup is explained in detail, including the brand names of materials used), a mention of R helps the reader in potentially recreating our calculations (maybe even by obtaining R scripts from us). Additionally, "R" is a scientific open source project, which lives from the support and contributions by the community, and added R functionality due to those contributions in turn directly benefits the whole scientific community. Citing open-source projects such as R in scientific papers increases their visibility and thus is beneficial for the scientific community. With the editor's permission, we would like to keep this reference.

Section 3 - I like the sensitivity discussion, especially made relevant to oceangraphic locations. However the description of many of the Figures reads like a data report in this section. “Figure X shows...“ It almost looks like some paragraphs are written by one author and some by another. The whole section would benefit from a revision that focused on the story that is being told. Section 3.2 - begins with ”Figure 2... It can be clearly seen.. that E.H. dominates”. The dominance of EH wasn’t clear to this reader from this figure. ?

Agreed. Section 3 will be reworked and streamlined. In detail:

- *large parts of section 3 will be moved to an appendix (see above: comment on plots and presentation of RP_{CO_2})*
- *Section 3 will be textually streamlined*
- *a structure using more subsections will be introduced to foster understanding*
- *some headlines will be renamed to become more “telling“*

- same paragraph line 5 - there is a “then“ that should be “than“

Correct. Should be ”... shallower THAN 500 m...”. This will be corrected in the revised version.

Figure 1 (and others) - y-axis labels “/ m“ makes it look like the units are ”to the power of -1” - suggest “/ “ removed

*Using the ”/ ”-notation is actually the mathematically correct way of labeling a plot. For example, SP_{O_2} is a quantity that consists of a value times a unit (i.e. SP_{O_2} = value * unit). What is displayed in the figure, however, is only the value. So, to come from the quantity SP_{O_2} to its value, one needs to **divide** SP_{O_2} by its unit. Which is exactly what is done in the legends in our plots. This is common practice in physical, mathematical and engineering papers and should be common practice in oceanographic papers as well. With the editor’s permission, we would like to keep the “/ “ in the axis labels.*

References

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