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Biogeosciences Discussions

Interactive comment on "Factors governing the pH in a heterotrophic, turbid, tidal estuary" *by* A. F. Hofmann et al.

A. F. Hofmann et al.

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Based on the constructive comments of all reviewers, we substantially improved our manuscript. The changes are too many to list individually and the most important, central improvements are summarized in our integrated reply to all referee comments which can be found in our top-level author comment "Integrated reply to referee comments". Here, we restrict ourselves to the outline of important changes based on the comments of reviewer # 5. Furthermore, we mention briefly why we do not agree with some of the comments of this reviewer. Also here, we restrict ourselves to the most important points.

Based on the comments of reviewer # 5, we added more information about used data (forcing, calibration, validation), about the consistency of pH and TA boundary values,

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and other model technicalities. We rephrased the introduction and made it more clear in general that the method is generic and can be applied to the open ocean as well (where acidification is an issue). We also added information about pH scale conversion (to the NBS scale for comparison to data). Additionally, we added references used for the T and S dependencies of the dissociation constants.

It needs to be noted that none of the equations presented in the present paper have been published in Soetaert et al. (2007). Soetaert et al. (2007) present equations that are similar to the equations in the present paper, yet they differ in several important points. Most importantly, the equations presented in Soetaert et al. (2007) are not based on the concept of total alkalinity, but the equations presented here are. Exactly explaining all differences goes beyond the scope of this reply, the interested reader is referred to Soetaert et al. (2007) and Hofmann et al. (2008a). Equivalents of Eqs 2 to 5 of the present manuscript (discussion version) have indeed been already presented in Hofmann et al. (2008a), but as in the present paper, the pH modelling method of Hofmann et al. (2008a) is extended, it fosters understanding to recapitulate these equations here. The model equations in tables 1 and 2 (discussion version) are already given in Hofmann et al. (2008b). To get the fully detailed picture of the model, Hofmann et al. (2008b) needs to be read, but to make this present paper at least somewhat self-sufficient and allow the reader of only the present paper at least a general understanding of the model, without having read Hofmann et al. (2008b), we included tables 1 and 2 in the present paper. We will not remove formulae from the materials and methods section, especially since other reviewers even demand that more details of the model need to be included. A suggestion which we followed in the revised version of the present paper.

As also mentioned by other anonymous reviewers and Pierre Regnier, the pH modelling method itself is one of the most important messages of the present paper and,

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therefore, we feel that the main equations deserve a central position in the body of the paper and not in the appendix (there is already an extensive appendix containing auxilary equations that are not vital for a general understanding of the modelling method).

It is true that the influence of (ocean) acidification on biogeochemical processes and organisms depends largely on changes of carbonate and other chemistry in the water and not just pH alone, but pH is a central variable, governing the speciation of acid base systems, therefore influencing e.g. the carbonate chemistry of natural waters. We therefore consider it valid to talk about the "potential impacts of pH changes on biogeochemical processes and organisms" even if this impact includes an intermediate step (via the influence of pH on carbonate and other chemistry). But, obviously, pH chemistry, its controls, effects, and feedbacks are complex. This is why we work on this subject.

Processes in the model have not been parameterized with true physiological parameters, but the model has been "fitted" (i.e. parameters were determined) to recreate water column concentration values (or literature parameter values of the same type have been used): see Hofmann et al. (2008b). Since water column concentrations are influenced by benthic processes as well, our parametrization of processes implicitly accounts for benthic processes as well (especially since we also include denitrification which is almost entirely a bethic process in the Scheldt nowadays as the water column is oxic). This issue has been discussed during the review process of Hofmann et al. (2008b) and is reflected in the last paragraph of section 4.1.1. of Hofmann et al. (2008b). Since the model underlying the present paper is exactly the same as the one underlying Hofmann et al. (2008b) and this issue has already been discussed there, we feel that re-opening this discussion would be out of scope of the current paper and review.

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Interactive Comment

Adsorption and desorption of protons to particles indeed is an interesting subject and might be of relevance for pH values in turbid estuaries like the Scheldt estuary. It already has crossed the minds of the authors to investigate this in an experimental fashion. However adding it to the current manuscript would be too much for one paper. This is something that needs to be resolved in further studies.

In the reference list of the current paper, there are numbers after the year of the publications. These numbers are "backreferences" indicating the page numbers where the particular reference has been made in the text. In the electronic version of the paper, these are hyperlinks bringing the reader right back to the position of the text where the particular reference has been made.

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