

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

**A. F. Hofmann et al.**

Received and published: 21 July 2009

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 # 1. 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 by reviewer # 1, we made it more clear that the model did not change from Hofmann et al. (2008b) to this manuscript. We also made more clear

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exactly what model runs have been done. We added more information about the technicalities of the model. We made more clear that the implicit and explicit method of pH modelling are "two ways to calculate the same thing" and that we show the "mistakes" one would make using the explicit method if one would not consider the K related terms. It is not a fitting of one model to the other, the underlying model and kinetic rate formulations are exactly the same (i.e. in both cases  $E_{\text{CO}_2}$  depends on pH). Both methods have to yield the same pH. If they don't, the modeller has made a mistake in implementing them. We show how large those mistakes are when different terms are omitted. Also, we split the estuary in three zones (upstream: low pH, midstream: rising pH, downstream: high pH) and constructed three separate yearly proton budgets. Furthermore, we added "variability bars" to fig 6 (discussion version), right panel, which describe the spatial and temporal variability of pH in the Scheldt (over the modelled area and one year). Additionally, we made all graphs, especially their legends, more readable. We explained exactly what averaging procedures we used. We also made more clear, how a changing hydrology (e.g. freshwater flow) influences estuarine pH chemistry. That means, we explain our model experiments which change the loadings at the boundaries (cf. fig 7 (discussion version)) in a much more accessible way. We made clear that boundary condition change for TA is actually calculated from pH boundary changes and constant DIC; but that TA data inside the estuary (as opposed to the boundaries) obtained from Frederic Gazeau (personal communication and Gazeau et al., 2005) have been used to calibrate the (constant) DIC boundary conditions. In general, we explained the way we calculate DIC and TA boundary conditions in much greater detail. (Which shows that there is no contradiction between Hofmann et al. (2008b) and the present paper.)

However, there are also comments of anonymous referee # 1 with which we do not fully agree or to which we want to reply in detail, while not including a respective part in the revised version of the paper.

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The current paper indeed is an extension of two previous Biogeosciences papers (Hofmann et al., 2008a,b). Hofmann et al. (2008b) presents an ecosystem model of the Scheldt estuary and Hofmann et al. (2008a) presents a method of quantitatively modelling the influences of kinetic processes on pH. The present paper basically is an application of the pH modelling method presented in Hofmann et al. (2008a) to the model presented in Hofmann et al. (2008b), while it also extends the pH modelling method to systems with time-variable acid-base dissociation constants. We are aware that to understand every last detail of the present paper, the reader must also read the two previous paper. However, we briefly repeated both, the gist of the Scheldt estuary model from Hofmann et al. (2008b) and the central formulae and ideas of the modelling method from Hofmann et al. (2008a) such that general understanding should be possible by only reading the present paper. As mentioned above, we added some more information about the model, but explaining every detail of the model and the pH modelling method again in the present paper would excessively increase the size of the present publication. Therefore, a certain need to read the two previous papers to get all the details will remain. Those three papers form a trilogy and are to be considered as a three parts of one story.

Referee #1 is left with an impression of "fuzzyness" because there seem to be differences between the models underlying Hofmann et al. (2008b) and the present paper. This seems to be the result of an unfortunate misunderstanding. Referee #1 obviously refers to the discussion version of Hofmann et al. (2008b) (since he/she refers to pages 87-88 which is correct for the BGD version but not for the BG version which has page numbers from 981 to 1006). In the BGD version of the model, we did not model primary production explicitly but modelled "net respiration" (i.e. production minus respiration). As a result of the revision process for Hofmann et al. (2008b), we changed the model in a way that primary production is modelled explicitly to gain more information (see discussion of Hofmann et al. (2008b) for details). The final BG version of Hofmann et al. (2008b) is based on this changed model and the present paper is as

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well. So, there is no difference between the model underlying Hofmann et al. (2008b) and the present paper.

For the present paper no further fitting was performed. The model underlying Hofmann et al. (2008b), which already contained an "implicit" pH modelling routine, was extended with the described "explicit" pH modelling routine that allows for a quantification of the influences of the modelled processes on the pH. Neither the forcings, the results for ammonium, oxygen, nitrate etc., nor the resulting pH profile along the estuary was changed by this. That means the model was run again with the same forcings as described in Hofmann et al. (2008b) and it then produced the same profiles for chemical species along the estuary, the same rates and the same pH. The only thing that changed is that we added another way of calculating the same thing (the pH profile) which additionally provides more information (the quantification of the influences of processes on the pH, i.e., information about proton cycling). In the revised version we made it more clear that the model did not change from Hofmann et al. (2008b) to the present paper: just an additional information yielding routine was added. Accordingly, adding the resulting profiles for ammonium, oxygen, nitrate etc. in the current paper as well would be an exact repetition of Hofmann et al. (2008b) and would dramatically increase the size of the present paper. We therefore think that it is not beneficial to add those profiles to the current paper. As mentioned above, Hofmann et al. (2008b), Hofmann et al. (2008a) and the present paper form a trilogy and for the complete picture with all details it is indeed necessary to read all three papers.

It is important to note that the explicit method is not "fitted" to the implicit method. The implicit and the explicit method are simply different ways of calculating the same thing, the pH profile in the estuary. It is not true that both methods should yield different results. Both methods describe exactly the same model, they are just two different

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mathematical ways of solving the same model. So if no mistake is made in either calculation, the results have to be exactly the same. Note that also if the implicit method is used to calculate pH, pH is still calculated and, e.g.,  $E_{\text{CO}_2}$  is a function of pH.

It is important to mention that it is not “wrong” to calculate TA boundary values from pH, DIC, T, and S. In fact it is the only way to make sure that modelled TA boundary values are consistent with both, available pH boundary measurements and the TA definition considered in the model. Because of this practise, theory tells us, artificially changing S boundary conditions also change TA boundary conditions. This has an effect on the experimental model run c). Any other model run, especially our baseline model run which has been used to create much of the output, is not affected by this, since both, pH and S boundary values are “true” values. Comparing the S-change induced TA boundary change in model run c) with year to year TA variations at the boundaries shows that the S effect on TA boundaries is insignificant. We therefore feel that extensively discussing this technical detail of the model is not necessary.

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Interactive comment on *Biogeosciences Discuss.*, 6, 197, 2009.

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