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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 Pierre Regnier. 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 Pierre Regnier we made a substantial change to the paper: we shifted the focus away from the model experiments that investigate the

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effect of changes in the boundary loadings for the mean estuarine pH more towards an explanation of the specific yearly averaged pH profile along the estuary. In the course of doing so, we also removed the "synopsis" section as demanded. Based on the comments of Pierre Regnier, we furthermore made more clear that we talk about a quantification of the influence of processes on the pH in a model where all processes are active at the same time (as opposed to model experiments where single processes are turned on and off). We clarified the differences between out approach and the works of Jourabchi et al. (2005) and Soetaert et al. (2007). We furthermore stressed the novel aspects of our approach: a mathematically transparent quantification of individual processes affecting pH in time-dependent models where those processes are active at the same time and dissociation constants are non time-constant (from the methodological point of view this is completely novel in this publication). We show an estuarine model as an example, but the approach is entirely generic and can be applied to any aquatic system. We comment on the shortcomings of the pH fit of the presented model of the Scheldt estuary. One of the interesting features of our methodology exactly is that we can find out that in certain circumstances e.g. denitrification can have a "visible" effect on C and N but not on H. (we added that in the discussion of the revised version of the current paper). Furthermore, we added some information about forcings, data, and model calibration and validation. Additionally, we included almost all of the helpful and numerous technical comments given by Pierre Regnier.

We feel that it is instructive that the current manuscript contains a brief recapitulation of the pH modelling method of Hofmann et al. (2008a), not only because it allows for a general understanding of the method even if Hofmann et al. (2008a) is not read, but also because it facilitates the explanation of the extension of the method to time-variable acid-base dissociation constants. We followed the referee's suggestion and expanded on the description of the method and the transition between formulae. However, we deemed it not suitable to use an extra, even simpler example model

to illustrate the transition from eqs 10, 11 towards eqs 13 - 22 (discussion version). We made it more clear that formulae from table 3 (discussion version) are plugged into equation 11 (discussion version) and then terms are simply regrouped such that terms featuring the same process rate end up in one group. These groups are then the process specific $\frac{dH^+}{dt}_i$ (in the revised version of the manuscript given in table 4).

It should be mentioned that the process rates given in Hofmann et al. (2008b) simply translate into the individual dH/dt terms presented in this paper. This is done by plugging the process rates given in Hofmann et al. (2008b) or obtained from the model, into the equations given in table 4 (revised version) This means that, if the rates as reported in Hofmann et al. (2008b) from any particular time and space in the model are plugged into eqs 13-22 (discussion version, or eqs in tab. 4 in the revised version respectively) together with the partial derivatives calculated with values for pH and total quantities at the same time and space in the model, then the dH/dt terms for the respective time and place in the model are obtained. Formulae for the modulating factors (partial derivatives of TA, especially dTA/dH) are given in the appendix of the present paper, and their meaning is explained in part in Hofmann et al. (2008a) and is further investigated in a manuscript the authors submitted to another journal (see also chapter 5 of the PhD thesis of A. Hofmann: http://igitur-archive.library.uu.nl/dissertations/2009-0513-200343/UUindex.html). There, also a discussion of the chemical meaning and interpretation of the modulating factors (partial derivatives of TA) in the process specific dH/dt terms and the specific form of the dH/dt equation is given. Such a treatment would be out of the scope of this paper.

A thorough investigation of the relation between the proton and the oxygen budget is out of the scope of this current paper, yet, it is an interesting subject for further studies which can employ the pH modelling methodology presented here. In our approach, transport is fully equivalent to any other physico-biogeochemical process and can be

treated in exactly the same way. We will not discuss possible discrepancies in C and nutrient budgets which have been reported in Hofmann et al. (2008b) with other references. This was the subject of Hofmann et al. (2008b) and is not part of the current paper. As our model area starts just downstream of the confluence of Scheldt and Rupel, our Q stands for the discharge of both of those rivers together. Downstream flow increase (i.e. lateral input) due to further tributaries has been calculated as explained in Hofmann et al. (2008b), section 2.2.6, "Physical condition forcings" (restated in the current revised paper).

References

Hofmann, A. F., Meysman, F. J. R., Soetaert, K., and Middelburg, J. J.: A step-by-step procedure for pH model construction in aquatic systems, Biogeosciences J1 - BG, 5, 227–251, 2008a.

Hofmann, A. F., Soetaert, K., and Middelburg, J. J.: Present nitrogen and carbon dynamics in the Scheldt estuary using a novel 1-D model, Biogeosciences J1 - BG, 5, 981–1006, 2008b.

Jourabchi, P., Van Cappellen, P., and Regnier, P.: Quantitative interpretation of pH distributions in aquatic sediments: A reaction-transport modeling approach, American Journal of Science, 305, 919–956, 2005.

Soetaert, K., Hofmann, A. F., Middelburg, J. J., Meysman, F. J., and Greenwood, J.: The effect of biogeochemical processes on pH, Marine Chemistry, 105, 30–51, 2007.

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