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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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First of all we would like to thank all referees for their elaborate and constructive criticism. We especially thank those referees who recognized that the main focus and the main value of this paper lies in the method of quantifying the contributions of modelled processes on the rate of change of the proton concentration in systems with time-variable acid-base dissociation constants. We also especially thank Pierre Regnier for calling our approach "mathematically transparent".

Especially with five scientists giving their reviews, some of them aiming in opposite directions, it is impossible to fully satisfy all reviewers. We used their suggestions and comments as inspirations to restructure and rewrite the paper. However, we tried to provide for a relatively smoth reading flow and a closed appearence. This means we

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had to omit several suggestions or pieces of information that some reviewers wanted in the paper - although, on their own, those pieces of information are valid and interesting.

Inspired by the many reviewer comments, the paper has been substantially changed - substantially improved in our view. The changes are manyfold, too many to list them all individually. Most importantly, the comments helped us to better structure the message of the manuscript - to make it a more consistent story. We made now clear, that the main message is the generic method of pH modelling: a method that allows for a quantification of the contributions of processes to the rate of change of the proton concentration in systems with time variable acid-base dissociation constants. This method can be used to investigate **proton cycling** in the respective system. The Scheldt estuary was used as a case study to apply the presented pH modelling method to. In dealing with the Scheldt estuary, we shifted the focus of attention slightly: away from a rather unconnected presentation of the "proton production and consumption along the estuary" (which actually is nothing else than **proton cycling** and is now termed that way) and model experiments which investigate the "factors responsible for changes in the mean estuarine pH" (which took up too much space in the discussion version and yielded too little valuable information) towards a more balanced and connected treatment. We now start with an investigation of the controls of the characteristic longitudinal pH profile in the estuary, followed by a treatment of proton production and consumption in the estuary (proton cycling) and the importance of different processes for that. Then, we discuss a related subject: the connection between proton cycling and CO_2 degassing. Finally, we briefly present results of the model experiments changing the boundary loadings that investigate the factors controlling the change in inter-annual mean estuarine pH. The treatment of "proton production in the estuary" itself has also been substantially improved from the discussion version: we better define what it actually is that we can investigate with our presented modelling method: **proton cycling**; we split the estuary up in three zones for total proton budgets; we calculate proton turnover times; we introduce total proton production (PP) and total proton consumption

rates (PC); we deal with the importance of the dissociation constant related terms in a better way. We show that PP and PC are orders of magnitude larger than the actual rate of change of protons (i.e. there is a high proton cycling intensity that is not reflected in actual pH changes). The terms associated with changes in the acid-base dissociation constants in the equation for the rate of change of protons are also orders of magintudes smaller than PP and PC, but comparable to the actual rate of change of protons. This explains why those terms are important if pH values are to be modelled, but can be neglected if proton cycling (i.e. PP and PC) is discussed.

As mentioned above, the main message of the paper is the description of our pH modelling method. We used this method to get a first glimpse at the pH in an example system: the Scheldt estuary. To that end, we applied it to an existing model which has been calibrated to generate yearly averaged output (Hofmann et al., 2008b). From that, we could obtain a first quantitative idea about which processes are how important for proton cycling at each point of the yearly averaged pH profile along the estuary, the estuary as a whole, and the up, mid, and downstream region - something that has never been done before. Additionally, we investigated the controls of the specific shape of the longitudinal pH profile, the connection between pH chemistry and CO_2 outgassing, got a first idea about the role of advective-dispersive transport for the pH chemistry of the estuary, and we shed light on the factors responsible for year to year changes in the volume averaged whole estuarine pH. We consider these results to be steps towards completely understanding pH in the Scheldt estuary - we do not claim that our results represent the final step. After all, our Scheldt model basically is a case study to validate our presented pH modelling method. Obviously, there are several scientifically valuable and interesting subjects to explore more, amongst others: quantitatively connecting the pH gradient (dH/dx) to the process rates (already work in progress), discussing the meaning of the "modulating factors" in our equation for the rate of change of protons (almost ready for resubmission), investigating the connection between the oxygen and proton budgets in detail, investigating the role of advective-dispersive transport more closely, investigating seasonal dynamics of pH, and applying

the presented pH modelling method to more elaborate models. However, all these ideas are out of the scope of the present publication as they cannot be treated in a few sentences. They can be, and most probably will be (some already are), the subject of further studies.

References

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.

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