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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.

Anonymous Referee #5

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General comments

The authors present an analysis of the drivers of pH dynamics in the Scheldt estuary. As it stands this is an interesting and valuable work but I feel could be improved as detailed below.

Major comments

As far as I can see, the equations underlying the model used in this paper have already to a large extent been published by Soetaert et al. (2007) and Hofmann et al. (2008a;b). If so, I suggest that the authors reduce the Material and Methods sections to the specifics of the paper. If not, I suggest that the equations are transferred to an annex section, so the reader is not discouraged by a soup of equations before arriving

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at the results and discussion.

One thing that is missing from the Material and Methods is information on the field data to force (upstream and downstream boundaries) and to validate the model. To my best knowledge, the only published data on pH and total alkalinity for the 2001-2004 period in the Scheldt estuary have been reported from January to December 2003 by Gazeau et al. (2005). Please specify originators of the data in 2001, 2002 and 2004. If the data are from different originators please specify if the internal consistency of the data-sets was checked or could be checked (traceable standards, equivalent instrumentation, etc).

Information on the precision and accuracy of the measured pH and total alkalinity data must be added to the Material and Methods section. This would help the reader to interpret for instance Fig. 3 and decide if the model validation is acceptable or not (within short-comings of measurements).

' dissociation constants '; appears at least 42 times in the text, although I could not work out from text which constants were actually used in the model. This could be an issue, since dissociation constants for carbonic acid are poorly constrained in brackish waters. The Mehrbach et al. (1973) constants are only valid until a salinity of about 15. Cai and Wang (1998) proposed equations to extrapolate theses constants between salinity 15 and salinity zero, while Millero et al. (2006) have produced a new set of constants based on measurements that fully cover the salinity range. It would be useful if the authors could check if the use of the different dissociations constants commonly used in estuarine environments has a significant impact on the simulation of pH.

Page 198 L 25 : Estuaries are naturally acid environments, and anthropogenic changes in carbonate chemistry in estuaries such as the Scheldt are most probably related to changes in organic and nutrient inputs, hence, oceanic acidification (related to the transfer of anthropogenic CO2 from the atmosphere to surface waters) is irrelevant for such estuarine environments.

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Page 198 L 25 : Furthermore, the potential impact of ocean acidification on marine organisms and communities depends on changes of whole carbonate chemistry (HCO3-, CO32-, CO2 and H+) and not solely on pH.

Page 202 Line 9 : The authors mention that the modelled pH is on the free scale which corresponds to minus log of the concentration of free protons. The pH measurements seem to have been made on the NBS scale which corresponds to minus log of the activity of protons. Hence, there is a conceptual difference between the two pH scales. Were the pH measured data manipulated to be comparable to the pH modelled data (or the way round) ? If so, please specify how this was done. If not, can the authors provide an estimate of the uncertainty arising from the comparison of values based on two different pH scales ?

There is no mention of benthic processes in the paper (remineralization, nitrification, denitrification). However, Gazeau et al. (2005) report that annual benthic net community production (NCP) is significant compared to pelagic NCP, respectively, -8 mmolC m-2 d-1 and -31 mmolC m-2 d-1. Hence, I would expect benthic processes to have a major impact in pH dynamics in the Scheldt estuary. Are benthic processes represented in the model ? If so, please mention if the relative impact of benthic and pelagic processes on pH is consistent with reported field measurements. If not, this needs to be mentioned and a few sentences on the potential impact of not representing benthic processes needs to be added.

All the figures and tables in the paper refer to annual averages. However, I would expect the relative contribution of biogeochemical processes on pH to change seasonally. During winter, the effects of transport and air-water CO2 exchange probably dominate as controlling factors on pH dynamics due to, respectively, high freshwater flow and higher wind speeds, while low temperatures probably reduce bacterial activity and related effect on pH. During other seasons, the effect on pH of transport is probably less important (lower freshwater flow), but biological activity probably becomes more important. Is there a specific reason to set aside the seasonal variability ? If so please state

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this reason. If not the inclusion of seasonality would be an useful addition to the paper.

It has been claimed that H+ adsorption/desorption from particles could influence pH in estuaries (Sarma et al. 2001). The Scheldt is a turbid estuary and could be a nice test case to check these claims. I would be grateful if the authors could look into this and allow to settle if this a significant process or not.

Minor comments

Page 199 L22 : air-water exchange of CO2

Pages 200, 203, 205, 207 : remove footnotes and include information in the main text

Page 207 : replace graphs by figures

All the references are odd with meaningless numbers after the year of publication . For instance 198 198, 199 199, 200 200, 201 201, 202 202, 203 203, 208 208, 214 214, 216 216, 228 228, 233 233, 235 in the Hofmann et al. (2008b) reference.

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