

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

### **Anonymous Referee #1**

Received and published: 2 March 2009

This paper deals with the explicit modelling of pH in a turbid tidal estuary in Netherlands (Schledt). It takes into account the main biogeochemical processes which produce or consume protons together with gas exchange and transport of water along the estuary. The paper is clearly written and straight to the point although some paragraph should be rewritten and explained better.

### General comments

Overall the paper is clear and present an original model, which is an extension of two former modelling efforts from the same authors: a previous modelling effort of pH (Biogeosciences, 5, 227-251, 2008a) and a paper dealing with C and N cycle in the Scheldt estuary (Biogeosciences, 5, 981-1006, 2008b). This paper presents a novel

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Discussion Paper

explicit modelling of pH which takes into account most biogeochemical reactions in the C and N cycle which influence pH (nitrification, denitrification, oxic mineralization of organic matter, CO<sub>2</sub> exchange, primary production). This new approach allows the authors to present and discuss quantitatively the main factors which influence pH and their interplay. This quantification is original and deserves publication although the paper needs substantial improvements and clarifications before it can reach the publishable state.

### Specific comments

As said in the introduction of the comment, the paper builds on 2 former papers on related topics. Therefore, a lot of references to these previous papers are made in the present paper which makes the reading very difficult and leaves an impression of fuzziness. This is especially true for the model runs section which was already very short in the previous paper (BGD-2008b). This section should be largely increased to present the way the model was run and how the fit to the data set was performed (see below). My understanding of this work is that it builds on the previous model outputs by Hoffman (2008b) and uses the adjustment to the data set and the rates calculated in this model to force the pH runs. If this is the case, then the main results of the previous model should be presented in this paper: (i) data and model fit (NH<sub>3</sub>, O<sub>2</sub>, NO<sub>3</sub> distributions along the estuary) (ii) rates of the main processes in the estuary. This would help the reader understanding the biogeochemistry of the estuary without having to read entirely the previous paper (2008b). The impression of fuzziness comes from a statement in the present paper. The role of primary production in the estuary seems to be quite important on pH distribution. Indeed, its effect on pH represents more than half the effect of the nitrification which is recognized as a major process (Fig. 6). Yet, this is in contradiction with the statement of paper 2008b in which primary production is neglected because of the turbidity of the water (p 87-88 of 2008b). It seems that, beyond the calculations that were performed for the previous paper, new runs and adjustments were performed producing new reaction rates (including primary production). If this is

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Discussion Paper



the case, then these new runs should be presented in the present paper including their fit to estuary concentration data and the rates of important biogeochemical processes.

#### Detailed comments

Methods 2.3 (p 206) for equation 12, the authors should state in the legend what the subscripts refer to. T for example stands for Transfer in this equation but T before stands for Temperature, other such as Rden, ROx, RNit should also be defined in the legend.

Model runs 2.7.1 (p 208): The author should state more explicitly what was done. Was the model run over time for all four years? What was the time step and how was the model output compared to data? On a yearly-averaged basis? If so, how do the time variations in one space point (time series) look like compared to the data? The authors provide not enough details to understand what was really done for model runs and their comparison to data.

Results 3.1 : why is it so important to fit the implicit model? Should both model not be different since  $\text{ECO}_2$  is a function of the real pH, hence interactively linked to it as in explicit model and not in the implicit one?

Results 3.2 and discussion 4.1: Figures 4a and 4b are not adequately described, although the different processes at work are well introduced. Instead of saying that nitrification is the main process governing pH in the estuary (which is true for the upstream region, but not downstream where  $\text{NH}_3$  is low), one should divide the estuary in two main zones dominated by a different set of processes. This division explains the sharp jump of pH from one zone to another which is otherwise not explained : the upstream region is indeed dominated by nitrification which acidifies the water and is larger than  $\text{ECO}_2$  hence producing acidic pH. In the downstream area, an import of protons produces  $\text{ECO}_2$  larger than oxic mineralization which is also counteracted by primary production. The author should rewrite this section according to these lines and split the estuary in two sections.

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Discussion Paper



For Figure 4 (as in Eq. 12), the authors should state in the legend what the subscripts refer to. T, for example, stands for Transfer, other such as Rden, ROx should also be defined in the legend.

One Table should be added to this paper: it is the Table with Redox reactions and their influence on pH: oxic mineralisation, primary production, denitrification, nitrification (See Hoffman et al., 2008b, Table 1)

Figure legends standing on the Figure are generally much too small (Fig. 4, Fig. 6, Fig. 7 is the worse, Fig. 8) and make the Figures unreadable. Indeed, the subscript of the subscript of  $dH/dt$  is of interest ( $dH/dtR_{xx}$ ) and is very difficult to read because of its small size. Figures should be redrawn and  $dH/dt$  removed and T or Rxx put in the legend only.

Result 3.3: There are no details on how and where the change of pH between 2001 and 2004 was calculated (I can not find it in the 2008b paper). Is it a single point annual average? Whole estuary average over the years? In any case, the method should be described again in this paper which main topic is pH and error bars or variability should be reported in order to provide a statistical sense to the observed variability.

Result 3.3 (p 212): Remove the sentence: these changes are caused by differences from 2003 to 2004. The authors should explain more why changes of pH are linked to the hydrology. To me, the drop in  $NH_3$  concentration together with freshwater flow explains most of the increase of pH observed as  $NH_3$  is a major source of proton for the upper estuary and nitrification provides protons to the lower estuary. Decreasing  $NH_3$  then acts as lowering the proton source and provides a more basic pH in the lower estuary. This should be stated better in the paper.

Result 3.3 (p 213): the paragraph from lines 6 to 18 is not clear to me. These sensitivity analysis should be presented in a clearer way

Discussion 4.1, p 214 lines 5-10. I would summarize the processes in another manner

[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)[Discussion Paper](#)

(see my comment above for Results 3.2 and discussion 4.1)

Discussion, p 214 lines 20-27: This statement is too general, but is only valid in oxic environments. Please refine or remove

Discussion, p 215: The use of the term buffer is inappropriate in the context of acid-base reactions as it has a restricted meaning of a solution which can absorb strong acid or base or be diluted without changing its pH by a large value. Here buffering implies a process which is the escape of CO<sub>2</sub>, hence no relation with the process of acid-base buffering. As it does counteract the addition of acid (in this case), one should talk about a negative feedback process.

Discussion p 216 line 8-14: this paragraph is puzzling. It is said that the effect of the freshwater flow for S could be an artefact; yet its influence on the sensitivity analysis is 22% and this is discussed only in the last sentence of the discussion. Furthermore, the authors state that it could be a problem in boundary conditions with TA being recalculated given SCO<sub>2</sub> and pH. Yet, on paragraph 2.7, it is clearly stated that TA was the boundary condition (but not SCO<sub>2</sub>). Where is the truth? Isn't there some confusion in the boundary conditions used? I think this problem with S effect should be presented before (in the result section) and discussed more thoroughly.

Conclusions: should be rewritten in full text instead of bullet points

---

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

**BGD**

6, S289–S293, 2009

---

Interactive  
Comment

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Discussion Paper

