

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

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This is a methodological paper aiming at calculating the respective contributions of transport and reaction processes on pH dynamics in estuarine systems. The method is then applied to a macrotidal estuary (The Scheldt) to establish whole ecosystem proton budgets. If the results are novel and interesting, I think that the authors should elaborate significantly further on the methodological aspects of their study, as well as on the validity and uncertainties of their budget estimates before this paper can be published. The introduction should also be modified significantly.

MAJOR COMMENTS

1. Introduction. I find that the introduction does not properly reflect the current knowl-

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edge about pH dynamics in natural systems (in particular, statements in line 22 of p 198 and line 27 of p 199). Part of the confusion comes from the fact that the authors do not distinguish pH studies carried out in estuaries from those performed in porous media (mainly sediments). Later statements in the text reflect in my opinion more closely what is currently known about pH: the paragraph between line 6 and 20 of p 200 indicates that others have already quantified the relative importance of individual processes on pH while p 214 shows that at least qualitative information about the relative importance of individual processes on estuarine pH profiles was already known. Note that the statement 'took steps in that direction' line 6 p 200 is vague and should be clarified. Based on the above, I think that the authors should 1. Be more specific in their statements about current knowledge; 2. Separate quantitative pH studies among different environments (estuaries, sediments, ...); 3. Provide complete referencing in the first paragraph; 4. Identify more specifically the novel aspects of this study. From my understanding, this is the first mathematically transparent quantification of individual processes affecting pH in an estuarine system, which from the methodological standpoint required including the influence of the non constant dissociation constants. As stated above, this is original material that warrants publication.

2. Methods. Section 2.4 is not needed. I would merge it with 2.5 and state in one sentence that the dependencies of TA on K are the new terms in the development. For the sake of clarity and accessibility to a broader audience, I would however 1. Expand briefly (in words) the description of the strategy that you intend to follow to quantify the individual terms $[dH/dt]_i$; 2. Expand on one of the equations 13-22 as an example of how you go from eq 11/12 to any of those equations (using info from Table 2).

3. Results and discussion. - 'Validation': The exact conditions of the simulations are not clearly defined and the model validation is only performed on a limited set of data (in particular, the model is seasonally-resolved, yet only yearly averaged forcing conditions and model results are presented). It would thus be useful to provide more details about the exact forcing conditions of the model (river discharge, temperature, concen-

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trations,...). Furthermore, the intra-annual variability in simulated and observed pH values in Fig. 3, complemented by a comparison with other variables of the carbonate system (at least TA, pCO₂ (?)), should be reported. The small, yet systematic deviation between yearly averaged model results and observations observed for the 4 years (under predicted pH around km 40 - over predicted pH beyond km 50) shown in Fig. 3 should also be briefly discussed, at least if it is of statistical significance.

- Methodology (the key novel feature of this paper): Process rates are plotted in Hofmann et al., 2008b. However, it is not clear how those translate into the individual dH/dt (eqs 13-22) terms reported along the estuarine gradient. For instance, in terms of C and N units, denitrification has a visible effect on the budgets reported in Hofmann et al 2008b, but this process is insignificant on the proton budget. A much more detailed discussion, imparting from the results reported in Hofmann et al., 2008b (rates should be reported in a way consistent with eqs 13-22), is definitely required to support the transition between the results reported in the companion paper and those shown in Fig. 4a, at least for the dominant contributions to dH/dt. In particular, what about the contribution of the partial derivative terms appearing in eqs 13-18? Providing more insights would also be useful in the context of the comparison between proton and oxygen budgets (line 19 and further, p 214). Since Fig 4a is the key fig of the paper, I think that the authors should elaborate on the explicit link between the major pH features observed in Fig. 3 and the various contributions to pH changes presented in Fig. 4a: They need to better distinguish between net proton production/consumption by biogeochemical processes and the influence of transport (avoid mixing terminology such as import/export and consumption/delivery for the latter, which is confusing). The authors should also comment on the total net proton prod/cons values along the gradient, which (slightly) deviate from 0.

- Budgets: I find the information in Fig 4, Table 5 & 6 and supporting text somewhat redundant and the information should thus be condensed (since % are reported in the text, Table 5 & 6 do not bring anything more than what is already shown in Fig.4). I

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also think that the discussion is obscured by the continuous referencing to 6 different locations: the spatial distribution is obvious in Fig 4 while the (well-known) volumetric effect is highlighted without reference to these 6 locations. In terms of the budget reported in Fig 5, the statements in line 1-10 of p 212 and in line 8 of p 214 are somewhat contradictory, especially with respect to primary production. You should also elaborate on the physical meaning of the transport contribution to dH/dt . I agree that the present results are generally consistent with those of Regnier et al. 1997 and Vanderborght et al., 2002. Yet, based on Hofmann et al., 2008b, some discrepancies with other (C and nutrient) recent budgets established for the summer period (e.g. Vanderborght et al., 2007) and for the year 2003 under fully transient conditions (Arndt et al., 2009, in press) may occur, especially concerning the contribution of primary production to the overall budget. This most likely arises from different estimates of this process in the lower estuary. In my opinion, uncertainties in volume integrated process rates are high in this area (low concentrations and large volumes, but also poorly constrained seaward boundary conditions) and, at the very minimum, statements about uncertainties in estimates should thus be made when the proton budgets are presented/discussed, especially because model validation in the present paper + Hofmann 2008b is limited. Since the model is seasonally resolved, I would also be interested to see the magnitude of standard deviations in whole estuary proton production/ consumption at the seasonal scale.

- Sensitivity analysis: This is an interesting section and results intuitively make sense. However, providing more information would help understand, substantiate and validate these results: 1) In Table 3, report DIC and pH at the boundaries (assuming that pH reported there is the model averaged pH. How was this calculated? Is the increasing trend also observed in the data?); 2) Report and discuss simulated (and measured) CO₂, TA, NH₄ along the estuarine gradient for the 4 individual years to explain further how changes in freshwater flow and boundary conditions impact on these profiles, and thus on pH dynamics (such information could also be useful to discuss further the methodology - see above).

- Synopsis: This section and figure 8 are not needed since this is already summarized in the preceding sections.

SPECIFIC COMMENTS

- Fig 2 p 234 longitudinal

- line 4, p 199 - unclear - rephrase

- line 5, p 200 - the justification will only be understood by few. I would remove it from the intro.

- Line 1 p 201 - independently, for given freshwater -

- Line 2-3 p 201 - unclear - rephrase

- Footnote p 203. The definition of X is not specific enough (see Table 2 for a better treatment). I do not understand the alkalinity statement

- Line 19 p 204. This is not a proper justification. You should justify that the effect of true pressure variations (M2 tide, spring-neap) are negligible

- Eq 12 p 206 / Eq 13 p 207. Subscript T should be replaced by Tr I guess. In eq. 13, I would replaced subscript i by j for consistency with Table 2.

- Table 2 p 228 - Define the conversion OM-> carb in the caption

- Line 8, p 208 - first 2001 values = 1/1/2001 ?

- Line 15-20 p 208: the statement on the influence of temperature is contradictory

- Line 26 p 208: their individual effect: specify exactly to what 'their' refers to.

- Table 3 p229: temperature should be reported. Q refers to the flow at upstream boundary: do you the total freshwater discharge or only the one from the Scheldt river ?

- Table 4 p 230. The table caption is unclear. Do the parameters listed in a-n remain

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constant or are changing too? This can hardly be inferred when T4 is referred to for the first time in the text (even though it is easier to understand it in the results section).

- Lines 10-15 p 209: the text is redundant with the fig. caption.
- Line 2 p 210 (and all further references to such statement): dH/dt is referred to as an influence on the proton concentration. Why influence (and not contribution to total proton change) ?
- Line 16 p 210: it is not the figure which is trumpet like shape.
- Fig 4 p 236: refer to fig 4a and b in the fig caption.
- Lines 23-25 p 211: It is mainly physical processes which dominate the volume integrated proton turnover in the mid-estuarine region. Any comment on this?
- Line 12 p 212: Statement unclear.
- Line 9 p 213 ... by influences via ... only.
- Fig 5 p 237. the y axis should read $\text{kmol H}^+/\text{yr}$. Subscript T should be Tr.
- Line 11 p 214 add comma ... degassing, which ...
- Line 12-13 p 214 remove supports (if it is fully consistent, it thus supports). ... yields more quantitative information.
- Line 14-18 p 214: I find this statement trivial.
- Lines 3-13 p 215: this is the third time that the relative contribution of processes to the proton balance is discussed in the results-discussion section. Please restructure. Remove parenthesis in line 12.

REFERENCES

All references are already in the ms. except for:

Arndt, Regnier and Vanderborght. Seasonally-resolved nutrient export fluxes and fil-

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