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Interactive comment on “A step-by-step procedure for pH model construction in aquatic systems” by A. F. Hofmann et al.

Anonymous Referee #2

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Hofmann et al. formulate kinetic models for the pH and other quantities in rivers and estuaries. The integration of the resulting equation system can be quite difficult because of the large range of characteristic time scales for the various processes involved (advection, diffusion, chemical reactions, air-water gas exchange; stiff systems of ordinary differential equations). The authors discuss several methods to tackle such problems. As an example they consider the Schelde estuary in Belgium under various scenarios.

The manuscript is largely readable but needs many revisions and is far too long (it should be shortened by at least 50%; compare my suggestions in the annotated manuscript). The authors should discuss what is really essential for a research paper, what is new and of interest for readers of BG.

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The term 'canonical transformation' has a fixed meaning in classical dynamics and thus should not be used in the current context. The term 'dynamical equilibria' should be replaced by 'steady state'. I am not in favour of terms like 'equilibrium reactions', 'equilibrium species', or 'equilibrium invariants'. Tables should be numbered in the order of referencing in the text (Table 14 is referenced first). A list of abbreviations might be useful.

Mention in introduction: Large range of time scales of processes causes numerical problems (stiff equations). Introduce approximations that reduce range of time scales and thereby make system of equations less stiff. The 4 approaches (FKA, FNA, OSA, DSA) discussed in the manuscript are different approximations and not just related by mathematical transformations. Which approximations have been made? What are the consequences for the equation systems and the results?

Appendix A: the criterion for exclusion of acid-base reactions could be expressed more clearly and shorter as follows:

"If the possible range of pH values is specified, say $\text{pH}_{\text{lower}} \leq \text{pH} \leq \text{pH}_{\text{upper}}$, and the total alkalinity over this range is above a characteristic value, TA_c , acid-base systems with low concentrations (pK may actually be inside specified pH range) and 'fully dissociated' acids or bases can be excluded. A simple criterion could read as follows. Consider an acid HA with total concentration A_{total} .

When $\text{pH}_{\text{lower}} \leq \text{pK}_{\text{HA}} \leq \text{pH}_{\text{upper}}$ (case1) the acid can be excluded from the simulation of pH if $A_{\text{total}}/\text{TAC} < \epsilon$ where ϵ is specified small number (for example, $\epsilon = 1e-5$).

When $\text{pK}_{\text{HA}} \leq \text{pH}_{\text{lower}}$ (case 2) one can estimate an upper limit of [HA] at pH_{lower} by $[\text{HA}]_{\text{pH}_{\text{lower}}} \leq 10^{(\text{pH}_{\text{lower}} - \text{pK}_{\text{HA}})} * A_{\text{total}}$. The number of protons provided by further dissociation of HA in the specified pH range cannot be larger than $[\text{HA}]_{\text{pH}_{\text{lower}}}$ and thus HA can be excluded when

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$[HA]_{pH_lower}/TA_c \leq 10^{(pH_lower-pK_HA)} * A_total/TA_c < \epsilon$.

An analog argumentation leads to the exclusion of basis with $pK_base > pK_upper$ (case 3):

$[base]_{pH_upper}/TA_c \leq 10^{(pK_base-pH_upper)} * base_total/TA_c < \epsilon$."

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