

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

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1 General comments

In our paper we provide a set of formulations to model the pH in any aquatic system, including aquatic sediments. The large difference in characteristic time scales of processes results in stiff equation systems and we identify this as the most important difficulty in pH modelling. We provide a recipe of sequential reformulations of the problem which overcomes the stiffness issue and other difficulties of pH modelling. We outline different methods to numerically solve the model at different reformulation stages and provide linkages to existing approaches.

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The goal of our manuscript is to document a general and systematic treatment of pH modelling. Rather than presenting one specific method, our aim is to show how existing approaches are linked and how they can be generalized. In order to do this, we need to mention historical approaches as well as alternative ways of treating certain aspects of the modelling process. We are aware that this results in a rather long manuscript that requires a committed reader. However, we believe that such a systematical synthesis of pH modelling is a valuable contribution to the scientific literature, and so, we decided not to shorten our manuscript by 50 % as requested by Anonymous Reviewer # 2. Because this a crucial point, we have contacted Anonymous Referee # 2, and explained the rationale in more detail. He acknowledged the value of our approach and agreed that the unshortened manuscript is worth publishing. (Anonymous Referee #2 has been asked to confirm this in a letter to the editor or in an online comment).

Another central point of criticism of Anonymous Referee # 2 is his claim that our different solution approaches represent different approximations and not just mathematical reformulations. Two major approximations have been made: To make the transition from the FKA to the FNA (the transformation into the canonical form) the local equilibrium assumption has been applied. This approximation has no influence on the results of the model, as long as the temporal model resolution is coarse enough, which in our case means that it stays on the timescale of our kinetic reactions. Furthermore, to reformulate the system into a form solvable by the DSA, the K^* 's of the system are assumed constant. This has been done out of didactical reasons to keep the mathematical expressions simple, but variable K^* 's can be integrated into the DSA as well.

Both of these approximations can also be made from the very beginning, the local equilibrium assumption can be included into the FKA by estimating very high forward and backward rate constants k_f and k_b such that their ratio equals the equilibrium

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constant K^* of the reaction in question ($K^* = \frac{k_f}{k_b}$) and the K^{**} 's can be assumed constant for all approaches. What remains is a chain of mathematical transformations with no further approximations involved (hence these are different reformulations and not different approximations). Our goal in the paper is (1) to show that these four different reformulations of the same pH model yield the same results and (2) to discuss the advantages and disadvantages of these reformulations.

As shown in Table 18 and in Fig. 6 of the manuscript (original and revised), there is a clear trade-off between reformulation effort and the numerical resources required (while exactly the same assumptions of local equilibrium and constant K^* 's are used in all approaches). The more the pH problem is initially reformulated, the less computation time is spent on actual pH simulations afterwards and the more (chemical) insight is gained.

2 Comments on the manuscript annotated by Anonymous Referee #2

We thank Anonymous Referee # 2 for the detailed annotation of our manuscript as well as for a fruitful personal discussion. They were very useful and not only helped to remove typesetting errors and language inconsistencies, but also helped to improve the manuscript by providing ideas to straighten out several weak points.

This led to following main improvements:

1. We gave an explicit rule of thumb to decide if the characteristic time scale of a process is “fast” or “slow” with respect to the time scale of the model.

2. We better explained why the apparent equilibrium reaction rates R_i^{diss} become mathematical unknowns.
3. We greatly improved Appendix A (the criterion when to exclude acid-base reactions from the system). The new figure follows a suggestion by Anonymous Referee # 2.
4. We improved the explanation of the differences between the influences of processes on the pH as calculated with the FKA and with the DSA.

3 Specific replies to online comments by Anonymous Referee #2

3.1 “canonical transformation”

This term is indeed already in use in Hamiltonian mechanics. We followed Anonymous Referee # 2 and changed the name of our procedure to “transformation into canonical form”.

3.2 “dynamical equilibria”

We changed “dynamical pH equilibrium” to “pH steady state”.

3.3 “equilibrium invariants”

We are in favour of terms like “equilibrium invariants”, “equilibrium species” and “equilibrium reactions” Since Bernard Boudreau (Referee # 1) seems to agree we decided to keep these terms.

3.4 Table numbering

It is indeed a cosmetic flaw of our manuscript that Table 14 is mentioned first. We nevertheless decided to keep Table 14 in the Results section since it contains much information about our example system which is not relevant to the main story we want to convey: a comprehensive guide to pH modelling. Placing this table up front would obstruct the view of the reader onto the essentials of our paper. However, we removed the reference to Table 14 in step 1 of our model generation procedure and replaced it with a reference to the Results section of the manuscript.

3.5 List of abbreviations

We explain all abbreviations in the text. To not extend the manuscript even more, we opted for not including a list of abbreviations.

3.6 Stiffness and approximations in introduction

We followed Anonymous Referee # 2 and mentioned the stiffness of the equation system as a central problem of pH modelling in the abstract and the introduction.

We added a paragraph discussing the approximations made for different reformulation steps to the discussion of the manuscript. (See also section 1 (General comments) in this document for this issue.)

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4, S2161–S2166, 2007

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3.7 Appendix A

Although they contain a sign error (see below) we followed the suggestions of Anonymous Referee # 2 and rewrote Appendix A.

Sign error:

Anonymous Referee # 2 estimates:

$$[\text{HA}]_{\text{lower}} \leq 10^{(pH_{\text{lower}} - pK_{\text{HA}}^*)} \cdot [\sum \text{A}] \quad (1)$$

However:

$$K^* = \frac{[\text{A}^-][\text{H}^+]}{[\text{HA}]} \quad (2)$$

$$\Rightarrow [\text{HA}] = \frac{[\text{H}^+]}{K^*} \cdot [\text{A}^-] \leq \frac{[\text{H}^+]}{K^*} \cdot [\sum \text{A}] \quad (3)$$

$$\Rightarrow [\text{HA}] \leq \frac{10^{-pH}}{10^{-pK^*}} \cdot [\sum \text{A}] \quad (4)$$

$$\Rightarrow [\text{HA}] \leq 10^{(-pH - (-pK^*))} \cdot [\sum \text{A}] \quad (5)$$

$$\Rightarrow [\text{HA}] \leq 10^{(pK^* - pH)} \cdot [\sum \text{A}] \quad (6)$$

which means:

$$[\text{HA}]_{\text{lower}} \leq 10^{(pK_{\text{HA}}^* - pH_{\text{lower}})} \cdot [\sum \text{A}] \quad (7)$$

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S2166

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