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Interactive comment on "The mathematics of the total alkalinity–pH equation: pathway to robust and universal solution algorithms" *by* G. Munhoven

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Many thanks to Mick Follows, to the anonymous reviewer and to Andy Ridgwell for their comments. I basically see two main points that the reviewers recommend to improve on. I am considering both for the revision of the manuscript. Andy Ridgwell provides a welcome illustrative example of a real-world failure of the *p*H calculation routine in his model.

Below, I present a short discussion and a few details about how I am planning to take your suggestions into account. I furthermore take the opportunity to add a few additional points that came up in personal discussions with other colleagues about the paper.

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Interactive Discussion

Discussion Paper

Reviewer's comment by the Anonymous Reviewer #1

On *"the step from the 'TA-DIC' to the 'TA-pH' problem"*

It should be noticed that, strictly speaking, the problem mentioned is actually transformed from a TA-DIC problem into a *p*H problem. I am aware that the name chosen for the equation that the paper revolves around is potentially misleading. Actually, TA (or Alk_T as it is denoted in the paper) and all of the other total concentrations (e.g., C_T, B_T, S_T, or any $[\Sigma\mathrm{A}]$) that appear in the equation are equally important; TA does not play any more prominent role than the others. The equation that I am studying here could actually have more concisely been called the *pH equation*. I thought this was too general a name and decided to further include *Total Alkalinity* in the name, in order to remind that the overall structure of the equation derives from the definition of total alkalinity.

In the revised manuscript, I will work out this aspect more clearly at the end of section 1 where the equation is introduced, and also elaborate on the TA-DIC to *p*H step in the description of the reported numerical experiments.

Reviewer's comment by Mick Follows

On *"the discussion of free vs seawater pH"*

Having re-read section 4 while preparing this reply, I must agree that readers without at least some prior knowledge will have difficulties to grasp the importance of considering the differences between the different *p*H scales. The revised manuscript will include a consistent introduction to the related issues, most of which can be traced back to the measurement procedures and interpretation of *p*H in seawater. I will furthermore also

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emphasize on the importance of considering the different concentration units used in the literature (molal – mol/kg-solvent, i.e., mol/kg-H_2O here – versus mol/kg-solution, i.e., mol/kg-seawater in our case).

Editorial comment by Andy Ridgwell

Example of a real-world ICAC failure

Thank you for providing that typical example of a failure of your *p*H solving routine. Presuming that you used the GENIE model with its ICAC-type procedure, it is clear that once Alk_T reaches sufficiently high values (as could happen when a sufficiently large amount of $Ca(OH)_2$ is dissolved in surface ocean water), ICAC methods become unconditionally divergent.

Additional Comments

Extra modelling environments and models

Alberto Borges has drawn my attention to the R-package AquaEnv by Hofmann et al. (2010, 2012). I will include it in the revised manuscript, the more since it also mentions difficulties that may be encountered with the ICAC method that is adopted therein (and for which the authors refer to (Follows et al., 2006)) when calculating *p*H for samples with a very low or zero total dissolved inorganic carbon concentration. Finally, in the revised manuscript, I will also mention the LOSCAR Model (Zeebe, 2012). LOSCAR appears to use the single iteration ICAC method of Follows et al. (2006) and Zeebe (2012) reports that when the model is started with very high Alk_T/C_T, negative $[H^+]$

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may be obtained, requiring the model run to be restarted with Alk_T and C_T in a lower ratio. That kind of failure is clearly explained by the results presented in the discussion paper and it can be safely avoided with the new algorithms presented here.

Spurious pre-compiler definitions in driver_acb.F90 and driver_acbw.F90

I discovered that the two driver programs `driver_acb.F90` and `driver_acbw.F90` contain the pre-compiler definition `CASE_ZHINI_SAFEBOUNDS` that is, however, never used in those programs. I will discard those definitions and adapt the comments for the revision.

References

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