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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

Anonymous Referee #1

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To the editor:

below please find our referee report on the manuscript

The mathematics of the total alkalinity–pH equation: pathway to robust and universal solution algorithms

by

Guy Munhoven.

Our guess is that Munhoven's implementation of his new algorithm that uses bracketing bounds, a good starting guess and a good choice of termination criteria will become a standard method in the future in 3-D models, as has been the OCMIP implementation

in the past.

The paper is very well written, although some parts might be enjoyed only by the mathematically inclined reader.

We recommend the paper for publication in Geoscientific Model Development.

To the author:

In the manuscript ‘ The mathematics of the total alkalinity–pH equation: pathway to robust and universal solution algorithms’ Guy Munhoven proposes a new fast and save (always converging iterative) method to calculate pH from total alkalinity (TA) for given total concentrations of acid-base systems (including dissolved inorganic carbon = DIC), temperature, and salinity. There are several methods already available to solve the TA-pH equation. However, non of these methods is optimal in terms of necessary arithmetic operations (or computer time) to reach an approximate solution of sufficient accurancy while ensuring convergence for all interesting conditions.

Guy Munhoven discusses five methods that have been proposed and used in global marine carbon cycle models and compares his new method in terms of convergence and requested computer time for example problems. His new method always converges and is faster than 4 out of the other 5 methods. The fastest method is 10% faster than Munhoven’s new method, however, it does not always converges.

Even aside from the issue of different empirical equilibrium constants and the sometimes inconsistent use of pH scales, the various methods in use create model-model differences in calculated pH values solely due to the methods applied. Some of the methods are also more numerically stable than others. There are a number of further issues that one has to deal with when choosing between the different methods for a practical application, e.g. a good choice of initial guesses for the iterative solution, and of convergence criteria. In this thicket of methods, the paper by Munhoven brings urgently needed clarity: Firstly, by providing an overview and classification of the dif-

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ferent approaches that are in use for this purpose; it wasn't clear to me, for example, that the simplified method by Follows et al. (2006) is a variant of the iterative method by Bacastow (1981). Munhoven compares the convergence and stability properties of these methods with a set of standard test cases. But secondly and more importantly, he presents two important results that are of high practical relevance, and that I have not seen before. The first is that he proves that the problem of finding the concentration of H+ or, equivalently, of CO2 from dissolved inorganic carbon and alkalinity - which can be written as the problem of finding a zero of a polynomial - has exactly one real and positive solution. This is not difficult to see when taking into account only carbonate alkalinity, but here it is generalized to arbitrary many acid-base systems. The proof is actually simple, and one wonders why no one has noticed it before. This has very practical consequences as it allows constructing failsafe iterative algorithms. The second achievement is that he provides a method to calculate bracketing bounds for the iterative solution of the polynomial equation in H+ that have the property that the polynomial has a positive value for one of the bounds, and a negative value for the other, such that the solution to the polynomial equation is guaranteed to lie in between. Such a boundary is needed if one wants to guarantee the iterative solution to converge. So far, modellers often choose the bracketing quite wide in the beginning of their model runs (which implies slow convergence) and then narrow them arbitrarily. Personally I have experienced several times that this led to convergence failure in my model runs, e.g. when an ocean circulation model produced spuriously low alkalinity. My guess is that Munhoven's implementation of his own algorithm that uses these bracketing bounds, a good starting guess and a good choice of termination criteria will become a standard method in the future in 3-D models, as has been the OCMIP implementation in the past.

The paper is very well written, although some parts might be enjoyed only by the mathematically inclined reader.

My single suggestion for change: Global biogeochemical models contain prognostic

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equations for DIC and TA from which all other quantities of the carbonate system have to be calculated if requested. It would be nice to show the step from the 'TA-DIC' to the 'TA-pH' problem.

Interactive comment on Geosci. Model Dev. Discuss., 6, 2087, 2013.