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Comment

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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The hydrogen ion/hydronium concentration participates in a majority of significant geochemical reactions at the earth's surface. As a consequence it has been utilized as a master variable in classic geochemical and environmental analyses (e.g. Garrels and Christ, 1965, Solutions, Minerals and Equilibria; Stumm and Morgan, 1996, Aquatic Chemistry), and it continues to be the object of considerable research interest.

The problem of predicting, as opposed to measuring, pH in aquatic environments is far from trivial. Even in closed, purely equilibrium systems, the presence of more than one protolytic species leads to a need to solve numerically a system of non-linear algebraic equations. Add finite-rate transport and non-equilibrium reactions and one has a recipe for computational difficulties.

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Hofmann et al. synthesize the approaches that have been taken to calculate pH and offer a clear, explicit strategy/algorithm for calculating pH in complex geochemical situations. They correctly point out that a fully kinetic model of pH will encounter numerical challenges, usually insurmountable in my experience. These problems result from the vastly different time scales of acid-base reactions, as compared to transport and redox and precipitation/dissolution reactions. They then plainly and intelligibly explain how the acid-base reaction terms can be treated as unknowns and replaced by mass-action laws for these reactions. They then explain that the resulting system of equations can be solved either directly, via a DAE solver (FNA), or via transformation and "operator splitting" (OSA), or further transformation and direct substitution (DSA). The method is logical, and neophytes will find great succor in this presentation. The example problems are informative and relevant.

No presentation is perfect, and this paper has a few minor flaws. Let me mention some of these, in the order that they appear in the text.

(1) p. 3727. The authors strive for rigor and generality, without needless complexity. However, they divide the transport term of eq (1), P_x , into an advective-dispersive transport, T_x , and a term for exchange of volatiles into the atmosphere, Ex . This precludes, a priori, any possible exchange with the bottom. Certainly benthic exchange should be included until that point, later in the paper, where that component is argued to be small. Other systems may have a large benthic contribution.

(2) I am not one of those who believes that it is both correct and sufficient to cite a recent reference as the source of an idea that is germane to an argument. The idea that, when some reactions are fast (compared to transport processes and other reactions) and reversible, they can be considered to be in local equilibrium is much older than suggested by the authors, e.g., Saatlink et al. (1998), Morel and Hering (1993), etc. The only acknowledgement of the ancestry of that idea is the reference to Aris and Mah (1963). The idea is older: Olander (1960, *AIChEJ* v. 6) models diffusion with equilibrium reactions. (Supposedly, Prigogine discusses the concept in an early

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book from the 1940s, but I cannot verify this.) Subsequently, the topic is discussed in papers by Secur and Beutler (1967, *AIChEJ* v. 13), Goddard et al. (1970, *Chem. Eng. J.* v. 25) and Otto and Quinn (1971, *Chem. Eng. J.* v. 26). The latter reference specifically deals with the carbonate system. The area was sufficiently well understood by the mid-1970s that Sherwood et al. included a discussion in their textbook *Mass Transfer* (1975, McGraw-Hill, p. 336-343). In our own field, Di Toro (1976, Chapter 9 in *Modeling Biochemical Processes in Aquatic Systems*, Ann Arbor Science, pp. 233-255) introduced many of the ideas in the current paper, including local equilibrium, equilibrium invariants, and etc. Failing to reference these earlier workers can give the impression of diminishing their contributions and falsely that the topic is of recent invention.

(3) p. 3734, line 5. OM decay is said to have a Monod-like dependence on the oxygen concentration. That is correct if the rate of OM decay is controlled by the oxidation step; however, if it is controlled by OM hydrolysis, this rate is independent of the oxidant concentration. Only the oxygen uptake rate in the oxygen conservation equation will exhibit such a Monod dependence. If true, this will not affect the result in any appreciable way.

(4) p. 3736-37 and again on p. 3754 (1st paragraph). The concept of equilibrium invariants, and their advantages, is old. This discussion is without references and gives the impression of something new. In aquatic geochemistry, they appear in the Di Toro paper given above. In sedimentary geochemistry, similar weighted quantities appear naturally in the analysis in Boudreau (1987, *GCA*; 1991, *GCA*), Boudreau and Canfield (1988, *JMR*; 1993, *GCA*). And the hydrology literature contains many other examples. Again, some acknowledgement of history would be nice.

(5) p. 3743. The footnote here needs to be placed much earlier.

(6) Total electro-neutrality was employed in CANDI because pH modelling was an afterthought. CANDI was as created originally to model OM and nutrients; thus it does not model invariants. It was "retro-fitted" to do pH using the kludge of total electro-neutrality.

This approach is not generally recommended by its author.

(7) Figure 6. Readers will love or hate this diagram. From my point of view, with no units and numerical values it conveys no more information than the words in the text, and it should be removed.

There are a number of minor mistakes in the writing, but it reads well.

OVERALL: This is a remarkably good synthesis of the problem and its solution; I can highly recommend its publication.

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