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Comment on egusphere-2022-676

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Community comment on "Oceanic Alkalinity and Titration Alkalinity and the small difference between them due to minor effects of sulfate, fluoride and phosphate in the acid titration of oceanic seawater" by Hein J. W. de Baar et al., EGU sphere, <https://doi.org/10.5194/egusphere-2022-676-CC2>, 2022

While it was interesting to read on the historical development of the alkalinity concept, and I appreciate the effort made by the authors to bring together so much pertinent information, there are several significant issues with the theoretical aspects of this manuscript. These issues mean that the manuscript adds to, rather than removes, confusion surrounding the alkalinity concept, and that the conclusions regarding the effects of various components on alkalinity (including phosphate and sulfate) are incorrect, or at best applicable to only one of multiple different alkalinity definitions that are treated here as if they were the same. Several studies that already clearly demystify the issues causing confusion here are either ignored (e.g., Middelburg et al., 2020), misrepresented (e.g., Chen et al., 1982), or not understood (e.g., Wolf-Gladrow et al., 2007).

[1] Multiple alkalinity definitions

The most fundamental issue is that two different definitions of alkalinity are compared and treated as if they were the same. These are called 'Oceanic Alkalinity' and 'Titration Alkalinity' in this manuscript. Oceanic Alkalinity, as defined here by equations (19) and (20), is similar (although not quite identical, it does treat phosphate in the same way) to the 'charge-balance alkalinity' of Middelburg et al. (2020), while Titration Alkalinity is the alkalinity of Dickson (1981) – it is not the right-hand side of equation (19), despite the claim on line 291. The Middelburg et al. review explains the differences between the two definitions, including how phosphate gain/loss does alter Dickson alkalinity, but not charge-balance alkalinity.

This difference appears to lead to the misunderstanding of the 'explicit conservative' equation of Wolf-Gladrow et al. (2007) and consequent confusion in section 5.1. Here, comparisons are made between the authors' Oceanic Alkalinity and the explicit

conservative equation. But the explicit conservative equation is based on, and consistent with, the Dickson (1981) definition, whilst Oceanic Alkalinity is not. It is therefore no surprise, and not a problem, that Oceanic Alkalinity and Wolf Gladrow et al.'s explicit conservative equation are not the same as each other.

Which definition should we use? One could choose either as long as one was consistent through the entire analysis (as noted by Middelburg et al.). The certified reference materials most widely used to calibrate alkalinity measurements are defined in terms of Dickson alkalinity (Dickson et al., 2003). All variants of the CO2SYS software are based on the Dickson alkalinity equation (Humphreys et al., 2022). So if one is using these tools, then one is implicitly using the Dickson alkalinity definition, and phosphate should be treated accordingly.

[2] Zero versus negligible effect

Another important issue is that at times the distinction is blurred between something having exactly zero effect on alkalinity and something having a negligibly small effect on alkalinity. This is a very important theoretical distinction, and arguing that the latter case is true for a particular system has no relevance for how it should be included in the alkalinity equation.

Related to the issue above, it seems there is also some inconsistency in how this logic is applied in the manuscript. In section 4.2 and around lines 910–914 it appears that the possible influences of Mg^{2+} and sulfate on alkalinity are ruled out because changes in these variables are too small to measure against the large background value and therefore cannot be verified. But on lines 61–65 the use of alkalinity in lieu of Ca^{2+} to detect $CaCO_3$ cycling is accepted. In reality there is no need for experimental verification, as this is a purely theoretical question: given an alkalinity equation we can calculate the exact effect of any given chemical reaction.

[3] Other, more minor points

With reference to section 2.1.2, I would note that studies that either do not mention phosphate, or that conclude that any phosphate effect in an experiment would be too small to measure, should not be portrayed as supporting any particular effect of total phosphate gain/loss on alkalinity.

If I have read section 2.2.2 correctly, the argument is, “there should not be a negative $[H_3PO_4]$ term in the Titration Alkalinity equation because $[H_3PO_4]$ increases through a titration.” But alkalinity is not defined in terms of whether things increase or decrease in concentration during a titration. For example, $[HSO_4^-]$ also increases during a titration, which the manuscript does accept as a negative term in the equation (lines 860–863) - as

indeed does $[H^+]$.

The points raised about needing to take care in selecting correct stoichiometric ratios for organic matter when calculating the effect of its production or remineralisation (e.g. section 5.2) are important and valuable to consider further. But they are not relevant to the core question of how changes in the various components actually affect alkalinity.

The conceptual explanation of how alkalinity is held constant during DIC uptake or loss during photosynthesis and respiration (section 2.2.3) is unhelpful and arguably incorrect. This is due to oversimplification in equation (23), specifically, neglecting the $-[H^+]$ term. The absence of this term makes it seem that one could remove HCO_3^- from solution and then maintain constant alkalinity by converting some HCO_3^- into CO_3^{2-} , as the latter has double the effect on alkalinity. It also implies that the removal or addition of DIC causes an initial change in alkalinity that is then (quickly) reversed by this conversion. However, both of these suggestions are false, as follows. First, the reaction by which the conversion occurs is: $HCO_3^- \rightleftharpoons CO_3^{2-} + H^+$. Thus converting HCO_3^- into CO_3^{2-} necessarily releases an H^+ , which has an exactly equal and opposite effect on alkalinity, thus there is no overall change in alkalinity from this reaction in either direction - if alkalinity were changed by DIC uptake, this reaction could not reverse that effect. But in fact, alkalinity is not affected at all by DIC uptake or production, even on the shortest possible timescale, regardless of which form of DIC is taken up or produced, under the standard assumption that charge is balanced with H^+ . Therefore, although there is indeed a shift in the balance of the different DIC species ($CO_2(aq)$, HCO_3^- and CO_3^{2-}) after DIC uptake/production, this shift has absolutely nothing to do with keeping alkalinity constant, as implied in the manuscript.

A valid mechanism by which changes in total phosphate might not affect total alkalinity (as defined by Dickson, 1981) would be through challenging the assumption that charge balance is always maintained by H^+ . If in fact some other ion that does not appear in Dickson's alkalinity equation were used (e.g., Na^+) to balance the appropriate fraction of the charge then there could be zero overall effect on alkalinity. This would be analogous to how DIC uptake for photosynthesis, charge-balanced by H^+ , does not affect alkalinity, while DIC uptake for calcification, charge-balanced by Ca^{2+} , does. However, I could not find any discussion of this aspect in the manuscript.

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