

First, and foremost, the authors are most grateful to the five colleagues that have provided their constructive comments.

Therefore, we now are quite busy making major revisions to our manuscript towards the revised version to be re-submitted and published as a regular article in Ocean Science. Meanwhile we are also studying the various other articles that were recommended in the five comments of the colleagues.

Perhaps it is useful to mention the rationale for submission of the discussion paper that invites such comments. Recently, it was noticed that one colleague had a different view on one aspect of Alkalinity than another colleague. However, each was convinced the own personal view was the only correct view. For a long time indeed there only was one alkalinity concept in the literature. Yet given the above apparent different views, it was deemed helpful to submit a discussion paper that invites colleagues to provide feedback towards eventually arriving at one commonly agreed exact definition of alkalinity.

Next Prof. Middelburg promptly by email sent his article Middelburg et al. (2020) and from this, and the further information provided by him, all of us learnt and came to realize that in fact there are several definitions of Alkalinity in the literature.

There exist at least three definitions as follows:

- a. what we called Oceanic Alkalinity, more or less the same as Charge Balance Alkalinity after Middelburg et al. (2020).
- b. Titration Alkalinity
- c. Total Alkalinity, after Dickson (1981)

Moreover, for those authors wishing to also take into account the effects of biological uptake/release of sulphate, magnesium, strontium and so forth, and combinations thereof, more versions of the definitions of Alkalinity do arise and do exist in the literature.

Middelburg et al. (2020) review the various approaches and definitions in the literature, in a non-judgmental style. From this style, it is now realized that every author, or team of authors, has the academic freedom of speech to write and publish their own approach and definitions. For example, for the effect of photosynthesis and its opposed respiration, numerous approaches are mentioned yielding calculative factors ranging from 1.06 to 1.36, where yet another approach relying on AOU for assessing such organic matter dynamics is also mentioned.

This notion that there exist several concepts and their definitions of alkalinity, and each is fine, is somewhat of a paradigm shift, this versus the preceding notion of there being one alkalinity that can be measured by titration.

Next, we may, or may not, soon observe the classical response of the scientific community, after Kuhn (1962). Briefly, after such paradigm shift, (almost) everyone states that, yes, they knew this for a long time, has always stated this. In this case, some or several ocean chemists would say they always knew that there are several concepts/definitions of alkalinity. Quite nicely, Kuhn (1962) was soon proven correct once two major revolutions

had taken place: 1) the double helix structure of DNA as per Watson and Crick (1963), and continental drift (evidence of geomagnetic reversals) after Vine and Matthews (1963).

*) Morley 1963 manuscript, also on geomagnetic reversals, first rejected by Nature, next rejected by J.Geophys.Res.: "*such speculation makes interesting talk at cocktail parties but it is not the sort of thing that ought to be published under serious scientific aegis*"

With regards to specific comments of Dr. Humphreys:

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).

Answer: Yes, the Middelburg et al (2020) article provides the paradigm shift that there are many different views and definitions of alkalinity, and all are fine. This Middelburg et al. (2020) article was overlooked in our discussion paper.

Chen et al (1982) was represented in our discussion paper. In this article, the view on the role of phosphate uptake/release was debated and changed a few times throughout the article. Yet unfortunately we had overlooked a final sentence that, after all, did mention that the release of one mole of H_3PO_4 due to organic matter decomposition decreases TA by one equivalent. We are grateful to Prof. Chen for having informed us about this final conclusive sentence in response to the discussion paper. The article of Wolf-Gladrow et al. (2007) we did not understand, and quite honestly there still remain some questions.

In our fully revised manuscript, we will show that there are still issues with alkalinity, which need to be removed.

[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.

Answer: Yes, indeed multiple definitions do exist and each is fine, see above. In our revised manuscript, we will follow the definition from Middelburg et al more closely. However, with regard to the phosphate issue we will add new interpretations trying to clarify this unresolved issue. One could of course use the CRMs, the CO2sys software and the Dickson definition of alkalinity and presume that if phosphate is treated in that way that everything is fine. However, if the theory behind phosphate is erroneous, this consistent array of applications will still lead to erroneous results in the eventual interpretation of alkalinity. "Which definition should we use? One could choose ..."
Indeed, there is full freedom of choice, and indeed best to clearly mention one's choice(s) and next be consistent.

[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.

Answer: In natural science there is deemed to be the combination of concept/theory and observation (measurement). Crudely stated: No concept no science, no measurement no science. On the other hand, we all know that some scientists are more focused on making observations, other are more focused on concept/theory.

The history of Alkalinity is an interesting example of first measurements being made, for at least one century already, and next slowly beginning to understand the underlying chemistry,

and the underlying theory having been developed. Therefore, measurements and their reproducibility really do matter.

Nobel-prize winner Kamerlingh Onnes having achieved the world's lowest temperatures in his laboratory, did have the motto: "Door meten tot weten". Quite soon the general public did shorten this to: "Meten is weten". In some sort of translations: By measurement to knowledge or briefly: To measure is to know.

Surely every scientist has the freedom of speech to write out the theory of any or all conceivable constituents of seawater affecting alkalinity. If so, then would one include those trace elements that occur in nanomolar to picomolar concentrations in seawater, and exhibit a charge. Here, the review chapter of Bruland et al. (2014) in their Table 1 provides data of all trace elements and their concentration ranges. Here are for example $\text{Al}(\text{OH})_4^-$ and $\text{Al}(\text{OH})_3^0$ in the 10^{-9} molar range, vanadate HVO_4^{2-} in the 10^{-7} molar range, chromate CrO_4^{2-} in the 3 to 5 nanomolar range, arsenate HASO_4^{2-} in the 17 to 25 nanomolar range as mentioned in an email message by Dickson, selenate SeO_4^{2-} in the 0.5 to 2.3 nanomolar range, tin in the $\text{SnO}(\text{OH})_3^-$ and $\text{Sn}(\text{OH})_4$ in the 1 to 20 picomolar range, and so forth. This shows that also theoreticians do not use the full, ultimately correct definition of alkalinity, but draw a line between significant or not, just like observationalists are doing. Only the position of the drawing line is different, where the one of the observationalists seems to be more realistic as sound science ultimately depends on what can be measured.

Ourselves being observationalists, going out to sea to make measurements, the reproducibility of the measurements is a bottom line of what constituents of seawater are worthwhile to take into consideration. The reproducibility or precision of alkalinity measurements at some 1 to 1.5 $\mu\text{mol.kg}^{-1}$ really is excellent at 0.04 to 0.06 %. Given this bottom line of some 1 to 1.5 $\mu\text{mol.kg}^{-1}$ it is realized that the NO_2^- anion would not really matter. The occasional nitrite concentrations in the surface ocean typically are in the 0 - 0.3 $\mu\text{mol kg}^{-1}$ range of which only 6% is the anion NO_2^- . At upper limit 0.3 $\mu\text{mol kg}^{-1}$ the 6% NO_2^- after titration to $\text{pH} = 4.5$ would be merely 0.018 $\mu\text{mol kg}^{-1}$. The corresponding proton consumption is well below the precision $\pm 1 \mu\text{mol kg}^{-1}$ of the Titration Alkalinity. Even at higher total nitrite in the Black Sea, the contribution of NO_2^- in the order of 0.03 to 0.04 $\mu\text{mol kg}^{-1}$ still is below the precision of the Alkalinity. Last but not least, as mentioned in the discussion paper, shipboard determinations for nitrate in fact measure the sum of $\text{NO}_3^- + \text{NO}_2^-$ and only by having available an additional analytical channel to detect nitrite alone, one is able to make the distinction between true nitrate = measured total - measured nitrite.

Similarly in the discussion paper was mentioned the uptake/release of magnesium with regards to the production/decomposition of chlorophyll, where only the very highest chlorophyll contents of algae would at most be equivalent to 0.77 $\mu\text{mol.kg}^{-1}$ seawater. This maximum value still is below the about 1 $\mu\text{mol.kg}^{-1}$ precision of the Alkalinity titration.

Indeed assimilation/dissolution of sulphate, magnesium and calcium by biota is not discernible from a dissolved tracer, this because of the very high background concentration in seawater. Nevertheless, among these three, the calcium is of greatest significance with regards to production or dissolution of CaCO_3 shells, hence with regards to preservation, or not, of marine calcareous deposits. Therefore, many efforts were made to somehow back-

calculate small changes in dissolved calcium from alkalinity, after salinity normalization plus "correction" for organic matter via nitrate. Notably, Brewer et al (1975) did pursue this, and in fact also consider sulphate effects and even cite a S:C ratio of 0.016 in marine organisms, but conclude the effects of sulphate are not discernible. Also, the above-mentioned article of Chen et al. (1982) in fact is also focusing on the same calcium problem as the Brewer et al (1975) article.

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.

Answer: Agree that not mentioning phosphate and so forth in an article in the literature, does not necessarily imply supporting/rejecting effect on alkalinity by the author(s) of such article. We changed this in the revised manuscript.

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 $[H^+]$.

Answer: The definition of Total Alkalinity is based on two inherent assumptions. When adhering to this Total Alkalinity concept then one arrives at different interpretation, as compared to other concepts of Alkalinity. Indeed some, major, terms like HCO_3^- and $2 CO_3^{2-}$ do account for their binding of the added hydrogen ions of the titration acid. The term HSO_4^- indeed is for the fact that some percentage of the dissolved sulphate does absorb some protons during the titration to formation of some HSO_4^- in the order of $\sim 90 \mu mol.kg^{-1}$.

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.

Answer: Next to presenting the classical Redfield-Ketchum-Richards equation we had mentioned that other such equations have since then evolved in the literature, and indeed these are not relevant to the core question. Meanwhile we found some more such equations, and these will also be duly included when revising the manuscript. However, this indeed is not the core question of the discussion paper.

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: $\text{HCO}_3^- \rightleftharpoons \text{CO}_3^{2-} + \text{H}^+$. 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 ($\text{CO}_2(\text{aq})$, 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.

Answer: Indeed, the short-cut conceptual explanation will be deleted. The reaction by which the conversion occurs is: $\text{HCO}_3^- \rightleftharpoons \text{CO}_3^{2-} + \text{H}^+$ and was given in the equation 11 of the discussion paper, yet later on the H^+ was overlooked.

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.

Answer: For such valid mechanism that charge balance is not always maintained by H^+ , one may be interested to see the Table 3 of Goldman and Brewer (1976) where the hypothesis of indeed Na^+ is mentioned, as alternative to H^+ . We intend to mention this in the revised version of the manuscript.

References

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