

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*"

Specific Responses

Below we have copied all comments of the reviewer, and below each comment/correction have written our response in italic print.

I do not feel that this manuscript should be published in its present form. It aims to resolve confusion in the literature, but although it does draw attention to potentially confusing aspects in our present-day description of the total alkalinity of seawater, it does not (I feel) resolve anything particularly clearly. Furthermore, I feel that the presentation suggests that the authors do not fully understand the concept of alkalinity in solutions such as seawater as it has already been presented in the literature.

Agree. On the basis of five received reviews and comments, and further reading in the literature, we now in retrospect realize several misunderstandings in our discussion paper. We will restructure the manuscript and include all comments and suggestions by the referees and commenters. We feel that there are enough confusing aspects on the alkalinity concept left to warrant the publication of our manuscript.

The authors are correct in noting that the importance of seawater alkalinity lies in the belief that it is a measurable parameter of the seawater acid-base system which, when expressed in micromoles per kilogram of seawater, is a conservative variable both on mixing and for changes in temperature and/or pressure. Changes in total alkalinity in the oceans result predominantly as a result of a variety of biogeochemical processes that affect the acid-base composition of the seawater itself. However, its value is not affected by the exchange of carbon dioxide gas between seawater and the atmosphere. Measurements of total alkalinity can thus be used to help study these biogeochemical processes, and can also be used to help calculate the state of the seawater acid-base system.

We fully agree and explain and discuss this in our manuscript.

However, the authors do not seem to comprehend (or at least do not discuss here) quite why it is that total alkalinity – a weighted sum of the amount contents of various base and acid species, see their eqn (24) – does indeed remain constant even when the various acid-dissociation constants are themselves changed by a change of temperature and pressure. Hence, every term in eqn (24) changes value with a change in temperature and/or pressure, but the particular weighted sum defined as total alkalinity does not. Nor do they seem to ask themselves why when carbon dioxide gas is added to seawater (the process of ocean acidification) and the pH changes, again every term in eqn (24) changes in value but still this particular weighted sum does not.

We certainly agree with this. Otherwise our discussion paper did NOT aim to discuss or explain that alkalinity remains constant. Similarly the discussion paper did NOT aim to discuss or explain the changes in relation to changes (increases) of DIC due to addition of carbon dioxide gas to seawater. In the introduction this was merely mentioned as to support why the discussion paper focusing on Alkalinity is of wider relevance for the world oceans,

for the precious planet and for human society at large. Otherwise in next further working on the necessary major revisions, we will make an effort to also mention these above suggested considerations.

The paper of Wolf-Gladrow et al. (2007) spends some considerable effort to point out that these phenomena are a consequence of the expression for total alkalinity – eqn (24) in this manuscript – being necessarily consistent with the charge balance expression for a seawater of known composition, and furthermore it is identical in value to a quantity Wolf-Gladrow et al. (2007) refer to as the explicitly conservative form of total alkalinity (insofar as it is a sum of terms that are themselves individually conservative). Sadly, the authors (despite many citations of this 2007 paper in this manuscript including a discussion in their §5.1) do not seem to have fully adsorbed this concept (see e.g. lines 1020–1021 where they fail to recognize this identity). Nor do they grasp its application to understanding how a particular biogeochemical process occurring in seawater can change the alkalinity of the seawater where it occurs.

The authors appear to view this latter question as a purely empirical concept, rather than one that can – in principle – be inferred from a mechanistic understanding of alkalinity. If one adopts the view described by Wolf-Gladrow et al. it is simple to view a change in seawater alkalinity as being a consequence of a flux of constituents between the seawater and another phase.

Agree in general. Given the above mentioned now realized academic freedom of speech, in retrospect any view or definition(s) on Alkalinity in any published article is fine. Therefore, in retrospect the Wolf-Gladrow et al. (2007) approach is just fine.

Otherwise, after reading the interesting article of Fraga and Alvarez-Salgado (2005), it is now realized that the Wolf-Gladrow et al. (2007) article is based on the approach and definitions of Dickson (1981), that in itself is based on two arbitrarily established inherent assumptions. Moreover, Wolf-Gladrow et al. (2007) do add a third inherent assumption of the nutrient- H^+ -compensation principle.

Quite interestingly, Fraga and Alvarez-Salgado (2005), do give much credit to the Dickson (1981) article, yet eventually choose to use the definition of Millero et al. (1995) instead of the Total Alkalinity definition after Dickson (1981). Presumably, by this choice, Fraga and Alvarez-Salgado (2005) did avoid the need to invoke inherent assumptions.

Such a flux must necessarily be charge-balanced, otherwise significant energy would be required for any macroscopic separation of charges.

For example, in the case of a micro-organism assimilating nitrate ion from the surrounding seawater (discussed in this manuscript), it is perhaps not apparent that uptake of an ion that itself is not involved in the acid-base chemistry of seawater can affect the total alkalinity, yet it does. The reason for this is that such a flux cannot take place in isolation, it is necessary (so as to ensure charge balance) that a cation be co-transported into the cell together with the nitrate anions (or an anion be exported). An empirical study (Brewer and Goldman, 1976) showed both that alkalinity increased on the uptake of nitrate (as would be expected if the co-transported ion was hydrogen ion – however, they explicitly suggested that OH^- was being excreted to achieve charge balance) and that the cellular content of cations such as Na^+ did not; the observed increase in alkalinity approximately corresponded to the decrease in nitrate ion. Over the years it has been shown that H^+ - transporter channels are very common in cell

membranes and have also been shown to be associated with nitrate uptake channels in a number of species.

Wolf-Gladrow et al. therefore assumed that such “proton pumps” would be ubiquitous (their §5.2) as they felt that pumping Na⁺ (for example) would lead to an excess building up in the cell. They then pointed out that a loss of nitrate ion from the seawater would increase their explicitly conservative form of total alkalinity (and thus, of course, the measurable total alkalinity).

All the above is very interesting, and given the now realization that every author(s) has the academic freedom of speech, we no longer have problems with the approach of Wolf-Gladrow et al. (2007). This being stated, we do not necessarily fully understand all of the above comments of reviewer Dickson, nor all of the inner workings of the Wolf-Gladrow et al. (2007) article. The treatise of Fraga and Alvarez-Salgado (2005) of such issues, however, does seem to clarify many aspects.

The authors however do not seem comfortable with generalizing this concept to discuss the uptake of inorganic phosphate by a photosynthesizing organism in seawater.

Indeed.

Wolf-Gladrow et al. (again assuming the effect of H⁺-transporter channels) point out that removal of any form of inorganic phosphate will have the same net effect, an increase of total alkalinity that is equivalent to the amount of phosphate removed (their §5.4). The authors deny that this is so without themselves providing a clear mechanism to address the need for charge balance.

My own view is presently more agnostic. A brief examination of the literature when preparing this review showed that transporter mechanisms exist to take up ionic forms of phosphate, and that either hydrogen ions or sodium ions can be co-transported to achieve charge balance (both systems have been observed) thus it is possible that on uptake of inorganic phosphate alkalinity might increase (for hydrogen ion uptake), or it could either not change or even decrease (for sodium ion uptake) – see the table below.

Net effect on the alkalinity of a seawater resulting from the uptake of n mol of inorganic phosphate depends on the cation that is co-transported. (Estimated from the *explicitly conservative form of total alkalinity*.)

| species | ΔA_T /mol when H ⁺ co-transported | ΔA_T /mol when Na ⁺ co-transported |
|---|--|---|
| H ₃ PO ₄ | + n | + n |
| H ₂ PO ₄ ⁻ | + n | 0 |
| HPO ₄ ²⁻ | + n | - n |
| PO ₄ ³⁻ | + n | - 2 n |

All this is very interesting. However given our background and perspective on the basis of measuring and interpreting dissolved constituents of seawater, we are not familiar with the above and by Wolf-Gladrow et al (2007) given considerations from the viewpoint of the functioning of a phytoplankton cell, here notably the functioning of transporter mechanisms across the cell wall for transport to and from the ambient seawater.

Given our background, we may be able to produce a significantly revised and improved manuscript that is based on treating Alkalinity from the realm and viewpoint of dissolved constituents in seawater.

Nevertheless, the authors are (as far as I know) correct in suggesting that in an oceanic environment with an assemblage of varying phytoplankton species we do not, as yet, know the quantitative effect on alkalinity of the uptake of inorganic phosphate.

Agree

The authors' discussion of sulfate uptake by phytoplankton is similarly confused. They again cite absence of evidence as indicative that there is inherently no effect, whereas two facts belie this: first there is clear evidence for sulfur as a constituent of at least some phytoplankton, even to the extent of showing up in average compositions for natural samples (see e.g. Hedges et al., 2002) as well as in particular phytoplankton species (e.g. those that can produce DMSP, DMSO, and DMS); second if sulfur is taken into phytoplankton cells from the surrounding seawater then it is almost certainly in an anionic form, and there will be a need for another ion to be transported either in or out of the cell to ensure charge balance. It is this co-transport that likely affects alkalinity, albeit immeasurably.

Indeed, due to the very high background concentration of dissolved sulphate, it is impossible to detect in the dissolved sulphate concentration any effect of uptake/release of sulphate. This is very different from the utilization of C, N and P by phytoplankton, where the dissolved tracers do provide an approach to verification if not even quantification.

Our lack of enthusiasm for including sulphate uptake/release as a nutrient element of plankton is because this cannot be quantified/verified versus a dissolved tracer, this due to the very high background concentration of sulphate obscuring any such effects. This is in contrast with uptake/release of nitrate or phosphate that can be verified versus their dissolved tracer concentrations. In the end our approach in the manuscript boils down to the fact that we are observationalists and to the principle that we include those species that can be measured to a significant level. This is opposite to the theoretical treatise of alkalinity as done in Wolf-Gladrow et al. and the comments by the referee. We will make this more clear in the revised manuscript.

It is, I feel this lack of appreciation of the tight link between charge balance and total alkalinity that guides them in their other discussion of a potentially confusing issue.

Agree. We should have and will from now on take into account the charge balance considerations.

How is it most helpful to simplify the expression for alkalinity that was promulgated by Dickson (1981)? A difficulty with both the Dickson and Wolf-Gladrow et al. approaches is that they assume that we know a priori all the acid-base systems that will be in a particular seawater. Even when we restrict ourselves to considering inorganic acid-base systems in either oxic (or anoxic) seawater, it is clearly appropriate to recognize that there are probably acid-base systems present at such low levels that they do not contribute meaningfully to the alkalinity of a particular sample.

Agree. This is exactly the right argument for our approach to only include those species that contribute significantly.

A suitable touchstone is likely related to the repeatability of the usual alkalinity titration method, but this varies from lab to lab with the lowest value with current equipment being $\sim 0.5 \mu\text{mol kg}^{-1}$; the authors assume a value three times this (but refer to it as an accuracy – line 215). My own preference would be significantly smaller even than this number, perhaps 150 nmol kg^{-1} . This choice for oxygenated seawaters essentially removes the majority of potential inorganic acid- base systems, leaving the carbonate system, the borate system, the water system, the silicate system, and the orthophosphate system

In the discussion paper was chosen a reproducibility of $\sim 1.5 \mu\text{mol kg}^{-1}$. In doing the revisions we have now lowered this somewhat to $\sim 1\text{--}1.5 \mu\text{mol kg}^{-1}$. Please be aware that two of the three authors still regularly go out to sea and make these alkalinity titration measurements, and in context of international programmes do communicate regularly with other colleagues doing alkalinity titrations.

As the referee mentions, this reproducibility varies from lab to lab with the lowest value with current equipment being $\sim 0.5 \mu\text{mol kg}^{-1}$. Given latter sentence, a 'typical' reproducibility of $\sim 1\text{--}1.5 \mu\text{mol kg}^{-1}$ would be quite representative. The own preference of the referee of perhaps $150 \text{ nmol kg}^{-1} = 0.15 \mu\text{mol kg}^{-1}$ is understood to be a wish of the referee for the future, rather than already a reality today. On the other hand, in case this $0.15 \mu\text{mol kg}^{-1}$ is already reality today than please let us know.

Anyway, in the revised manuscript we can easily add some text paragraph on such improved reproducibilities $\sim 0.5 \mu\text{mol kg}^{-1}$ or even $0.15 \mu\text{mol kg}^{-1}$ and briefly discuss their implications for perhaps the need to include one or more extra acid/base systems.

(of course, the ammonia system and the nitrite system may also be above this level in certain oceanic samples where nitrogen redox processes are occurring).

In order to keep the discussion paper concise and relatively simple it was in principle restricted to well oxygenated seawater, where the ammonia system and the nitrite system would not play a role. Nevertheless, there was a separate section on these reduced constituents. In general these two systems of ammonia and nitrite are not a problem, except perhaps that the nitrite effect on alkalinity is deemed to be less than the reproducibility of titration of alkalinity. In the revised manuscript we will now also mention what the implications would be when assuming (see above) a tenfold improved reproducibility at $\sim 0.15 \mu\text{mol kg}^{-1}$ that would imply a significant effect of nitrite, when the latter nitrite is present in the seawater sample.

The orthophosphate system has certainly been responsible for some confusion. It used to be common to write the orthophosphate contribution to alkalinity as

$$A_p^* = [\text{H}_2\text{PO}_4^-] + 2[\text{HPO}_4^{2-}] + 3[\text{PO}_4^{3-}] .$$

This was done, I suspect, by analogy with the carbonate system where the terms appear to be charge-weighted. In contrast, Dickson (1981) proposed that the appropriate alkalinity contribution would be

$$A_p = -[\text{H}_3\text{PO}_4] + [\text{HPO}_4^{2-}] + 2[\text{PO}_4^{3-}] ,$$

where $[\text{H}_2\text{PO}_4^-]$ has been chosen as the “zero level of protons”. A comparison of these shows that $A_p^* = A_p + P_T$, where P_T is the total amount content of the orthophosphate acid-base system in seawater. Nevertheless, choosing one form or the other has little practical effect for natural seawaters, for which $P_T < 4 \mu\text{mol kg}^{-1}$, as long as the definition is used consistently, both in the titration, as well as in any subsequent speciation calculations.

The authors seem to accept unquestioningly the form recommended by Dickson (A_p), but note that the negative weighting of H_3PO_4 in this expression is potentially confusing and furthermore that even at the lowest pH in an alkalinity titration the maximum value of $\text{H}_3\text{PO}_4 \sim 0.15 \mu\text{mol kg}^{-1}$ and thus can surely be neglected. Both comments are correct.

However, I believe that explicitly omitting this term is misguided. Its existence makes clear the explicit choice of $[\text{H}_2\text{PO}_4^-]$ as the “zero level of protons” for this acid-base system (omitting it might leave a novice unclear about quite how the chosen weightings for orthophosphate species in the alkalinity expression occur). As I note above, I believe that it is clearer yet to explicitly omit consideration of entire acid-base systems when their total amount content is below a specified threshold rather than to omit an individual species from the alkalinity expression.

Agree. In this case, yes indeed either omit all four phosphate species, or include all four phosphate species. While the overall effect of the four phosphate species on alkalinity is relatively small, it happens to be just about significant versus an assumed reproducibility of some $\sim 1\text{--}1.5 \mu\text{mol kg}^{-1}$ (or even better $0.15 \mu\text{mol kg}^{-1}$) for the titration of alkalinity.

Furthermore, I would note that without that species (and its sign) explicitly in the expression for total alkalinity it is not as obvious that adding phosphoric acid to a seawater does reduce the alkalinity by an equivalent amount (the opposite of the discussion above for uptake of phosphate species) as is, of course, suggested by the sign.

Agree that phosphate does belong to the definition of total alkalinity.

There are many aspects of this manuscript that I feel are not necessary; others I found confusingly expressed (for example the putative benefits of what they call Oceanic Alkalinity, and how it varies from the concept described by Soetart et al. 2007 and Middelburg, 2020 – which was not mentioned); there are also some egregious typos). I do not discuss any of these here (in this already rather long review).

In doing the revisions we will better define Oceanic Alkalinity that is more or less the same as charge balance alkalinity by Middelburg et al. (2020). On the one hand perhaps one could do without this concept and describe only the Alkalinity as obtained by acid titration. On the other hand the Oceanic Alkalinity approach does exist in the literature, notably after Broecker and Peng (1982) and we feel this OA therefore is better also described in our manuscript.

It is the lack of appreciation for the importance of charge balance when discussing alkalinity that I found most problematic, and which I emphasize throughout this review.

Agree and we will in doing the revisions give more appreciation for the importance of charge balance.