

Response to comments of Prof. Middelburg

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.

De Baar and co-workers identified some confusion in the literature regarding alkalinity. Although de Baar et al. resolved some of the confusion, they might have misunderstood, or at least they appear to have miscommunicated, some of theoretical underpinnings. This comment aims to resolve some of issues identified.

Indeed, due to the comments of five colleagues, and further reading in the literature, it is now realized that our discussion paper did comprise several of our misunderstandings. These will be resolved in the revised manuscript.

It is important to distinguish between (1) titration alkalinity that is quantified by titration with a strong acid, (2) total alkalinity as defined by Dickson (1981) which is based on a proton balance and (3) ocean alkalinity which is based on a charge balance concept. The latter alkalinity is also known as excess negative charge or charge balance alkalinity (e.g., Zeebe and Wolf-Gladrow, 2001; Soetaert et al., 2007).

We fully agree and will apply these in the revised manuscript.

The titration alkalinity of a solution can be quantified by recording changes in pH or E (mV) values as a function of acid added. The measured titration curve is then used to identify the equivalence point corresponding to the titration alkalinity, either by numerical differentiation (no chemical model needed), or by curve fitting or Gran plots using chemical insights.

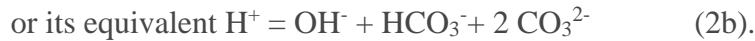
We agree. Otherwise, in our (mis)understanding for curve fitting there is also not really a chemical model needed, as to say as input into the curve fitting. Nowadays in the era with computer, as compared to what reviewer Dickson with some sense of humor defines as the BC period (Before Computers), the Gran plot approach has become obsolete. Otherwise, latter Gran plot approach of Dyrssen (1965) at that time was a major step forward, and recognized as such in text line 478 of the discussion paper as one of three benchmark articles.

The total alkalinity based on proton balances and the charge balance alkalinity is identical for some systems, but different for other systems such as seawater. To illustrate this, let us consider the system H₂O-CO₂ (the reasoning below is based on Middelburg, 2019 and Middelburg et al., 2020). This system has five unknown species (H⁺, OH⁻, CO₃²⁻, HCO₃⁻ and H₂CO₃), which are related by four relations: the self-ionisation of water, the first and second dissociation equilibria of carbonic acid and the total quantity of carbonic acid added. To solve this system with 5 unknowns and 4 relations, one needs to introduce one additional relation. There are two options: a proton balance or a charge balance.

Waters are uncharged and the positive charge of the proton should balance negative charges of hydroxide, bicarbonate and carbonate ions:



Alternatively, one can establish a proton balance given by the sum of protons released when water and carbonic acid dissociate to their equilibrium distribution (e.g., Butler, 1964):

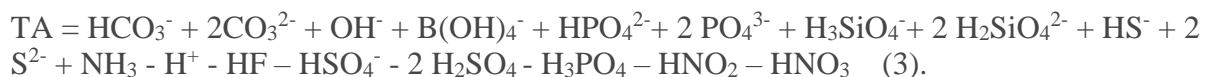


The species H_2O and H_2CO_3 are the zero level of protons for this system, with species on the left-hand side having excess protons and those on the right-hand side a deficiency in protons. The alkalinity of this system ($\text{OH}^- + \text{HCO}_3^- + 2\text{CO}_3^{2-} - \text{H}^+$) is identical irrespective whether a charge-balance or proton-balance approach is adopted. This is not necessarily the case for some more complex systems such as seawater, as will be shown below.

All agreed. On the basis of improved insights it now appears that in the case of oceanic seawater, that the charge balance description (our Oceanic Alkalinity) is not exactly the same as the Alkalinity value obtained from the acid titration method. Briefly, for (i) the HSO_4^- , (ii) the fluoride, and (iii) the phosphate species, there are differences, that quite fortunately can be quantified in an exact manner. Not surprisingly these same three constituents are the so-called proton donors as defined by Dickson et al. (1981).

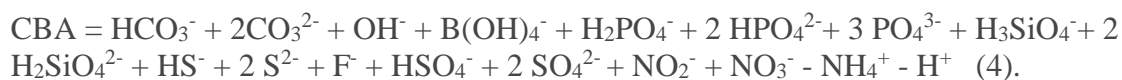
Dickson (1981) defined the alkalinity (TA) as follows: “The total alkalinity of a natural water is thus defined as the number of moles of hydrogen ion equivalent to the excess of proton acceptors (bases formed from weak acids with a dissociation constant $K \leq 10^{-4.5}$ and zero ionic strength) over proton donors (acids with $K > 10^{-4.5}$) in one kilogram of sample”.

Dickson’s TA is based on a proton balance approach and a well-defined zero level of protons ($\text{pK}=4.5$). For seawater containing carbonic acid, borate, phosphate, silicate, ammonia, hydrogen sulfide, fluoride, sulfate, nitrate and nitrite, the TA would then read:



Note that this equation lacks the species serving as zero-level of protons (the dominant species at $\text{pH}=4.5$: H_2CO_3 , $\text{B}(\text{OH})_3$, H_2PO_4^- , H_4SiO_4 , H_2S , NH_4^+ , F^- , SO_4^{2-} , NO_2^- and NO_3^-). The sign is positive for all species deficient in protons relative to the reference species and negative for those having more protons than the reference species. Using Dickson’s rationale, this equation can be easily extended provided the pK values of the additional components are known.

The charge balance alkalinity (or excess negative charge or ocean alkalinity) for the very same system would read (Soetaert et al, 2007):



It is evident that the proton-balance or total alkalinity (eq. 3) and charge-balance alkalinity (eq. 4) are different for ocean water (Zeebe and Wolf-Gladrow, 2001; Middelburg, 2019; Middelburg et al., 2020). Specifically,

$$\text{TA} = \text{CBA} + \sum \text{NH}_3 - \sum \text{NO}_3 - \sum \text{NO}_2 - \sum \text{PO}_4 - 2\sum \text{SO}_4 - \sum \text{F} \quad (5)$$

in which the \sum refers to the total concentrations of ammonia, nitrate, nitrite, phosphate, sulfate, and fluoride species, respectively. This difference is caused by the charge of the components at the zero-proton level of Dickson's TA definition (e.g., H_2PO_4^- , F^- , NH_4^+ , SO_4^{2-} , NO_2^- and NO_3^-). Consequently, acid-base systems that are uncharged at $\text{pK}=4.5$ (e.g., borate, silicate, and hydrogen sulfide) do not contribute to this difference.

We agree with all the above. Otherwise, from further reading, notably the article of Fraga and Alvarez-Salgado (2005), it is now realized that the approach and definitions of Dickson et al. (1981) are based on two arbitrarily established inherent assumptions. For details on this notion of Fraga and Alvarez-Salgado (2005), see our response to Fiz Perez. To keep this response within reasonable limits we have refrained from here copying such paragraphs from our response to Fiz Perez. Otherwise, as a matter of fact, these two assumptions are hard to understand and indeed have led to confusion on our discussion paper and probably within parts of the community of biogeochemists.

It appears that most confusion on seawater alkalinity is related to (1) neglecting the difference between CBA and TA and (2) incomplete understanding of the zero-proton level concept underlying Dickson's TA. The discussion paper by De Baar et al. is an example showing these confusions.

To keep this comment within reasonable limits, the focus will be on phosphate. At $\text{pH}=4.5$, H_2PO_4^- dominates dissolved phosphate speciation and is the adopted zero-proton level; this implies that H_3PO_4 should come with a negative sign in the TA equation and that one HPO_4^{2-} and two PO_4^{3-} (with positive signs) should be included. De Baar et al.'s suggestion to omit H_3PO_4 is based on a misunderstanding of the zero-proton level concept.

They also argue that phosphate uptake or release by organisms can be ignored. This misconception appears to be related to their unclear distinction between TA and CBA. Any process (biological or chemical involving phase transfer, e.g. primary production, mineral formation/dissolution) that releases/removes nitrite, nitrate, phosphate, sulfate or fluoride does impact alkalinity because charge must be conserved.

Agree. Otherwise, now, after all the five constructive comments, and further literature, we still experience this adopted zero-proton level to be very confusing. The same for the assumption of proton donors in relation to its K value of $10^{-4.5}$ criterion. Our revised manuscript shall point this out and we think it is useful to clarify this once and for all.

Butler, J.N. (1964) Solubility and pH Calculations. Reading Mass: Addison-Wesley Publishing Company Inc.

Dickson, A. G. (1981), An exact definition of total alkalinity and a procedure for the estimation of alkalinity and total inorganic carbon from titration data, Deep Sea Res. Part A, 28, 609– 623, doi:10.1016/0198-0149(81)90121-7.

Middelburg, J.J., (2019) Marine Carbon Biogeochemistry. A primer for Earth System scientists. Springer Verlag.

Middelburg, J. J., Soetaert, K., & Hagens, M. (2020). Ocean alkalinity, buffering and biogeochemical processes. *Reviews of Geophysics*, 58, e2019RG000681.
<https://doi.org/10.1029/2019RG000681>

Soetaert, K., Hofmann, A. F., Middelburg, J. J., Meysman, F. J. R., & Greenwood, J. (2007), The effect of biogeochemical processes on pH, *Mar. Chem.*, 105, 30– 51, doi:10.1016/j.marchem.2006.12.012.

Zeebe, R. E., & Wolf-Gladrow, D. (2001), *CO₂ in Seawater: Equilibrium, Kinetics, Isotopes*, Elsevier Oceanography Series, 360 pp., Elsevier Science B.V.

The above citations Middelburg (2019) Middelburg et al. (2020), Soetaert et al. (2007) are available to us and surely will further be taken into account. For example, the Soetart et al. (2007) is now mentioned in our response to Fiz Perez.