

Response to Prof. Wolf-Gladrow, Dr. Klaas, Dr. Zeebe

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

Therefore we now are quite busy making major revisions to our discussion paper towards the revised version to be re-submitted and published as a regular article in the Ocean Science journal. Meanwhile we also are 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 (1) commonly agreed exact definition of alkalinity.

Next Prof. Middelburg promptly by email did send to us his article by Middelburg et al. (2020) and from this, and the further information provided by him, all of us did learn and come to realize that in fact there are several definitions 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 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. At least for us, authors of the discussion paper, this surely is a paradigm shift, attributed to the article of Middelburg et al. (2020).

Next, we may, or may not, soon observe, the classical response of the scientific community, after Kuhn (1962). Briefly, after such paradigm shift or scientific revolution, (almost) everyone states that, yes, he/she knew this for a long time, has always stated this. In this case, some or several of ocean chemist 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). The latter case I had studied in 1977 for a term paper in context of a PhD route, where before this revolution (almost) all geoscientists did firmly reject\*, and after the revolution (almost) all did state they had always known this.

The three authors of the discussion paper together have done more than 80 years working in chemical oceanography, each with considerable experience in measuring alkalinity, yet only now have learned that there is a difference between Ocean Alkalinity (charge balance alkalinity) and the analytical value obtained by acid titration. If nothing else, this illustrates that alkalinity of seawater is (i) either a difficult concept, or (ii) not well explained in the literature, or a combination of these two obstacles. The alternative explanation would be that all three of us are dummies and/or lay people, but that would be too easy conclusions for assessing three people each holding a PhD in chemical oceanography.

\*) 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 found at least 20 different definitions of alkalinity!" Ernst Maier-Reimer (1990ies)

*This statement was already known from the book by Zeebe and Wolf-Gladrow (2001), yet there anonymous, now nice to know this was made by the late Ernst Maier-Reimer.*

"...alkalinity, one of the most central but perhaps not the best understood concept in aquatic chemistry." Morel and Hering (1993, p.157)

*We will now also carefully read their description of alkalinity. This is towards our own improved understanding.*

Several pertinent and insightful comments (reviews by Fiz Perez and Andrew Dickson, comments by Matthew Humphreys and Jack Middleburg) on the paper by deBaar et al. have been already posted and thus we will add only a few, mostly complementary, remarks.

*The above mentioned other comments have now been complemented by our responses. Given the deadline for these responses, more time is needed to further study the subject, and meanwhile do the necessary major revisions of the manuscript to be transformed from a discussion paper into a final article.*

In the literature different definitions of alkalinity are found and it can be confusing to relate them to each other. Some of the expressions for alkalinity are just approximations to more exact expressions and these approximations were convenient before (personal) computers and easy-to-use software for the calculation of carbonate system components were available. Also, to obtain insight into various relationships and processes and for teaching it is still useful to apply approximations that allow derivation of analytical results (compare, for example, Broecker & Peng, Tracers in the Sea, 1982).

*Yes, on the one hand Broecker & Peng, Tracers in the Sea (1982) did here and there, presumably for educational purposes, apply approximations (simplifications). On the other hand, it is our impression that since then several authors have in their articles ascribed more such approximations than actually is written in print in that textbook. This also applies when in one part of the book a simplified approach is taken by ignoring some constituents of overall alkalinity, whereas elsewhere in the textbook the role of one of such, in one place omitted, constituent, is mentioned and explained.*

For the *definition* of alkalinity (and *expressions* are consequences of definitions) there are at least two starting points:

1. **Titration alkalinity** as developed over many decades: from recognizing peculiar response of seawater to addition of strong acids in the 19th century, the notion of proton acceptors by Rakestraw (1949), Dyrssen & Sillén (1967), among others, to the currently most exact and widely accepted definition by Dickson (1981). The development of the alkalinity concept in marine chemistry has been described in detail by Dickson (1992). Titration alkalinity is a quantity that *can be measured* by titration.

*Agree, and in the discussion paper some of the above historical developments were also mentioned, yet largely by merely referring indeed to Dickson (1992). Otherwise it is now realized that Total Alkalinity of Dickson (1981), is not exactly the same as the value that one obtains by acid titration of a seawater sample. When considering only the good old major constituents, there is agreement. However, for the full equation of Total Alkalinity (Dickson, 1981) there are differences. Thus far such differences have hardly been realized, if at all; even the recent article of Middelburg et al. (2020) is not always making a clear distinction, yet the recent comment of Middelburg on our discussion paper does point this out. This in turn did make us think about this, to be studied and reflected on further towards a correct and clear wording in the revised manuscript now in preparation.*

2. **The separation into strong ('fully dissociated') and weak ions (e.g., de Baar et al., Eqs. 18 and 19).** This approach has been used by Broecker & Peng (1982) and has influenced many colleagues especially in (bio)geochemistry. Broecker & Peng were champions of approximate expressions (compare Box further below) for alkalinity that allowed valid insight to geochemical and biogeochemical processes.

*See above response that perhaps Broecker and Peng (1982) did not apply as many approximate expressions as some colleagues have suggested afterwards.*

Such approximations were still in use when computer power and software was no longer limiting calculations of carbonate system components anymore (compare, for example, Sarmiento & Gruber, 2006).

*Some approximations may, or may not, have remained in use for educational purposes. Sarmiento and Gruber (2006) in their excellent textbook that in several aspects is an improved successor of Broecker and Peng (1982), and indeed relying more on results based on computer power by others or themselves, are mentioning alkalinity in many text parts at many different pages.*

*On the other hand, in their description of Alkalinity (their pages 323 and beyond), there is simplification by using a criterion that the contributions of minor constituents are usually well below one percent, and therefore neglected. This can be seen in their equation 8.2.8. that*

merely mentions "minor bases" and in the subsequent text is defined to be "total alkalinity" that is operationally defined by titration (see Dickson, 1981 for an exact definition of alkalinity). Indeed when ignoring the minor bases the total alkalinity is equal to alkalinity obtained by titration. However, today, we have become aware that, when taking into account all the minor bases, that total alkalinity is not necessarily the same as what is obtained by acid titration.

Similarly the equation (8.2.9.) that is more or less the same as what we did call Oceanic Alkalinity in our discussion paper, does merely mention "minor cations" and "minor anions".

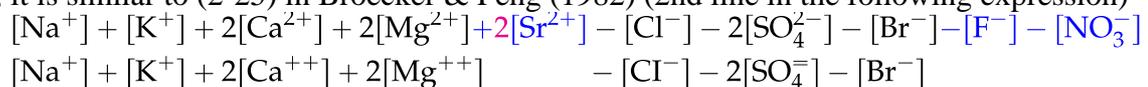
The nice thing about this approach of Sarmiento and Gruber (2006) is that, by ignoring the minor players, the Oceanic Alkalinity is the same as Total Alkalinity and the same as Titration Alkalinity. This is fine for the educational objective, and/or focusing only on the major role of alkalinity without bothering the readership with the 'ballast' of the nitty-gritty details of the minor players.

Perhaps, in retrospect, this treatment by Sarmiento and Gruber (2006) may, unconsciously and unwittingly, have led us into the mistake in the discussion paper, that Oceanic Alkalinity equals the values that is obtained by acid titration. Thanks due to the various referee comments, we now realize that there are differences between Oceanic Alkalinity, Total Alkalinity and Titration Alkalinity. Surely here "the devil is in the detail".

Otherwise, we have as yet not verified all the other mentions of alkalinity in this textbook. Perhaps some are approximations, and others are very exact thanks to computer power and software.

As a matter of fact, other textbooks also sometimes give a straightforward text, that by reading further is presumably intended as an approximation. For example, Zeebe and Wolf-Gladrow (2001) at the bottom of their page 51 mention in their item 4. as follows: Uptake of one mole of nitrate by algae ....., such that alkalinity increases by one mole (term:  $[\text{NO}_3^-]$ ). On the other hand in their Appendix C.1. at their page 280 under item 2. the uptake of one mole of phosphate is also mentioned for causing an increase of alkalinity by one mole.

The 'Oceanic Alkalinity' expression of de Baar et al. (Eq. 20) (1st line in the following expression) follows from the alkalinity definition based on the separation of strong and weak ions; it is similar to (2-25) in Broecker & Peng (1982) (2nd line in the following expression)



except for 3 additional terms (in blue) by de Baar et al. (which again shows the approximate character of the Broecker & Peng expression); an obvious typo (missing 2 in front of Sr) has been corrected.

Thanks for pointing out the obvious typo omission of missing 2 in front of Sr.

Table 2-5 at page 64 of Broecker and Peng (1982) indeed does not list strontium, fluoride and nitrate. On the other hand the role of nitrate is next treated explicitly in a paragraph in the bottom half of text at page 67. In the further text at page 68 (by way of an example) the role of nitrate is again mentioned, and in small print that explains Figure 2-9 at page 70, and Table 2-6 also includes nitrate.

Oceanic Alkalinity is not measured because the small difference between two large numbers (sum over all strong anions times their charges and sum all strong cations times their charges) yields a small difference with an unacceptable large uncertainty (de Baar, Eq. 21).

From the publications of Broecker & Peng (1982) and others (for example, Sarmiento & Gruber, 2006) as well as the current manuscript by de Baar et al. one could get the impression that alkalinity is just based on ions, i.e., on counting and adding charges, and that measured alkalinity and the alkalinity in terms of strong ions are just the two sides of the same medal. Unfortunately, things in the real world are a bit more complicated.

The fact that titration alkalinity is more than adding ion concentrations times their charges is obvious from the alkalinity expression of Dickson (1981) that is based on the concepts of proton acceptors and proton donors:

$$\begin{aligned}
 \text{TA} = & [\text{HCO}_3^-] + 2[\text{CO}_3^{2-}] + [\text{B}(\text{OH})_4^-] + [\text{OH}^-] \\
 & + [\text{HPO}_4^{2-}] + 2[\text{PO}_4^{3-}] + [\text{H}_3\text{SiO}_4^-] \\
 & + [\text{NH}_3] + [\text{HS}^-] + \dots \\
 & - [\text{H}^+] - [\text{HSO}_4^-] - [\text{HF}] - [\text{H}_3\text{PO}_4] - [\text{HNO}_2] + \dots
 \end{aligned} \tag{1}$$

(slightly revised by Dickson: the term  $[\text{S}^{2-}]$  has been dropped). At least two things are remarkable in Dickson's expression:

1. Some of the coefficients are not equal to the negative of elementary charges of the corresponding ions; for example  $2 [\text{PO}_4^{3-}]$  (instead of  $3 [\text{PO}_4^{3-}]$ ). These are *not typos*. The derivation of these coefficients is discussed at length in Wolf-Gladrow et al. (2007).
2. Neutral compounds show up!

Because of these facts, Oceanic Alkalinity and Dickson's titration alkalinity can not be consistent with each other.

*Due to the several comments and by further reading of more articles, it is now realized that Oceanic Alkalinity does not exactly agree with Total Alkalinity (Dickson, 1981) and alkalinity by titration. We account for such comments in the revised manuscript.*

Wolf-Gladrow et al. (2007) combined titration alkalinity (Dickson's definition) with overall charge balance (all ions, not only the 'strong ions').  $\text{TA}^{(ec)}$  (Eq. 32 in Wolf-Gladrow et al., 2007) is *not a new definition* because it is based on and consistent with Dickson (1981).

*From the various comments we have now become aware that alkalinity by titration is not necessarily exactly the same as Total Alkalinity (Dickson, 1981).*

*It would be nice to be informed what the meaning is of the superscript  $(ec)$  in  $\text{TA}^{(ec)}$ . Our guesses thus far have been unsuccessful.*

What came as a surprise were a few 'additional terms' as, for example, the total phosphate concentration (in addition to strong ions).

Changes of any term in  $\text{TA}^{(ec)}$  (including the 'additional terms') by biogeochemical processes will have corresponding impacts on the value of the measured titration alkalinity and consequently on other carbonate system parameters as, for example,  $[\text{CO}_2]$ . [Changes in total phosphate or total sulphate will change  \$\text{TA}^{\(ec\)}\$  and thus Dickson's titration alkalinity with consequences for other carbonate system parameters.](#)

*Admittedly, we still do not fully understand the above.*

Even if the impact of variation of phosphate or sulphate in ocean waters is often small (compared to other processes like carbonate precipitation or dissolution, nitrate uptake by phytoplankton), an exact definition of total alkalinity should be general enough to apply it other situations as, for example, in pore waters of marine sediments (sulphate reduction!) or in lab experiments with modified seawater compositions.

*Fraga and Alvarez-Salgado (2005) have, among others, extensively described the role of uptake of sulphate by phytoplankton. They also outline the organic sulfur compound DMSP that thus is produced within the plankton cell. Given the usually quite dynamic wax and wane of phytoplankton blooms, one does realize that several intracellular constituents would by rapid decomposition (grazing or otherwise) largely be returned to seawater. This would be likely for the Mg central atom of chlorophyll a, because latter chlorophyll is deemed to be quite unstable once a phytoplankton cell has died. Similarly perhaps for intracellular organic sulfur compounds that become released again in the ambient seawater and may presumably become rapidly oxidized again to dissolved sulfate. In other words, any changes in alkalinity in surface waters due to uptake of N, P, S, Mg and so forth, may perhaps in time frames of one or a few weeks become nullified again due to the rapid turnover of algal biomass in the surface water ecosystem. If so, then an alkalinity definition based on uptake by algae in surface waters, may not necessarily be general enough to also apply in notably deep waters. Now for uptake and remineralization of N and P we do have deep water tracers dissolved nitrate and phosphate, that do provide some guideline for an alkalinity equation being valid also in deep waters. For S the immense background concentration of dissolved sulphate does prevent a similar approach for assessing a general definition to be valid also in deep waters. However, we have yet to read the article of Kanamori, S., & Ikegami, H. (1982) that we were told does somehow take this sulphate effect into account.*

*Kanamori, S., & Ikegami, H. (1982). Calcium:alkalinity relationship in the North Pacific. Journal of Oceanography, 38, 57–62. <https://doi.org/10.1007/bf02110291>*

*Otherwise, after reading this 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.*

Critical technical comments (mainly with respect to Wolf-Gladrow et al., 2007):

(1) The main misunderstanding in the de Baar et al. manuscript concerns Eq. 31 of Wolf-Gladrow et al. (2007) identical to Eq. 43 here (except ellipses are missing): These equations **DO NOT** describe the explicit conservative expression for total alkalinity! As clearly stated by Wolf-Gladrow et al. (2007), they describe the overall charge balance, i.e. the sum of *all* ions times their charges (compare also with Eq. 30 in Wolf-Gladrow et al., 2007). Hence, they **DO NOT** contain any electrically neutral compounds.

*This we have now noted. Otherwise in now doing major revisions for transforming the discussion paper into a regular article, the Wolf-Gladrow et al. (2007) article would be mentioned only briefly without such details as were in the discussion paper.*

(2) The explicit expression of TA in Wolf-Gladrow et al. (2007) is derived by combining the overall charge balance (Eq. 31, Wolf-Gladrow et al., 2007) with Dickson's titration alkalinity (Eq. 28 in Wolf-Gladrow et al., 2007; slightly modified compared to the 1981 version).

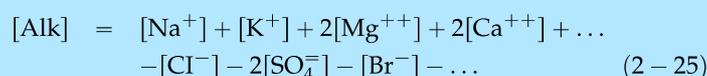
(3) In contrast, de Baar et al. combine their Oceanic Alkalinity (Eq. 20) with Dickson's titration alkalinity (Eq. 24 in this manuscript; original version from 1981). Thus it is not surprising, that equations 43 and 44 in this manuscript differ from each other, mainly because Oceanic Alkalinity (Eq. 20) is different from the overall charge balance (Eq.43).

*Agree, from the several comments received on the discussion paper we now realize that Oceanic Alkalinity is different.*

1: Excursus (introduction of alkalinity in Broecker & Peng, 1982, p. 67)



where Alk is the alkalinity of the water (that is, the excess positive charge to be balanced by  $\text{CO}_3^{2-}$  and  $\text{HCO}_3^-$  ions). The alkalinity is given by:



Obviously, the authors were aware that these expressions are approximations only, as, for example, the contribution of borate is obviously missing when they first defined alkalinity on p. 67; it was added in a later chapter. The main interest of Broecker & Peng in that chapter was to study the impact of  $\text{CaCO}_3$  precipitation or dissolution on the marine carbonate system (the right-hand side of 2-24 is called 'carbonate alkalinity'). The expressions were introduced as theoretical constructs to address these questions and not to provide an exact definition of total alkalinity or to guide measurements of alkalinity. The article of Dickson (1981) is not cited in Broecker & Peng (1982) which could be explained by the proximity of the publication dates.

*Indeed these equations (2-24) and (2-25) of Broecker and Peng (1982) were not complete omitting some other constituents which presumably were not needed to make the arguments in their text.*

*Whether or not at the time, Broecker and Peng (1982) were aware of the Dickson (1981) article, we will never know because the late Broecker is not with us anymore. Otherwise another referee did comment that one should not make interpretations about the knowledge and intentions of Broecker and Peng (1982). This was on another issue of alkalinity, yet one does not know why Dickson (1981) is not mentioned in the textbook of Broecker and Peng (1982).*