



EGUsphere, community comment CC1  
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## **Comment on egusphere-2022-676: Seawater alkalinity: less confusion than argued by de Baar et al.**

Jack Middelburg

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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-CC1>, 2022

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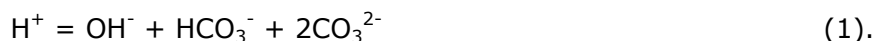
De Baar and co-workers identified some confusion in the literature regarding alkalinity. Although de Baar et al. resolved some of the confusion, they might have misunderstood, or at least they appear to have miscommunicated, some of theoretical underpinnings. This comment aims to resolve some of issues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

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).

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.

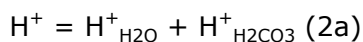
The total alkalinity based on proton balances and the charge balance alkalinity is identical for some systems, but different for other systems such as seawater. To illustrate this, let us consider the system H<sub>2</sub>O-CO<sub>2</sub> (the reasoning below is based on Middelburg, 2019 and Middelburg et al., 2020). This system has five unknown species (H<sup>+</sup>, OH<sup>-</sup>, CO<sub>3</sub><sup>2-</sup>, HCO<sub>3</sub><sup>-</sup> and H<sub>2</sub>CO<sub>3</sub>), 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,

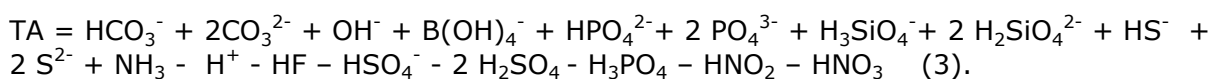
1964):



or its equivalent  $H^+ = OH^- + HCO_3^- + 2 CO_3^{2-}$  (2b).

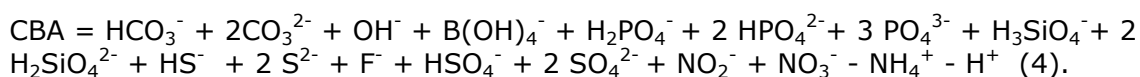
The species  $H_2O$  and  $H_2CO_3$  are the zero level of protons for this system, with species on the left-hand side having excess protons and those on the right-hand side a deficiency in protons. The alkalinity of this system ( $OH^- + HCO_3^- + 2CO_3^{2-} - H^+$ ) is identical irrespective whether 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.

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 ( $pK=4.5$ ). For seawater containing carbonic acid, borate, phosphate, silicate, ammonia, hydrogen sulfide, fluoride, sulfate, nitrate and nitrite, the TA would then read:

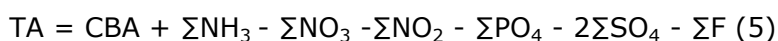


Note that this equation lacks the species serving as zero-level of protons (the dominant species at  $pH=4.5$ :  $H_2CO_3$ ,  $B(OH)_3$ ,  $H_2PO_4^-$ ,  $H_4SiO_4$ ,  $H_2S$ ,  $NH_4^+$ ,  $F^-$ ,  $SO_4^{2-}$ ,  $NO_2^-$  and  $NO_3^-$ ). The sign is positive for all species deficient in protons relative 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,



in which the  $\Sigma$  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  $pK=4.5$  (e.g., borate, silicate, and hydrogen sulfide) do not contribute to this difference.

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 pH=4.5,  $\text{H}_2\text{PO}_4^-$  dominates dissolved phosphate speciation and is the adopted zero-proton level; this implies that  $\text{H}_3\text{PO}_4$  should come with a negative sign in the TA equation and that one  $\text{HPO}_4^{2-}$  and two  $\text{PO}_4^{3-}$  (with positive signs) should be included. De Baar et al.'s suggestion to omit  $\text{H}_3\text{PO}_4$  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.

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