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

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

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.

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).

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.

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. 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).

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)

$$
\begin{array}{l}
[\mathrm{Na^+}] + [\mathrm{K^+}] + 2[\mathrm{Ca^{2+}}] + 2[\mathrm{Mg^{2+}}] + 2[\mathrm{Sr^{2+}}] - [\mathrm{Cl^-}] - 2[\mathrm{SO_4^{2-}}] - [\mathrm{Br^-}] - [\mathrm{F^-}] - [\mathrm{NO_3^-}] \\
[\mathrm{Na^+}] + [\mathrm{K^+}] + 2[\mathrm{Ca^{++}}] + 2[\mathrm{Mg^{++}}] \qquad\qquad - [\mathrm{Cl^-}] - 2[\mathrm{SO_4^{=}}] - [\mathrm{Br^-}]
\end{array}
$$

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

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:

$$\begin{aligned} \mathrm{TA} \;=\; & [\mathrm{HCO_3^-}] + 2[\mathrm{CO_3^{2-}}] + [\mathrm{B(OH)_4^-}] + [\mathrm{OH^-}] \\ & + [\mathrm{HPO_4^{2-}}] + 2[\mathrm{PO_4^{3-}}] + [\mathrm{H_3SiO_4^-}] \\ & + [\mathrm{NH_3}] + [\mathrm{HS^-}] + \ldots \\ & - [\mathrm{H^+}] - [\mathrm{HSO_4^-}] - [\mathrm{HF}] - [\mathrm{H_3PO_4}] - [\mathrm{HNO_2}] + \ldots \end{aligned} \qquad (1)$$

(slightly revised by Dickson: the term $[\mathrm{S^{2-}}]$ 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 $[\mathrm{PO_4^{3-}}]$ (instead of 3 $[\mathrm{PO_4^{3-}}]$). 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.

Wolf-Gladrow et al. (2007) combined titration alkalinity (Dickson's definition) with overall charge balance (all ions, not only the 'strong ions'). $\mathrm{TA^{(ec)}}$ (Eq. 32 in Wolf-Gladrow et al., 2007) is *not a new definition* because it is based on and consistent with Dickson (1981). 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 $\mathrm{TA^{(ec)}}$ (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, $[\mathrm{CO_2}]$. Changes in total phosphate or total sulphate will change $\mathrm{TA^{(ec)}}$ and thus Dickson's titration alkalinity with consequences for other carbonate system parameters.

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.

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.

(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).

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

$$[\mathrm{Alk}] = [\mathrm{HCO}_3^-] + 2[\mathrm{CO}_3^{2-}] \qquad (2-24)$$

where Alk is the alkalinity of the water (that is, the excess positive charge to be balanced by CO_3^{2-} and HCO_3^- ions). The alkalinity is given by:

$$\begin{aligned}[\mathrm{Alk}] \quad = \quad & [\mathrm{Na}^+] + [\mathrm{K}^+] + 2[\mathrm{Mg}^{++}] + 2[\mathrm{Ca}^{++}] + \ldots \\ & -[\mathrm{CI}^-] - 2[\mathrm{SO}_4^=] - [\mathrm{Br}^-] - \ldots \qquad (2-25)\end{aligned}$$

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 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.

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