

Review of “*On the true and the perceived minor interactions of dissolved phosphate and dissolved sulphate and some other constituents with the Alkalinity of oceanic seawater.*”

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.

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.

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.

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. 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  $\text{OH}^-$  was being excreted to achieve charge balance) and that the cellular content of cations such as  $\text{Na}^+$  did not; the observed increase in alkalinity approximately corresponded to the decrease in nitrate ion. Over the years it has been shown that  $\text{H}^+$ -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  $\text{Na}^+$  (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).

The authors however do not seem comfortable with generalizing this concept to discuss the uptake of inorganic phosphate by a photosynthesizing organism in seawater. Wolf-Gladrow *et al.* (again assuming the effect of  $\text{H}^+$ -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	$\Delta A_T/\text{mol}$ when $\text{H}^+$ co-transported	$\Delta A_T/\text{mol}$ when $\text{Na}^+$ co-transported
$\text{H}_3\text{PO}_4$	$+n$	$+n$
$\text{H}_2\text{PO}_4^-$	$+n$	0
$\text{HPO}_4^{2-}$	$+n$	$-n$
$\text{PO}_4^{3-}$	$+n$	$-2n$

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.

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.

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. 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. 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  $150 \text{ nmol kg}^{-1}$ . 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 (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).

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  $[\text{H}_3\text{PO}_4]$  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.

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.

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).

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.



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