

The salinity normalization of marine inorganic carbon chemistry data

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[1] Normalization to a constant salinity (S) is widely used for the adjustment of marine inorganic carbon chemistry data such as total alkalinity (A_T) and total dissolved inorganic carbon (C_T). This procedure traces back to the earliest studies in marine chemistry, but ignores the influence of riverine input of alkalinity and of dissolution of biogenic carbonates in the ocean. We tested different adjustment possibilities for A_T and conclude that in most parts of the surface ocean the normalization concept does not reflect relationships which represent reality. In this paper, we propose a salinity adjustment based on a constant and region-specific term for $S = 0$, which expresses river run off, upwelling from below the lysocline, calcification, and lateral sea surface water exchange. One application of the normalization concept is its extension to A_T and also C_T predictions and implementation in models. We give a brief discussion on the usage of such extensions. **INDEX TERMS:** 4825 Oceanography: Biological and Chemical: Geochemistry; 1635 Global Change: Oceans (4203); 1724 History of Geophysics: Ocean sciences; 4806 Oceanography: Biological and Chemical: Carbon cycling. **Citation:** Friis, K., A. Körtzinger, and D. W. R. Wallace, The salinity normalization of marine inorganic carbon chemistry data, *Geophys. Res. Lett.*, 30(2), 1085, doi:10.1029/2002GL015898, 2003.

1. Introduction

[2] The importance of the marine CO_2 system for the global carbon cycle [e.g., *Bacastow and Keeling, 1973*] has motivated intense field studies of ocean inorganic carbon distribution starting with GEOSECS in 1972–73 and continuing through the 1990s [e.g., *Wallace, 2001*].

[3] Here we critically assess a widely used but potentially biasing treatment of such data: The traditional salinity normalization. This method of adjustment of marine CO_2 system parameters such as total alkalinity (A_T) and total dissolved inorganic carbon (C_T) is widely employed [e.g., *Koczy, 1956; Postma, 1964; Edmond, 1974; Brewer, 1978; Chen and Millero, 1979; Poisson and Chen, 1987; Broecker and Peng, 1992; Archer and Meier-Reimer, 1994; Bates et al., 1995; Millero et al., 1998; Lee et al., 2000*]. The traditional normalization is a simple transformation of a measured value (X) to some reference salinity based on the measured salinity (S^{ref}) (variously the mean salinity of the data in question or a salinity of 35):

$$nX = \frac{X}{S} \cdot S^{\text{ref}} \quad (1)$$

Originally the normalization was applied to A_T values only, but later it was extended to C_T [*Postma, 1964*] and calcium

concentrations [*Horibe et al., 1974*]. The great importance of the traditional normalization concept lies in its widespread applications including: (I) comparisons between samples with different salinity, (II) constructing nX -predictor equations as an empirical approach to describe the marine CO_2 system, (III) techniques used for identifying anthropogenic CO_2 , and (IV) estimates of oceanic carbon transport carried by freshwater [see review by *Robbins, 2001*]. In the following we present a geochemical aspects of the traditional salinity normalization, demonstrate its usage and shortcomings, and propose an alternative. For the evaluation of the normalization concept we concentrate on A_T as a model parameter. However our critics applies similarly to the treatment of C_T data.

2. Geochemical Aspects

[4] The key processes involved in alkalinity cycling are illustrated in Figure 1. Surface alkalinity in the ocean does not behave strictly conservatively. Within the ocean, the total alkalinity can be altered as a result of, physical 'processes involving freshwater addition (dilution) or removal (evaporation, sea-ice formation) and, biogeochemical processes'. The major (but not only) biogeochemical process that affects seawater alkalinity is the cycling of carbonate minerals. Within the ocean interior, alkalinity is strongly affected by the formation and dissolution of solid carbonate minerals both in the water column and within ocean sediments. For many studies it is desirable to characterize and quantify such

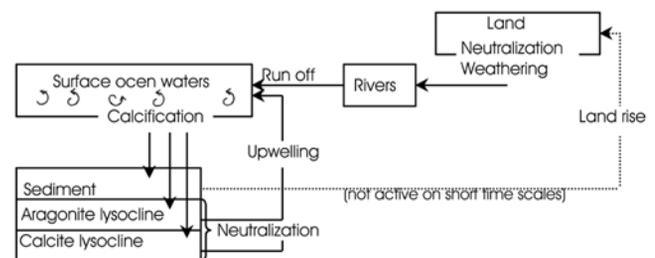


Figure 1. Schematic diagram of the relevant biogeochemical processes, that control the dissolved carbonate salt (calcium carbonate as major part) inventory of the ocean. Neutralization is the reaction of solid carbonates with carbonic acid [$\text{CaCO}_3 + \text{H}_2\text{CO}_3 \rightarrow \text{Ca}^{2+} + 2 \text{HCO}_3^-$]. In context of this diagram weathering is the reaction of silicate minerals with carbonic acid [e.g. $\text{NaCaAlSi}_x\text{O}_{(2x+3)} + 2 \text{H}_2\text{CO}_3 \rightarrow \text{NaAlSi}_x(\text{OH})_2\text{O}_{(2x+1)} + \text{Ca}^{2+} + 2 \text{HCO}_3^-$]. Alkalinity was historically explained as 'being a measure of its potential carbonate of lime' [*Dittmar, 1884*]. This interpretation has survived since the carbonate alkalinity represents the major portion (~95%) of the actual total seawater alkalinity definition.

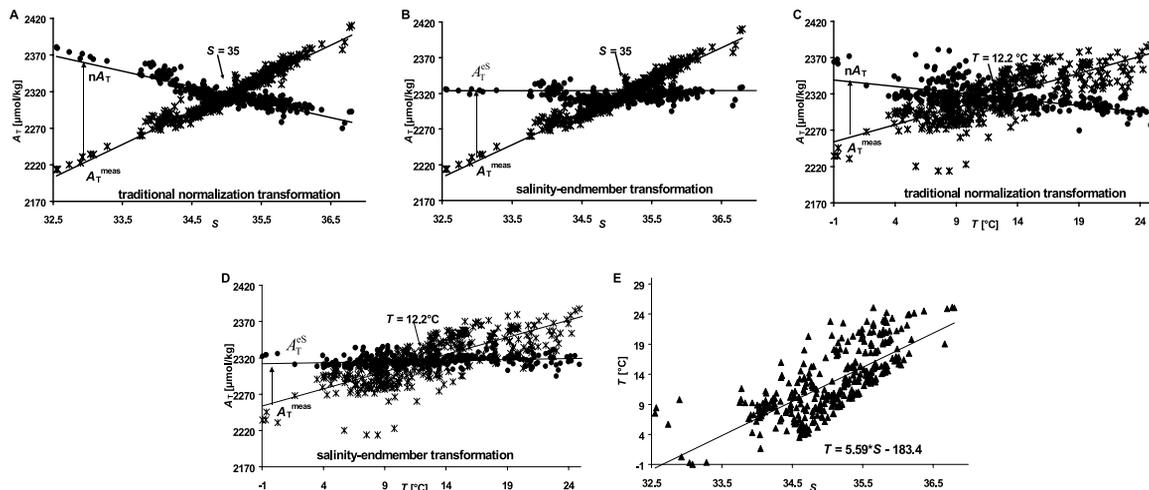


Figure 2. A–E: Relationship between alkalinity, temperature (T) and salinity (S) of the ‘combined’ data set (Atlantic between 30°S – 54°S , and north of 40°N excluding Norwegian and Greenland Sea): (A) Measured (A_T^{meas} , crosses) and conventional normalized alkalinity (nA_T , dots) versus S ; (B) Measured alkalinity (A_T^{meas} , crosses) and alkalinity normalized using equation 2, #6 (A_T^{S} , dots) versus S ; (C) A_T^{meas} and nA_T versus T ; (D) A_T^{meas} and A_T^{S} versus T , using equation 2, #6; (E) T – S correlation.

biogeochemical processes and hence some means of separating their effect from the effect of physical factors is required.

3. Data

[5] *Millero et al.* [1998] identify surface alkalinity regimes in the world ocean. In this paper we concentrate on their regimes 2 and 6 in the Atlantic, including the Labrador Sea, but excluding the regions north of the Denmark Strait and the Iceland-Scotland Ridge. Hence we combine data from the following regions ($n = 356$): SAVE (30 – 54°S , 15 – 60°W ; Takahshi pers.com.; *SAVE*, 1992), *R/V MALCOLM BALDRIGE* cruise (41 – 64°N , $\sim 20^{\circ}\text{W}$; OACES, 1997), *R/V METEOR 39* cruise (41 – 62°N , 10 – 60°W ; *Schott et al.*, 1999), and *R/V METEOR 45* cruise (41 – 65°N , 10 – 60°W ; *Schott et al.*, 2000). The accuracy is similar for all data sets with $\pm 4 \mu\text{mol/kg}$ for SAVE [*Gruber et al.*, 1996], $\pm 4.8 \mu\text{mol/kg}$ for OACES [*Castle et al.*, 1998], $\pm 3.5 \mu\text{mol/kg}$ for *METEOR 39* [*Schott et al.*, 1999] and $\pm 2.0 \mu\text{mol/kg}$ for *METEOR 45*. In order to place our results in a more global context we also make use of the eWOCE Atlas [*Schlitzer*, 2000] and data from the Bermuda Atlantic Time-series study [*Bates*, 2002]. We define surface alkalinity as the alkalinity of samples collected in the upper 50 m of the water column.

4. Relationship Between Sea Surface Alkalinity and Salinity/Temperature

[6] Based on the combined SAVE, OACES and *R/V METEOR* surface data, we examined several different linear relationships of traditionally normalized and measured A_T with temperature and/or salinity (Table 1). Relationships #2 to #4 employ A_T values that have been traditionally normalized to a constant salinity of 35. Relationships #1 and #5 to #7 use the original non-normalized A_T values. Plots of relationships #1 to #6 are shown in Figures 2A–2D.

[7] Measured alkalinity usually shows a strong salinity dependence. This is also true for traditionally normalized alkalinity (Figure 2), and this indicates immediately that there are problems with the normalization procedure. The change in sign of the slope indicates over-correction by the normalization scheme.

[8] For relationship #6 (Figure 2B) A_T data have been normalized to a salinity of 35 using a non-zero freshwater endmember [$A_T^{\text{S}=0} = 728.3 \mu\text{mol/kg}$] according to equation (2):

$$A_T^{\text{S}} = \frac{A_T^{\text{meas}} - A_T^{\text{S}=0}}{S_{\text{meas}} - S^{\text{ref}}} \cdot S^{\text{ref}} + A_T^{\text{S}=0} \quad (2)$$

No salinity-dependence of the adjusted A_T^{S} values can be observed (Figure 2B). Figure 2D also shows that A_T^{S} is independent of temperature. It thus appears that temperature doesn’t play a major role for surface water A_T predictions. The anti-correlation of nA_T with temperature (Figure 2C), which has been utilized frequently in the literature [e.g., *Chen and Millero*, 1979] can be explained

Table 1. Characteristics of empirical surface alkalinity relationships. These are derived from the ‘combined’ North Atlantic data set ($n = 356$) and have the general form $nA_T = m_T T + m_S S + b_0$ for traditionally normalized (nA_T) and non-normalized alkalinity (A_T) [$b_0 = A_T^{\text{S}=0}$]

| Id | parameter/ parametrization | σ | $m_T \pm (\sigma^2)$ | $m_S \pm (\sigma^2)$ | $b_0 \pm (\sigma^2)$ |
|----|-------------------------------|----------|----------------------|----------------------|----------------------|
| #1 | A_T | 33.4 | – | – | 2316.8 – |
| #2 | nA_T | 18.2 | – | 66.2 – | 0.0 – |
| #3 | $nA_T = f(T)$ | 13.8 | $-1.7 (0.02)$ | – | 2336.9 (3.8) |
| #4 | $nA_T = f(S)$ | 7.4 | – | $-21.1 (0.4)$ | 3056.3 (39.6) |
| #5 | $A_T = f(T)$ | 20.4 | $4.8 (0.04)$ | – | 2258.0 (5.6) |
| #6 | $A_T = f(S)$ | 7.2 | – | $45.4 (0.3)$ | 728.3 (38.4) |
| #7 | $A_T = f(T, S)$ | 6.7 | $0.7 (0.01)$ | $41.2 (0.6)$ | 865.2 (51.6) |

Also shown are standard deviations (σ) of the alkalinity fits as well as variances (σ^2) of m_T , m_S and b_0 .

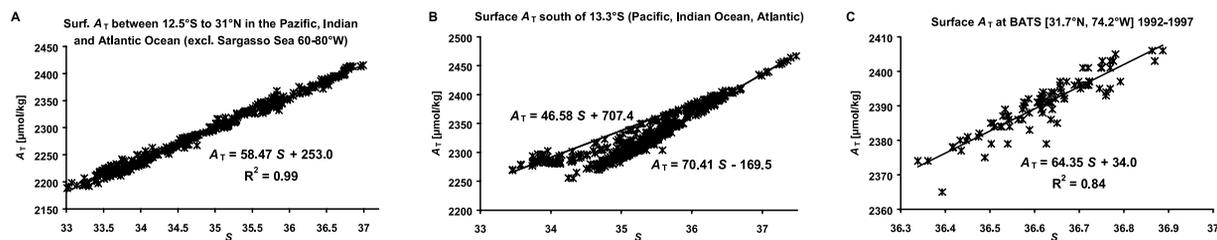


Figure 3. A–C: A_T – S relationship for samples from upper 20 m. Panel A and B are based on data of the eWOCE-Atlas [Schlitzer, 2000]. Data prior to 1980 are not included. Panel C uses data from the Bermuda Atlantic Time Series site [Bates, 2002] that are excluded in Panel A, and where the A_T – S correlation reveals an endmember value that is close to zero.

by the nA_T – S anti-correlation (Figure 2A) and the T – S -correlation (Figure 2E). The associative law creates a nA_T – T -correlation due to the strong correlation of T and S .

[9] Therefore we propose equation (2) for the normalization of A_T to a constant salinity. The corresponding A_T – S relationship #6, (Figures 2A and 2B) is usually very tight and yields standard deviations (here $\pm 7.2 \mu\text{mol kg}^{-1}$) which compare favorably to the typical accuracy of A_T measurements at sea ($\pm 4 \mu\text{mol kg}^{-1}$). Even though a bivariate linear regression approach of A_T yields significant salinity and temperature correlations (#7) and provides the smallest standard deviation ($\pm 6.7 \mu\text{mol kg}^{-1}$) an adjustment procedure based purely on the A_T – S algorithm (#6) appears adequate. This relation is able to account for the main processes determining alkalinity: Evaporation and precipitation as well as a salinity-proportional parts of mixing/upwelling and a non-zero endmember. The A_T – S relationship #6 may be preferred to the A_T – S – T relationship #7 since it avoids potential artifacts due to the seasonal temperature cycle. The alkalinity endmember (intercept) of the A_T – S relationship integrates the signals from riverine alkalinity input, deep water upwelling from beyond the lysocline(s), calcification (see Figure 1) and water mass exchange of surface waters with differing A_T – S characteristics.

[10] In fact, it is not surprising that non-zero endmember terms are found, since the size of the flux estimates of the global hydrological cycle (Figure 1) can give a rough idea of the importance of the conservative^(c) and non-conservative^(nc) processes effecting alkalinity. Baumgartner and Reichel [1975] estimated oceanic water exchanges of $425 \cdot 10^3 \text{ km}^3 \text{ yr}^{-1}$ for evaporation^(c), $385 \cdot 10^3 \text{ km}^3 \text{ yr}^{-1}$ for precipitation^(c), leaving a balance of $40 \cdot 10^3 \text{ km}^3 \text{ yr}^{-1}$ contributed by river water input^(nc). Estimates of deep water upwelling^{(c) + (nc)} across the 3.5°C isotherm are on the order of 30 Sv [Macdonald and Wunsch, 1996], or about $950 \cdot 10^3 \text{ km}^3 \text{ yr}^{-1}$. Even though only part of this upwelling originates from below the lysocline (especially in the Atlantic), this large upward displacement of water inevitably has significant implications for the alkalinity budget in the surface ocean.

[11] Together with other constraints (e.g., data on river water hardness) the A_T – S relationship may even become an important tool to identify and perhaps quantify some of the processes that redistribute alkalinity in the ocean in a manner not proportional to salinity.

[12] It is not the intention of this concept study to provide a comprehensive description of the global sea surface alkalinity field. However, the quick availability of

carbon chemistry data makes it possible to put the above results for the North Atlantic in a more global perspective. We find a tight A_T – S -correlation for the tropics and subtropics (12.5°S to 31°N ; excluding area of Figure 3C) (Figure 3A). In contrast a variable endmember situation is found for latitudes south of 13.3°S (Figure 3B). Finally, data from the Bermuda Atlantic Time-series study (BATS) reveal an A_T – S relationship with no significant intercept (Figure 3C), and therefore no bias is produced with the traditional normalization. It is interesting to note that on the one hand tropical/subtropical regions are characterized by the same surface A_T – S relationship in the Pacific, Indian and Atlantic Ocean (Figure 3A). On the other hand, the Sargasso Sea is an exception to the same rule. At the BATS site in the eye of the Sargasso Sea A_T changes can be explained by seasonal evaporation/precipitation only. Upwelling and continental riverine inputs of alkalinity appear to play a minor role. This can be explained by station's location in the center of the subtropical gyre, i.e. in a convergent surface water regime, and by its remoteness with respect to riverine alkalinity inputs. In spite of the very consistent picture for the low latitudes, no global A_T – S relationship can be provided as the situation becomes more complex in high latitudes where multiple endmembers and significantly smaller slopes/higher intercepts are found.

5. Discussion and Conclusion

[13] The traditional normalization concept (equation 1) has been widely used for descriptions of the CO_2 -system. Our study shows that this normalization is usually not able to adjust surface A_T (nor any other carbonate parameter) for salinity variations. - A correct traditional adjustment at the BATS site appears to be the exception rather than the rule.

[14] Basically the traditional normalization is used as first step in more complex procedures or for direct interpretations. A detailed picture of all errors associated with this normalization exceeds the focus of this study. Nevertheless principle conclusions can be drawn.

[15] In high northern latitudes, or more precisely in all regions with a positive $A_T^S=0$ value, sea surface A_T adjustments to a salinity of 35 yields a value for nA_T which significantly departs from reality. For example, the salinity normalization using relationship #2 (Figure 2A) over(under)-estimates the alkalinity by about $21 \mu\text{mol kg}^{-1}$ per salinity unit below (above) S^{ref} . The usefulness of global sea surface maps for nA_T [Millero et al., 1998] and nC_T [Lee et al., 2000] is therefore restricted.

[16] In fact, normalization creates artificial variance in alkalinity distributions. In turn this spurious correlation with oceanographic parameters which are salinity-correlated but unrelated with alkalinity cycling and will create errors of interpretation. For example, recognition of the spurious nature of nA_T vs. T correlation helps explain why, significant nA_T - T relationships are not found in equatorial regions [Millero *et al.*, 1998] where temperature and salinity are not strongly correlated [Schlitzer, 2000].

[17] The traditional normalization approach is used in the widely applied technique of Poisson and Chen [1987] for quantifying anthropogenic CO_2 . We would like to briefly note that despite our critique of this normalization, the errors arising from its use, for this specific application, are not large. The reason for this is that this technique uses a 'baseline' developed from temperature dependant surface parametrizations of traditionally normalized C_T and A_T data, which are applied identically to industrial and preindustrial values. Because temperature and salinity below the mixed layer fall into narrow ranges, the T - S -dependent errors associated with the normalization mainly cancel out. Correspondingly, the largest errors occur in the mixed layer only.

[18] Based on the present findings we suggest that the traditional normalization concept should no longer be used, and if so only under well-defined circumstances taking into consideration local relationships, that allow an endmember term for $S = 0$. More generally we propose the use of an empirical relationships of the form $A_T = m_S S + A_T^S$ for the adjustment of surface alkalinity data.

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