

Title: Temperature effect on seawater  $f\text{CO}_2$  revisited: theoretical basis, uncertainty analysis, and implications for parameterising carbonic

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General comments:

The paper studies the sensitivity of seawater carbon dioxide fugacity ( $f\text{CO}_2$ ) to temperature because it is crucial for the accurate measurements needed in constructing global carbon budgets and understanding the variability of  $\text{CO}_2$  flux between air and sea. So far, the normalization or correction for temperature impact on  $f\text{CO}_2$  has been done using an experimental determination (Takahashi et al. 1993) and alternatively using the equations of the carbonate system in seawater (i.e. Wanninkhof et al. 2020). The author discusses that the two are not fully compatible or that it is possible to improve their small discrepancies. The authors present a new approach based on marine carbonate system equations and the van 't Hoff equation that shows a different proportional relationship between  $\ln(f\text{CO}_2)$  and temperature. It is argued that this approach is consistent with experimental and field data, and offers lower uncertainty in the temperature sensitivity of  $f\text{CO}_2$ . Their results may have more important implications for regional budgets and significant temperature adjustments, they are unlikely to affect global air-sea  $\text{CO}_2$  flux budgets.

In my opinion the manuscript presents some very important errors in the theoretical approach and the improvement it proposes to evaluate the effect of temperature on  $f\text{CO}_2$  does not improve the proposal of Wanninkhof et al. (2022). One might think that it could be presented as a useful alternative anyway, but my doubt is whether this could lead many readers to some confusion.

Minor comments

Line 47.- "it is driven by a global mean  $\Delta f\text{CO}_2$  of less than  $10 \mu\text{atm}$ " This needs a citation.

Line 64. Also, is use in the analysis of GOBMs to decomposed the biological and the temperature effects over the  $p\text{CO}_2$  seasonal cycle (i.e. Rodgers et al. 2023)

Linea 71-99.- The author strongly emphasizes that the derivative of  $f\text{CO}_2$  with respect to temperature cannot be theoretically linear. This is somewhat obvious, but it does not exclude that given a temperature interval, such as the one described in the APPENDIX of the Takahashi et al. (1993) article ranging from 2 to 24, the inverse function of Kelvin temperature and centigrade temperature are correlated with an  $R^2=0.9995$ , which implies an error of less than 2% in the estimation of the dependent variable by not using an inverse function of kelvin temperature. The additional exercise performed by these same authors of fitting to a quadratic function decreases this error to 0.04%. Therefore, I believe that the use of the linear function is overly criticized, although it is true that the use of the Takahashi et al.' factor should be restricted to the 2 to 24°C range and for relatively small temperature changes so as not to result in somewhat biased  $f\text{CO}_2$  estimates.

Line 98-99.- The author is aware that it is possible to use an approximate alkalinity to obtain a new  $f\text{CO}_2$  at another temperature without producing an error greater than  $2 \mu\text{atm}$ . Since the salinity is known, any climatology can generate an alkalinity with an error of  $\pm 20 \mu\text{mol/kg}$ , it would generate

a new  $f\text{CO}_2$  with an error of less than  $0.3 \mu\text{atm}$  for a temperature change of  $10^\circ\text{C}$ . Therefore, the use of CO2SYS as proposed by Wanninkhoff et al 2022 is more than sufficient.

Line 105. Please, show or evaluate the "big differences".

Line 108.- "thus indicating some deficiency with the measurements of Takahashi et al. 1993". The weaknesses of the Takahashi et al. (1993) measurements are not evaluated throughout the article. After all, they are the ones used throughout the article as a reference for other types of parameterizations.

Line 111: "we aim to provide this missing theoretical basis by developing a new functional form for how  $f\text{CO}_2$  and thus  $v$  vary with temperature' Are you saying that the measurements and statistical adjustments made by Takahashi et al. 1993 show a lack of theoretical basis? Honestly, they simply made a linear fit because for that temperature range it would be practically identical to a fit vs  $1/t_k$ .

Line 162-163. "Takahashi et al. (1993) did not give a theoretical basis for either of the forms (linear and quadratic; Eqs. 5 and 6) that they fitted to their dataset nor did they give any reason to choose one over the other." It does not seem very necessary to provide any kind of theoretical basis when the high-quality measures of Takahashi et al. 1993, shows that  $p\text{CO}_2$  values correlate with  $r^2=0.9999$ . The same  $r^2$  that would come out using the CO2SYS with the same configuration shown in the article.

Line 177 "In typical seawater, the approximations in Eqs. (12) and (13) are more than 99% accurate for  $\tau_c$  and more than 97% accurate" I honestly believe that this is where the author makes a big mistake because this approach has important consequences. The  $C_T/A_T$  ratio is key in his approximation. It is true that for  $C_T/A_T$  ratios  $<0.9$  the approximation is quite correct and the van't Hoff model would work well, but for  $C_T/A_T$  values  $>0.9$  equation 11 is going to present very low carbonate concentration (even lower than  $\text{CO}_2$  concentrations and with high  $p\text{CO}_2$  values generating very high biases when van't Hoff model is applied). The strange thing is that this is not indicated until very late in the article and is somewhat overlooked.

Line 300-303. "At each grid point, we computed the mean across all years separately for each month for temperature, salinity,  $A_T$  and  $\tau_c$ . We then used PyCO2SYS to calculate  $f\text{CO}_2$  from these variables at 50 evenly spaced temperatures from  $-1.8$  to  $35.83^\circ\text{C}$  (i.e., the range of the OceanSODA-ETZH data product) at each month and grid point. Next, we fit Eq. (19) to the generated  $t$  and  $f\text{CO}_2$  data to find the best fitting  $b_h$  value at each point." To be the key part of the way to obtain the equation 35 I think it is poorly explained. Especially because the equation first obtains 50  $f\text{CO}_2$  data by applying the CO2SYS equations, and then adjusting it to the van't Hoff equation which would only be applicable with high precision with low  $C_T/A_T$  values, i.e. with low  $f\text{CO}_2$  values which implies a low error in its adjustment. On the contrary, for high  $C_T/A_T$  values (high  $f\text{CO}_2$  values) the application of equation 19 already deviates from equation 11, and the biases generated amplify the errors in the  $f\text{CO}_2$  estimates using  $b_h$ . (Fig 3b).

Line 305-66 “The coefficients and their variance-covariance matrix are provided in the Supplementary Information (Supp. Tables 1-2).” It would be more informative for the reader to include the uncertainties of each of the coefficients and their level of significance.

Line 352. Legend Figure 1 “a) Variation of  $f\text{CO}_2$  with temperature according to the measurements of Takahashi et al. (1993)”. The legend is misleading. The variations of  $f\text{CO}_2$  with temperature are not described, but the anomaly of  $f\text{CO}_2$  with respect to that estimated using various parameterizations, including the two proposed by Takahashi et al. 1993.

Line 413. Figure 2. How can it be explained that if the coefficient obtained from van't Hoff called 'b<sub>h</sub> fitted' shows a behavior so different, and worse, from the b<sub>h</sub> parameterized van't Hoff coefficient considering that it is derived from that one. And on the other hand, the proposed parameterized b<sub>h</sub> enhancement is no better than the application of  $U_{Lu00}$  as proposed by Wanninkof et al 2022.

Line 433 Figure 3. Figure 3a clearly shows that the proposed estimate (b<sub>h</sub> van't Hoff) of  $f\text{CO}_2$  changes due to temperature changes does not improve on the more accurate alternative of direct application of CO2SYS when the  $C_T/A_T$  ratio > 0.95. The legend to Figure 3b shows the RMSE of b<sub>h</sub>, but the units is  $\text{K}^{-1}$  and not the erroneously written  $\mu\text{atm}^{-1}$ .

Line 435 “the b<sub>h</sub> fit is less than 1  $\mu\text{atm}$ ”. The b<sub>h</sub> unit is  $\text{J mol}^{-1}$  such as is indicated in Line 202.

Line 449 “parameterisations. However, while these issues might contribute a component of the discrepancy – i.e., the main pattern with  $\text{RMSD} \sim 1 \mu\text{atm}$  seen for  $T_C/A_T$  less than  $\sim 0.95$  – there is no reason to expect their influence to be correlated with  $T_C/A_T$ , so they cannot be the entire explanation.” How is it not possible that the author himself seems unaware of the limitations of equation 19 which proceeds from a strong simplification of equation 11? Just at  $C_T/A_T$  values below  $\sim 0.95$ , the term removed from equation 1 becomes determinant because the denominator tends to zero. We are in the environment of the first equivalence point where carbonate concentrations are equal to  $\text{CO}_2$  concentrations.

Line 452-457 “Inaccuracies in the approximations  $A_x$  and/or  $T_x$ , used in generating Eq. (19), likely also play a role at higher  $T_C/A_T$ . The fraction of  $T_C$  comprised of  $[\text{CO}_2(\text{aq})]$ , which is ignored in  $T_x$ , increases with  $T_C/A_T$ , while the fraction of non-carbonate alkalinity, ignored in  $A_x$ , decreases with increasing  $T_C/A_T$ . Consequently, the approximation that  $[\text{HCO}_3^-]^2/[\text{CO}_3^{2-}]$  is constant across different temperatures (Eq. 16), which emerges from the definitions of  $A_x$  and  $T_x$  (Eqs. 12-15), becomes less accurate with increasing  $T_C/A_T$ . The  $T_x$  approximation may be the problem here rather than  $A_x$ , because the  $\text{RMSD}$  of the b<sub>h</sub> fit is positively correlated with the error in  $T_x$  but negatively correlated with the error in  $A_x$  (Supp. Fig. 3).” Clearly the problem is the denominator of equation 11, and certainly it is the 'Inaccuracies in the approximations  $A_x$  and/or  $T_x$ , used in generating Eq. (19),’ There is not the slightest doubt and this calls into question the usefulness of b<sub>h</sub> and in the background of this whole article. Why use an alternative parameterization to avoid using CO2SYS which is always going to be less accurate even if we have inaccuracies in the equilibrium constants?

Line 520 “But we now know that  $\nu$  should follow a particular curvature that can be represented with only one adjustable parameter ( $b_h$ )” Sure? The equation 19 is a simplification of equation 11. On the one hand, the equation 11 contains more factors than the apparent equilibrium constants of the marine carbonate equilibrium and therefore does not have to follow exactly the van't Hoff equation. On the other hand, the apparent (or empirical) carbonic acid constants ( $K_1$  and  $K_2$ ) as well as the  $\text{CO}_2$  saturation ( $K^0$ ) contain more summands than the one given by the van't Hoff equation which are polynomial functions of the kelvin temperature.

Line 575 (Figure 5) and 594-597. “The SB21 parameterisation (Schockman and Byrne, 2021) consists of new, spectrophotometric measurements of the product  $K_1 \cdot K_2^*$  which ...  $k_2^*$ , which resulted in overall virtually zero variability in total  $\nu$ . This low variability in total  $\nu$  is echoed by the Su20 parameterisation (Sulpis et al., 2020), which is based on field observations where  $\Delta\tau$ ,  $\tau_c$ , pH and  $f\text{CO}_2$  were measured simultaneously, but the low variability is arrived at in a different way, with rather different distributions for the individual  $K_1^*$  and  $K_2^*$  effects”. **Interesting figure.** Obviously, the probability curves represent the spatial distribution of the ocean surface and this is strongly dependent on latitude. But looking at a relative perspective when comparing one set of constants with others, it is interesting to note that both the Schockman & Byrne 'Mehrbach' option (SB21) and Sulpis 2020 (Su20) show virtually no spatial variability with values very close to that estimated by Takahashi et al. (1993). This is an interesting aspect of this study.

Line 664 Conclusions. This epigraph is too long, and in some parts, it is rather a new discussion.

#### References

Rodgers, K. B., Schwinger, J., Fassbender, A. J., Landschützer, P., Yamaguchi, R., Frenzel, H., et al. (2023). Seasonal variability of the surface ocean carbon cycle: a synthesis. *Global Biogeochemical Cycles*, 37, e2023GB007798. <https://doi.org/10.1029/2023GB007798>