

Review with figure:

EGUsphere

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

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Reviewer Rik Wanninkhof, AOML

Matthew Humphreys provides a physical chemical basis to the frequently used empirical relationship of $f\text{CO}_2$ with temperature along with an thorough uncertainty analysis. He has incorporated the results into the PyCO2SYS software. The temperature relationship is frequently used to correct surface water $f\text{CO}_2$ measurements to *in situ* temperatures. Based on the uncertainty analysis presented, the uncertainty for this correction can be reduced from 0.24 % to 0.06 %.

The manuscript is exhaustive and laid out in a coherent fashion. It is well-referenced and thoroughly researched. Non-the-less it is a challenging read and final results and conclusions are not always clearly laid out. For instance, the equations to determine the temperature dependence are not that clearly laid out. That is, it would be useful if an additional equation was added after Eqns. 19-21 where the numerical values constants for b_h and R were included. A central premise of the work is that the proper functionality for the temperature dependence is $1/T$, following the van t'Hoff relationship, rather than t which is well-founded but the fit of a $1/T$ relationship to the experimental data of Takahashi et al. 1993 is worse than a linear fit with t . At the end of the manuscript the author correctly states that over a narrow range the functionality of $1/T$ versus t is very similar.

As pointed out by others, the temperature dependence will depend on the bicarbonate and carbonate concentrations of the seawater. This is also described in this manuscript (eqn12-18) but never emphasized. The important point is that no single simple equation can predict $f\text{CO}_2$ solely based on temperature but that information on TA and DIC needs to be implicitly included. It might be worth emphasizing that knowledge or estimate of TA and DIC will decrease the uncertainty in the $\ln(f\text{CO}_2\text{-}T)$ relationship.

One aspect that is not emphasized is why this empirical single $f\text{CO}_2$ -temperature dependence developed by Takahashi based on a single seawater composition “works” for the surface ocean as described in Wanninkhof et al. 2022:” The theoretical temperature dependence expressed as $\partial \ln(f\text{CO}_2\text{w})/\partial T = B_0 + B_1 T$ shows a stronger dependency at lower temperatures, and weaker dependency at low TA/DIC values (Fig. 4). These conditions often go hand-in-hand in the surface ocean. That is, surface waters of the world's oceans have lower temperatures and lower TA/DIC at higher latitudes such that the two factors will oppose each other.”

For experimental data and verification the paper relies heavily on the $p\text{CO}_2$ -temperature relationship of Takahashi that was derived from 1 seawater sample and 8 measurements at 7 temperatures from 2-25 C. The paper also assumes that deviations from a linear trend are likely at higher temperatures and suggests, correctly, that more systematic studies have to be undertaken. While several groups have undertaken such studies, they have failed to publish it in

the open literature. A notable exception is that of Lee and Millero (1995) that provides measurements from 5-30 C and obtains a linear dependence very similar to the of Takahashi et (1993) (see attached figure) particularly if the sample at 5 C is omitted that is questionable (Lee personal comm, 1996). Of note are that the 30 C value falls in line with other points, but that the temperature dependence using a polynomial fit is twice that of Takahashi.

Comments by line number

Line 11: omit "purely"

Line 25 and beyond : Besides the constants the concentrations of the species will impact the relationship as well

Line 47: global mean $\Delta fCO_2 \approx -5 \mu atm$ (Fay et al., 2024)

Line 50 and beyond: "minimum accuracy of 0.5 %." since ΔfCO_2 is often the quantity of interest it is commonly expressed as $< 2 \mu atm$ for "climate quality" rather than a %

Line 55: state that the surface seawater is equilibrated with an enclosed headspace and the headspace is measured. That is fCO_2 is fundamentally a gas phase property

Line 59: This criterium is for SOCAT dataset flags of A and B; SOCAT accepts all fCO_2 measurements

Line 65: Of note is that fCO_2 is also measured on discrete samples at fixed temperature usually 20 C by select groups. In these case conversion to fCO_2 at in situ temperatures is much greater.

Line 73: replace: "measured" by "reported"

Line 93: insert "v," after "calculating"

Line 109: Note that Takahashi et al. 2009 provide the equation as well including the integrated form

Sections 2.1 and 2.3: Very nice description of physical basis and uncertainties

Line 139: note that 8 measurements were taken at 7 temperatures.

Line 331: Note Lee and Millero (1996) have a measurement at 30 C that could be used to spot-check the difference between u_l and u_q above about 25 C

Line 335-340: the issue that the proposed fit does not do as well as the original is a significant point, even if both fall within the calculated uncertainty. Again the Lee and Millero (1996) measurements could shed some light on the fundamental issue if the proposed equations have shortcomings.

Line 427: Section 3.1.3 I found this section confusing in part because the previous sections discuss fitting with experimental data while this section discusses using the Lueker constants. I had expected that the author would use the experimental data presented in Table 3 of the paper of Lueker et al. which would be a good test of their parameterizations as the tests were done at several temperatures and varying fCO_2 , TA and DIC.

Line 455: This point could be empathized "Consequently, the approximation that $[HCO_3^-]_2/[CO_3^{2-}]$ 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 TC/AT.

Line 675 and before:" but this does not account for variability in u through space and time" [while this is explained in the introduction], strictly speaking u varies with temperature and chemical composition, not space and time.

Lee, K., and F. J. Millero, 1995: Thermodynamic studies of the carbonate system in seawater. *Deep-Sea Res.*, **42**, 2035-2061.

Takahashi, T., and Coauthors, 2009: Climatological mean and decadal change in surface ocean pCO₂, and net sea-air CO₂ flux over the global oceans. *Deep -Sea Res II*, **2009**, 554-577.

Note should be L&M, 1995

