Matthew Humphreys provides a physical chemical basis to the frequently used empirical relationship of fCO2 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 fCO2 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 %.

➢ I am grateful to the reviewer for taking the time to carefully read the manuscript and provide thoughtful and constructive feedback.

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.

➢ Thank you for these comments. I have rewritten many of the trickier parts of the paper to try to make them easier to follow.

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.

➢ I am reluctant to add a series of equations with the numerical values for b_h filled in because there would be potentially so many of them. There is the theoretical b_h value, the b_h value fitted to the Takahashi et al. (1993) dataset, now also the b_h value fitted to the Lee and Millero (1995) dataset, and a continuous spectrum of possible b_h values from the parameterisation. All the equations would be identical except for that value. The value for R is also prone to occasional revision. That said, I think that the underlying problem here may be that it's difficult for the reader to keep track of all the different b_h values. As such, I've added a table (Table 1) to assist with this, which hopefully fixes the problem in a different way.

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.

➢ The fit to 1/T indeed has a higher (i.e., worse) RMSD than the fit to T. But the 1/T fit is still not inconsistent with the uncertainty in the measurements. If multiple possible fits (linear, quadratic, 1/T) all fall within the uncertainty window, then especially when there are so few data points to compare against, I don't think it's really valid to simply say that the one with the lowest RMSD must be 'correct'. See also related comment below on lines 335-340.
➢ Nevertheless, the revised manuscript takes a more critical view of the agreement (or lack thereof) between the new form and the Takahashi et al. (1993) measurements, thanks in a large part to this reviewer's suggestion to also look at Lee and Millero (1995).

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 fCO2 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(fCO2-T) relationship.

➢ Yes, I think this is an important point that was not made clearly enough in the preprint. This is emphasised more with a new paragraph towards the end of Section 3.1.3. Related to comment on line 455 below.

One aspect that is not emphasized is why this empirical single fCO2-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 ∂ln(fCO2w)/∂T = B0 + B1 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."

➢ This is indeed an interesting point. A new figure (Fig. 7) and an additional paragraph of text at the end of Sect. 3.3.1 have been added to discuss it further.

For experimental data and verification the paper relies heavily on the pCO2-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.

➢ Thank you for bringing this dataset to my attention. It has been incorporated in the manuscript and leads to my taking a more critical view of the agreement between the model and these measurements. See also related comment on line 331.
➢ However, it is worth mentioning that the Lee and Millero (1995) measurements don't seem to be consistent with anything other than Takahashi et al. (1993), and because of the different TC/AT they shouldn't be as consistent with Takahashi et al. (1993) as they are, so they have been rather tricky to integrate into the analysis.

Comments by line number

Line 11: omit "purely"

➢ Done.

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

➢ Updated text.

Line 47: global mean ΔfCO2 ≈ -5 μatm (Fay et al., 2024)

➢ Thank you! Reference added and value updated.

Line 50 and beyond: "minimum accuracy of 0.5 %. " since ΔfCO2 is often the quantity of interest it is commonly expressed as < 2 μatm for "climate quality" rather than a %

➢ Added equivalent μatm value here. I have retained the 0.5% too because this is how it is 'officially' expressed by Newton et al.

Line 55: state that the surface seawater is equilibrated with an enclosed headspace and the headspace is measured. That is fCO2 is fundamentally a gas phase property

➢ Text updated.

Line 59: This criterium is for SOCAT dataset flags of A and B; SOCAT accepts all fCO2 measurements

➢ Text updated.

Line 65: Of note is that fCO2 is also measured on discrete samples at fixed temperature usually 20 ℃ by select groups. In these case conversion to fCO2 at in situ temperatures is much greater.

➢ Added this example to the list.

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

➢ Done.

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

➢ Done.

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

➢ I'm not sure I understand how this comment fits with the text here, so I haven't changed anything.

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

➢ Thank you!

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

➢ Done.

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

➢ Thanks. See response to comment above "For experimental data and verification…"

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.

➢ Agreed. See response to comment above "A central premise of the work…"

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 fCO2, TA and DIC.

➢ It's not really possible to perform this analysis using the suggested experimental data directly, because in order to test the parameterisation we need $f\text{CO}_2$ values for multiple temperatures where salinity, DIC and alkalinity are all held constant. In the Lueker et al. dataset, DIC is rather different for every measurement, and there is some variability in salinity and alkalinity too. I have updated the explanation of this section and moved it to an earlier place in the R&D to try to make it flow better and less confusing.

Line 455: This point could be empathized "Consequently, the approximation that [HCO3–]2/[CO32–] is constant across different temperatures (Eq. 16), which emerges from the definitions of Ax and Tx (Eqs. 12-15), becomes less accurate with increasing TC/AT.

➢ I have reworked this text and emphasised this point more. See also response to comment above "As pointed out by others…"

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

➢ Agreed, text updated.

*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.*