

Response to reviewer 1

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 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. Wanninkof 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 CO_2 flux budgets.

- My thanks to the reviewer for reading the manuscript and providing comments. I agree with the summary above.

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 Wanninkof 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.

- A number of the points presented as problems by the reviewer are either misunderstandings or do not take into account the evidence presented. This must stem from the original manuscript not having been written clearly enough, so I thank the reviewer for highlighting the points of potential confusion, and have revised the manuscript aiming to make these aspects clearer, in particular with the restructuring of the first part of the R&D (Sect. 3.1).

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.

- Value updated with 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)

- Thanks, citation added.

Line 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.

- I agree completely with the restrictions that the reviewer suggests should be applied to using the Takahashi et al. adjustment approach. However, these restrictions are not a solution: there is a lot of ocean outside the 2 to 24 °C range, and many applications where adjustments over large temperature ranges are required. Fixing this problem requires understanding how the t - $f\text{CO}_2$ relationship should behave, which is the main aim of this paper.

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 μatm . 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 μatm for a temperature change of 10°C. Therefore, the use of CO2SYS as proposed by Wanninkhoff et al 2022 is more than sufficient.

- The method that the reviewer suggests (estimating alkalinity from salinity) is not proposed by Wanninkhoff et al.; that study only considers cases where TA and DIC had been directly measured alongside $f\text{CO}_2$. Indeed, the complete method suggested by the reviewer has not to my knowledge been peer reviewed nor robustly assessed. A calculation with PyCO2SYS confirms that an uncertainty of 20 $\mu\text{mol/kg}$ in alkalinity would indeed propagate through to an uncertainty of less than 0.3 μatm in $f\text{CO}_2$ adjusted by 10 °C (conditions: alkalinity = 2250 $\mu\text{mol/kg}$, $f\text{CO}_2$ = 400 μatm , temperature = 15 → 25 °C, salinity = 35). However, this uncertainty budget is far from complete. It ignores the uncertainties in the equilibrium constants of the CO_2 system which are used in these calculations. While these uncertainties are very poorly known, using the set proposed by Orr et al. (2018) inflates the total uncertainty in corrected $f\text{CO}_2$ by 100 times, to around 16 μatm . The adjusted $f\text{CO}_2$ value can also vary by $\pm 10 \mu\text{atm}$ or more depending on which parameterisations are selected for the equilibrium constants. I have added extra text to the introduction here to point out this problem (although using a slightly different set of numbers; lines 100-113).
- More fundamentally, the method suggested by the reviewer does not deliver any scientific understanding of how temperature and $f\text{CO}_2$ are related, but rather takes more of an engineering approach with (Py)CO2SYS as a black-box tool, which doesn't provide any conceptual insight into how we expect the system to behave.

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

- Added a value based on Fig. 3a from McGillis and Wanninkhoff (2006).

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.

- The only ‘deficiency’ being referred to here is the lack of data above 25 °C. Other than the uncertainty in the alkalinity value, which is mentioned, I am not aware of any other weaknesses of these measurements that should be discussed here.

Line 111: “we aim to provide this missing theoretical basis by developing a new functional form for how $f\text{CO}_2$ and thus u vary with temperature’ Are you saying that the measurements and statistical adjustments made by Takahashi et al. 1993 show a lack of theoretical basis?

- The choice to fit the measurements with linear and quadratic equations lacks a theoretical basis. The fitted forms are empirical, having been selected because they appeared to fit the data, without understanding why.

Honestly, they simply made a linear fit because for that temperature range it would be practically identical to a fit vs $1/t_k$.

- While the two fits are indeed very similar for the temperature range of the experiment, Takahashi et al. (1993) did not appear to consider a $1/t_k$ form, nor did they show that they knew this would be theoretically justified.

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 CO_2SYS with the same configuration shown in the article.

- There are a few reasons why a theoretical basis is desirable, which I have attempted to make clearer in the revised manuscript: predictability, uncertainty propagation, and philosophical.
- Predictability: the linear fit does indeed perform very well within the range of the Takahashi et al. dataset, but it disagrees significantly with CO_2SYS outside that range. However, the new form proposed here, still fitted only to the Takahashi dataset, agrees very well with CO_2SYS even far outside of the range of the measurement data.
- Uncertainty propagation: as discussed in Section 3.2, accurate uncertainty propagation requires a meaningful and well-fitting model.
- Finally, the philosophical case is that, it is useful to know why something works, not just that it works (same as for the second bullet point of my response to ‘lines 98-99’ above).

Line 177 “In typical seawater, the approximations in Eqs. (12) and (13) are more than 99% accurate for TC 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 CT/AT ratio is key in his approximation. It is true that for CT/AT ratios <0.9 the approximation is quite correct and the van’t Hoff model would work well, but for CT/AT values >0.9 equation 11 is going to present very low carbonate concentration (even lower than 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.

- I realise this must arise from things not having been presented clearly enough in the previous manuscript, but the reviewer’s assertion that the approximation will not work does not stand up to the evidence presented in the manuscript that the approximation does in fact work rather well, such as being able to very closely reproduce the t - $f\text{CO}_2$ relationship calculated with CO2SYS, with less than 1 μatm RMSD in $f\text{CO}_2$ for over 97% of the global surface ocean. There is no evidence for the ‘big mistake’ suggested by the reviewer.
- As mentioned in the manuscript, the approximations have been previously used successfully for getting a first-order understanding of a closely related marine carbonate system problem (Humphreys et al., 2018), equivalently to how they are being used here.
- The corresponding section has been expanded for clarity and brought forward to the very start of the R&D (Sec. 3.1.3 and Fig. 3 have become Sect. 3.1.1 and Fig. 1).

Line 300-303. “At each grid point, we computed the mean across all years separately for each month for temperature, salinity, AT and TC. We then used PyCO2SYS to calculate $f\text{CO}_2$ from these variables at 50 evenly spaced temperatures from -1.8 to 35.83 °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 bh value at each point.” To be the key part of the way to obtain the equation 35 I think it is poorly explained.

- I have expanded the explanation in the text to make this clearer.

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 CT/AT values, i.e. with low $f\text{CO}_2$ values which implies a low error in its adjustment. On the contrary, for high CT/AT 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 bh . (Fig 3b).

- I am not certain what the reviewer is trying to say here. Yes, the approximation is worse at the higher CT/AT values that occur in less than 3% of the global surface ocean, and this is discussed in Sect. 3.1.1 and illustrated in Fig. 1 (which were Sect. 3.1.3 and Fig. 3 of the original manuscript).

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.

- The uncertainties in the coefficients are already provided in Supp. Table 2. For the level of significance, I added an extra column to Supp. Table 1, which contains the coefficient values for normalised predictors, and added a note to the caption explaining that the relative magnitudes of these normalised coefficients show the relative importance of each coefficient to the fit.
- During this process I noticed that values for coefficients u_2 - u_5 were not entered into Supp. Tables 1 and 2 in the correct order, so this has also been corrected.

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

fCO₂ with temperature are not described, but the anomaly of fCO₂ with respect to that estimated using various parameterizations, including the two proposed by Takahashi et al. 1993.

- The rest of the partially quoted sentence resolves the misunderstanding here, as it states, "... all normalised to the linear fit". I have moved this phrase to earlier in the sentence to make it more obvious.

Line 413. Figure 2. How can it be explained that if the coefficient obtained from van't Hoff called 'b_h fitted' shows a behavior so different, and worse, from the b_h parameterized van't Hoff coefficient considering that it is derived from that one.

- The 'b_h fitted' curve uses a single b_h value as fitted to the Takahashi et al. (1993) dataset globally. This does not account for variability of b_h with the hydrographic conditions. The 'b_h parameterised' curve uses a variable b_h value based on the parameterisation in Eq. (35).

And on the other hand, the proposed parameterized b_h enhancement is no better than the application of uLu00 as proposed by Wanninkhof et al 2022.

- The parameterised b_h is indeed equal to or slightly better (closer to zero) than Lu00 throughout the Δt range. But the method of Wanninkhof et al. requires a second marine carbonate system variable.

Line 433 Figure 3. Figure 3a clearly shows that the proposed estimate (b_h van't Hoff) of fCO₂ changes due to temperature changes does not improve on the more accurate alternative of direct application of CO₂SYS when the CT/AT ratio > 0.95.

- Correct, and this was stated in lines 429-430 of the originally submitted manuscript and is discussed in Sect. 3.1.1 of the revised manuscript. Again, the aim is not to improve on CO₂SYS, but to find something that approaches the same accuracy without needing a second carbonate system variable.

The legend to Figure 3b shows the RMSE of b_h, but the units is K⁻¹ and not the erroneously written μatm⁻¹.

- The unit of the RMSD is indeed μatm as written (not μatm⁻¹ and not K⁻¹). This is the same as for the following reviewer comment.

Line 435 "the b_h fit is less than 1 μatm". The b_h unit is J mol⁻¹ such as is indicated in Line 202.

- As for the previous reviewer comment, the unit is correct, the RMSD is for fCO₂ calculated with the b_h fit – sentence updated to clarify.

Line 449 "parameterisations. However, while these issues might contribute a component of the discrepancy – i.e., the main pattern with RMSD ~ 1 μatm seen for TC/AT less than ~0.95 – there is no reason to expect their influence to be correlated with TC/AT, 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 CT/AT values below ~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 CO_2 concentrations.

- The author is well aware of these limitations, as they were discussed in the very next sentence in the manuscript (which is quoted by the reviewer directly below: lines 452-457). The corresponding section has been revised for improved clarity.

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 TC/AT . The fraction of TC comprised of $[\text{CO}_2(\text{aq})]$, which is ignored in T_x , increases with TC/AT , while the fraction of non-carbonate alkalinity, ignored in A_x , decreases with increasing TC/AT . Consequently, the approximation that $[\text{HCO}_3^-]/[\text{CO}_3^{2-}]$ 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 TC/AT . The T_x approximation may be the problem here rather than A_x , because the RMSD of the bh 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..

- Up to here, the reviewer is correct (and is agreeing with the manuscript)...

... and this calls into question the usefulness of bh and in the background of this whole article.

- ... but this is not a valid conclusion. This is essentially the same point as the reviewer made earlier on line 177, so please refer to that response.

Why use an alternative parameterization to avoid using CO_2SYS which is always going to be less accurate even if we have indeterminacies in the equilibrium constants?

- Alternatives to solving the complete marine carbonate system are useful because $f\text{CO}_2$ measurements are often not accompanied by a second carbonate system parameter.
- The reviewer’s statement that the approach presented here is ‘always going to be less accurate’ is unfounded and currently false; uncertainties in the equilibrium constants significantly increase the uncertainty in carbonate system calculations; see my reply to the reviewer’s comment on lines 98-99.

Line 520 “But we now know that u should follow a particular curvature that can be represented with only one adjustable parameter (bh)” 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 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.

- Yes, here the phrasing was not clear that I am referring to the first-order form of u , which can be modelled well with equation 19. Added “to first order” to the sentence to clarify this.

Line 575 (Figure 5) and 594-597. “The SB21 parameterisation (Schockman and Byrne, 2021) consists of new, spectrophotometric measurements of the product $K1 \cdot K2^*$ which ... $k2^*$, which resulted in overall virtually zero variability in total u . This low variability in total u is echoed by the Su20 parameterisation (Sulpis et al., 2020), which is based on field observations where AT, TC, pH and fCO_2 were measured simultaneously, but the low variability is arrived at in a different way, with rather different distributions for the individual $K1^*$ and $K2^*$ 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.

- This is interesting (and indeed already mentioned in the manuscript, lines 594-599 of the original), although I'm not sure that it delivers any new insight. Neither of these parameterisations fits the Takahashi et al. (1993) dataset very well (Supp. Fig. 2). I added a note to emphasise this point to the section.

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

- It has been shortened with some parts relocated to other sections.

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>

Humphreys, M. P., Daniels, C. J., Wolf-Gladrow, D. A., Tyrrell, T., and Achterberg, E. P.: On the influence of marine biogeochemical processes over CO_2 exchange between the atmosphere and ocean, *Mar. Chem.*, 199, 1–11, <https://doi.org/10.1016/j.marchem.2017.12.006>, 2018.

Orr, J. C., Epitalon, J.-M., Dickson, A. G., and Gattuso, J.-P.: Routine uncertainty propagation for the marine carbon dioxide system, *Mar. Chem.*, 207, 84–107, <https://doi.org/10.1016/j.marchem.2018.10.006>, 2018.

Response to reviewer 2

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

- 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 fCO_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 $\ln(fCO_2-T)$ 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 $\partial \ln(f\text{CO}_2\text{w})/\partial T = B_0 + B_1 T$ 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.”

- 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 $\Delta f\text{CO}_2 \approx -5 \mu\text{atm}$ (Fay et al., 2024)

- Thank you! Reference added and value updated.

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 %

- 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 fCO_2 is fundamentally a gas phase property

- Text updated.

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

- Text updated.

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.

- Added this example to the list.

Line 73: replace: “measured” by “reported”

- Done.

Line 93: insert “v, “ 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 v_l and v_q 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 $f\text{CO}_2$, 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 $[\text{HCO}_3^-]/[\text{CO}_3^{2-}]$ 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 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 v through space and time” [while this is explained in the introduction], strictly speaking v 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 $p\text{CO}_2$, and net sea-air CO_2 flux over the global oceans. Deep -Sea Res II, 2009, 554-577.