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Simulated anthropogenic CO_2 uptake and acidification of the Mediterranean Sea

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1 Response to Referee #2

We thank Referee #2 for constructive comments, which have helped improve the manuscript. Below the Referee comments are repeated (in gray) and our responses follow (in black).

1.1)

This paper discusses model results from a model that simulates the ventilation and circulation of the Mediterranean Sea, with emphasis on two passive tracers (CFC-12 and DIC). The paper does a careful and very nice comparison of model results to data based results. It also calculates fluxes of anthropogenic carbon through the Strait of Gibraltar, and draw relevant conclusions on the ocean acidification of the Mediterranean Sea. The paper is very well written and an effort to join model and observational estimates in a common frame-work. The paper certainly merits publication in BG.

Many thanks for these positive remarks.

However, I do have some concerns about the model / data comparison that needs serious attention, and a number of minor suggestions that should be easy to correct. The most serious considerations concerns 1) the comparison of data based TTD derived estimates with the modeled deltaDIC and TTD(MW), and 2) the conclusion of the lower limit for Cant storage in the Mediterranean Sea. 1) I wonder why the model have 10 umol/kg lower Cant in the surface (section 3.5). The TTD method assumes (per definition) that the age of the surface water is zero, and the anthropogenic carbon content is only a matter of thermodynamics with a given alkalinity, temperature and pCO2. The 68 umol/kg of surface Cant is roughly what you would expect from thermodynamic considerations of the carbonate system. This suggests to me that the model finds kinetic restrictions to the saturation of Cant so that the air-sea equilibrium has changed over the anthropogenic time-period with roughly 15%. Can you verify or comment on this. It is surprising that such a large deltadeltapCO2 is found.

Data-based methods such as TTD do indeed assume that the change in ocean pCO_2 is identical to the change in atmospheric pCO_2. But this assumption must be wrong in the real ocean. If it were true, then the air-sea difference ($\Delta\delta pCO_2$) must always be zero, which implies that the air-sea flux of anthropogenic CO_2 must likewise be zero (see equation 5 in our submitted manuscript). Certainly, the anthropogenic CO_2 flux cannot be zero given that all data-based and modeling approaches indicate that the ocean does indeed contain substantial amounts of anthropogenic C_T.

The notion that the ocean $p\mathrm{CO}_2$ increase exactly follows that in the atmosphere, comes in part from measured or calculated $p\mathrm{CO}_2$ at 3 time-series stations (BATS, HOT, and ESTOC), where calculated atmospheric and oceanic trends are not significantly different (Bindoff et al., 2007). However, these stations are all located in subtropical gyres where both the air-sea flux of anthropogenic CO_2 and the corresponding air-sea disequilibrium are the lowest (Figure 2 in Sarmiento et al. (1992)). In short, the subtropical gyres are the worst place to look if one is trying to detect a non-zero air-sea disequilibrium ($\Delta\delta$pCO_2); it would be much better to look in the high latitudes, such as in the Southern Ocean. Although data-based methods that estimate anthropogenic C_T in the ocean find it convenient to assume that $\Delta\delta\mathrm{pCO}_2 = 0$, it has been recognized for years by some members of that community that that basic assumption does not hold in the real ocean (Orr et al., 2001). The lingering question then is how much of an error does that erroneous assumption imply? We think our simulations and particularly our tests of TTD in the model world offer a quantitative response for the Mediterranean Sea.

The reviewer is correct that our model's air-sea disequilibrium reaches 15% and even more in some places. In terms of the air-sea difference in δpCO_2, our $\Delta\delta$pCO_2 varies between 14 and 20 ppm in 2001, equivalent to the ocean $p\mathrm{CO}_2$ increase lagging that in the atmospheric by 20% since 1850 (Fig. 1 in this response). But we do not find those numbers surprising. They fall well within the 6-to-40 ppm range estimated by a global model (Figure 2 in Sarmiento et al. (1992)).

1.2)

Why do you conclude that the TTD(MW) is an overestimate, and not the other way around (i.e. the deltaDIC from the model) an underestimate? I am not saying that is the case, but it is strange to me that the model is able to reproduce the surface CFC-12 concentrations very well, but the TTD(MW) is still lower than the observational based TTD values? Are you using the same routines and supporting variable values for these calculations? The base of this question is: why is the TTD(data) different from the TTD(MW) when the CFC-12 values are the same?

We think that the TTD approach in the model world provides an overestimate of the δDIC because it assumes that the air-sea disequilibrium in anthropogenic CO_2 is null ($\Delta\delta pCO_2 = 0$), as elaborated above. That is, its oceanic $\delta p CO_2$ is too high, making its δDIC too high. There is no evidence to suggest that at the surface the simulated δDIC is too low (inconsistent with the model world circulation, ocean chemistry, and atmospheric CO_2). The chemistry is straightforward and well constrained, following best practices. The simulated flux of anthropogenic CO_2 is relatively insensitive to the gas exchange coefficient (Sarmiento et al., 1992). Ocean biology does not play a role, by definition. In the revised version of the manuscript, we will thoroughly discuss these concerns raised by Referee #2.

As described in the manuscript, coefficients for our perturbation approach were derived using the same carbonate chemistry routine (carb from seacarb) with the set of constants recommended for best practices, as used in our simple tests that assumed thermodynamic equilibrium.

Actually, the δC_T estimated by applying the TTD approach in model world (TTD(MW)) is similar to the TTD estimate of δC_T from observational data (TTD(data)) as shown in Fig. 2 (in this response) when CFC-12 concentrations are similar. In those cases, differences remain less than 10%.

2) We know that the model underestimates the strength of the deep overturning circulation in the Mediterranean from the too low CFC-12 values in the model. The model is roughly half of the observations over close to 2000 meter depth interval. Presumable the too low CFC-12 concentration in the model corresponds to a too low Cant concentration in the model. However, no attempt is made to quantify this difference. I can imagine many ways to do this, from "tuning" the model to match observations (of CFC-12), or more simple calculations based on relationship between CFC-12 and Cant for the Med. At any rate this should be done for the model Cant inventory calculations. As it stands now you present a value of Cant that you KNOW is an underestimate and state since this is lower than the TTD(data) estimate, the TTD(data) estimate has to be an upper limit. You might be correct with that statement, but it is not proven with the current data. Also, the point brought up above (1) suggest that the model Cant inventory is an underestimate by even more than the too low CFC-12 values suggest. These two points requires some careful analysis and discussion, and might have implications for discussion on pH and flux through the Strait of Gibraltar.

In the revised manuscript we will offer a more careful analysis and discussion. For now, let us try to clarify what seems to us as misunderstandings of our approach and our conclusions.

Concerning our approach, we simulate CFC-12 and compare it to observations to evaluate the simulated circulation, particularly the model's ventilation of deep waters. That is standard practice in the modeling community. Our goal was never to use the CFC-12 data to actually adjust and tune the model. Tuning a general circulation model is a huge task, unlike simple box models. To do what is suggested by Referree #2, tuning our general circulation model with the CFC-12 data, would require implementing an adjoint or inverse approach. Moreover, it would change the overall approach from being prognostic (predictive) to being diagnostic. For our simulations, the model must be prognostic, i.e., free to be perturbed by realistic, interannually varying boundary conditions (e.g., heat and water fluxes as well as wind fields). Furthermore, an inverse approach typically alters temperatures and salinities below the surface, necessarily with subsurface artificial additions or subtractions of heat and salt which are completely unphysical. For these reasons then, we stay with prognostic modeling approach for this study.

Although both CFC-12 and anthropogenic CO_2 can be treated as passive, transient tracers, they have different solubilities, air-sea equilibration times, atmospheric histories, and penetration depths. Hence we consider it inappropriate to adjust simulated δC_T results by using CFC-12 results. Philisophically, we think it is of greater value to know that a model is a lower limit than to try to adjust it in inexact ways to be a "best estimate" with unknown uncertainties and biases. Bracketting the real behavior seems more rigorous to us than to go for a best estimate.

As for our conclusions, unlike what is stated by Referee #2, we do not consider that TTD(data) is an upper limit just because its estimates are higher than those from the model. Rather, we consider that TTD overestimates $\delta\mathrm{C}_T$ because in the model world it overestimates simulated anthropogenic C_T. Furthermore, we know that at least part of the cause is that TTD assumes $\Delta\delta p\mathrm{CO}_2 = 0$. That the latter must be non-zero can be demonstrated by even the simplest of box models with finite gas exchange, and by the basic equation $F = \mathrm{kg}\,\Delta\delta p\mathrm{CO_2}$, as discussed previously.

We will do our best to clarify the misunderstandings raised by Referee #2 in the revised manuscript.

Specific comments:

Abstract and possibly elsewhere: Are you referring to uptake (as in air-sea exchange) or to increased interior storage of DIC? The term uptake is maybe not what you want to say, please check and modify. Maybe storage would be a better word to use.

Good point. We will clarify differences between storage and uptake in the revised manuscript.

Page 6464, line 18:I am not sure the “south of” is correct here. I suggest to leave that out since the deep water is/was actually formed in the Adriatic and in the Aegean (including south of the Aegean during the EMT).

Good advice, which we will follow in the revised manuscript.

Figure 1: The sections of the two Cant estimates are identical, so why is the average profile of TrOCA much more shallow than the TTD profile? Please make them comparable.

The average profile of TrOCA is much shallower the that of TTD on each section because the TrOCA method requires more variables to make the computation; TTD only needs CFC-12. That is, some of TrOCA input variables were not available in the deeper bottles. We will clarify the cause of this difference in the revised manuscript.

Supplementary material: I do appreciate that you publish the scripts used for the calculations and the constants. However, please put some effort into making this easily readable in a pdf version as well (keep the dat and R files since I assume they can be directly read by the code).

We will provide a listing of the R script as a PDF file and include that in the Supplementary Material of the revised manuscript.

I could not find table A1, for instance.

Table A1 refers to that in Wanninkhof (1992), not ours. We used the standard approach to cite an already published table (Wanninkhof 1992, Table A1), as advised in the Guide to Authors. If there is a better way, we would be happy to change our text.

Page 6471, line 20: Please remove "exactly", same for page 6473, line 5.

We will remove "exactly" from the revised manuscript.

Page 6474, line 11: Do you mean that the DIC was in equilibrium with the atmosphere, rather than the alkalinity? Please reformulate.

Thanks for pointing out this confusion. We meant that for the purposes of our perturbation apporach, we assume that preindustrial C_T is in thermodynamic equilibrium with both prescribed surface alkalinity and atmospheric xCO_2. We will clarify this point in the revised manuscript.

Section 3.4: Would it be appropriate to call this section "modelled deltaCT inventory"?

Good suggestion. In the revised manuscript, we will rename this section to "Simulated δC_T inventory".

Page 6478, line 25: Please state that (again) that you are referring to modelling "data" wrt poor ventilation; the observations seems to be different.

We do not understand why this sentence is confusing to the Referee. We state that "let us simply compare model results to the TTD data-based estimates of δC_T estimated from observations". Nonetheless, we will try to clarify further in the revised manuscript.

Section 3.5: I had some problems keeping the "model underestimate the data based estimates" terminology in this section. Maybe it would help rephrasing (on several occasions) to state "the model deltaCT is lower than the data based TTD results", or something like that.

This rephrasing does seem an improvement and will be considered more generally for the revised manuscript.

Page 2478,line 25: change “ estimated from” to “ based on”.

In the revised manuscript, we will make this change as well as remove “data-based” to avoid redundancy.

Section 3.6: The low Cant in the modelled surface, see above discussion on low Cant in the surface, also impact this discussion that might need to be reconsidered.

We will modify this discussion to clarify the general points we have made above about the comparison of simulated δC_T with the corresponding TTD data-based estimates.

Figure 14: Please change legend in the right hand panel to “deltaDIC TTD(MW)”

We will make this change in the revised manuscript.

Page 6488, line 3: add “poorly ventilated vs. observations- It could be appropriate to cite studies comparing various data based Cant estimates somewhere in the discussion where the TrOCA, DeltaC* and TTD results are compared (for instance (Yool et al., 2010;Álvarez et al., 2009;Vázquez-Rodríguez et al.,2009)).

In the revised manuscript, we will cite these studies, although they did not include comparison of these techniques applied to data in the Mediterranean Sea. In the Med Sea there is generally larger disagreement, e.g., between TTD and TrOCA (see Fig. 1 in the submitted manuscript).

References

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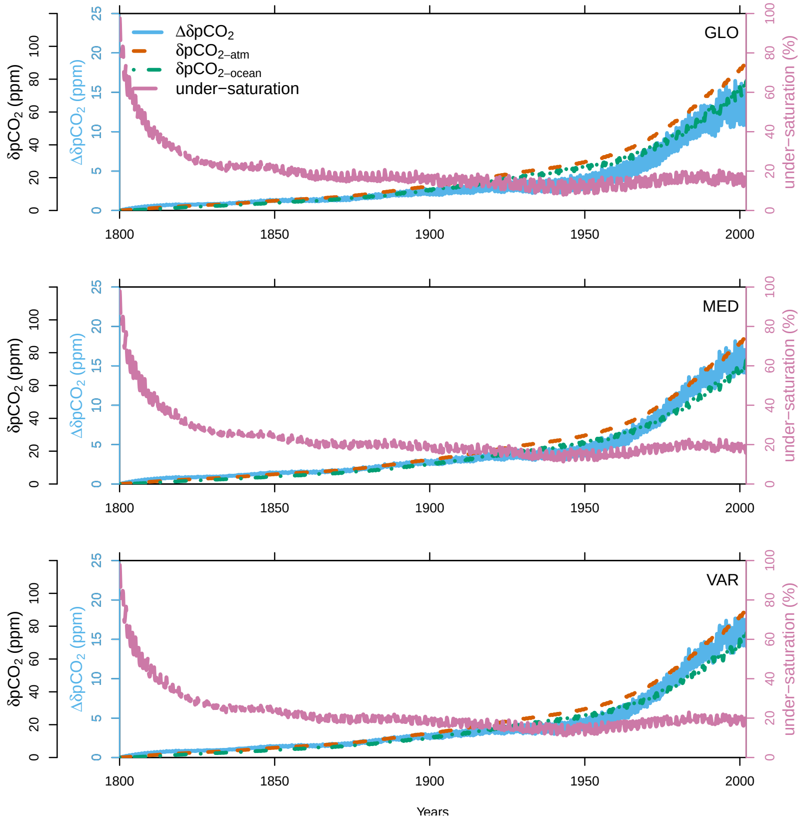

Figure 1. Temporal evolution from 1800 to 2001 of spatially avarage δpCO$_2$ (in ppm) in the atmosphere (dashed orange), the ocean (dashed-dotted green), and their difference difference $\Delta\delta$pCO$_2$ (solid light-blue line). Also shown is the corresponding percent undersaturation of oceanic δpCO$_2$ (long dashed purple), defined as $100\left(1-\left(\frac{\delta pCO_{2\,oc}}{\delta pCO_{2\,atm}}\right)\right)$.

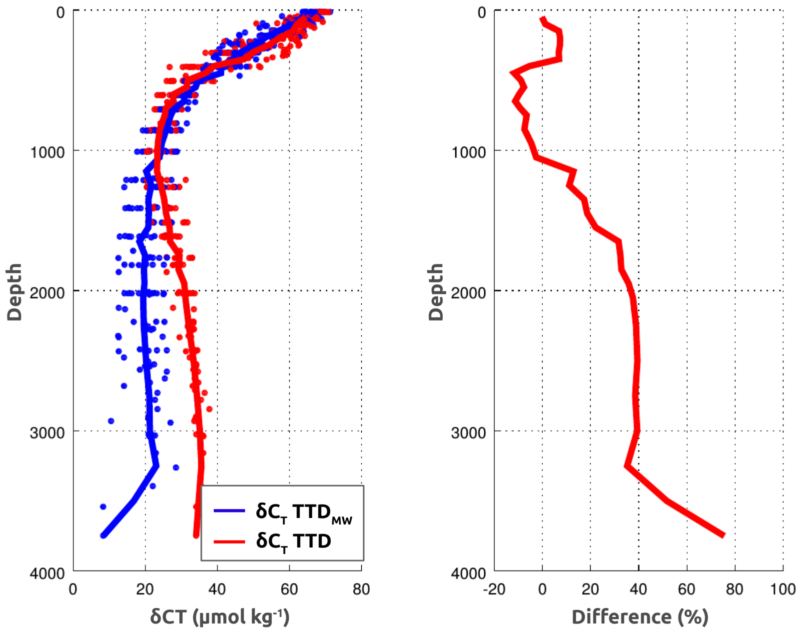

Figure 2. Average profiles of δC_T from the TTD approach using model results (TTD_{MW}, blue) and observational data (TTD, red). Shown are (left) all data (and corresponding model output) along the METEOR 51/2 section (points) and averages (solid lines), and (right) the percent difference betweeen the two averages.