Simulated anthropogenic CO₂ uptake and acidification of the Mediterranean Sea

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1 Response to Referee #1 (Marta Alvarez)

We are grateful for the assessment by Referee #1, whose comments are repeated below (in gray) with each one followed by our response (in black).

This work deals with a relevant topic for the Mediterranean Sea environment. This marginal sea suffers a high human pressure in different social, economical and environmental issues. The present work tries to estimate the anthropogenic CO2 uptake and storage and the directly derived pH decrease (acidification) in the water column in this practically closed system using a modelling approach. This issue is of particular interest to the referee. I agree that the work tries to address relevant questions for the oceanographic community working the MedSea but also for policy makers and it deserves publication in Biogeosciences but first it needs some MAJOR IMPROVEMENTS regarding the comments below.

We are happy that Referee #1 feels that this work should be published after some revisions.

I guess that applying your model results to one or other data base in the Mediterranean Sea is not a major issue if the cruises are recent and coherent in the CO2 data. Although I am biased, I really miss some reference to Álvarez et al. (Oc. Science 2014), this data was available in CDIAC from mid 2012 [http://cdiac.ornl.gov/oceans/Coastal/Meteor_Med_Sea.html] and it could have been used to get a better resolution of alkalinity, combining both 2001 and 2011 data sets. I am aware of other basin-scale cruises but the data is not so easily available. Although no TTD results are available for the 2011 data set, the directly measured tracer concentrations are contained in the data base.

Unfortunately, Alvarez et al. (2014) was not published before we designed our simulations, ran them, and compared them with the TTD data-based estimates. Nor does that publication provide a relationship for total alkalinity vs. salinity in the Med Sea. Our objective was not to derive a new salinity-alkalinity relationship, a noble goal but not within our remit of simulating anthropogenic CO₂ uptake. Instead, we used the published surface salinity-alkalinity relationship from Schneider et al. (2007) to derive the coefficients used for the perturbation approach in one of our 3 simulations (VAR). Results from the other 2 simulations do not depend on a variable salinity. Another reason for that was that the same salinity-alkalinity relationship was
used in the TTD method of Schneider et al. (2010), which provided internal consistency with the rest of the study. We consider that the carbonate system and hydrographic data collected on the older 2001 cruise (METEOR M51/2) was of high quality and adequate for our purposes. Regardless of these concerns, we have now read Alvarez et al. (2014) and will cite it in the revised manuscript.

1) One of my main concerns is commented in the Introduction, last paragraph in page 6464 and first paragraph in page 6465: the MedSea is warming and getting saltier at higher rates than any other ocean, ventilation of deep waters is much faster as well, in addition, it has a very peculiar CO2 chemistry (Álvarez et al., 2014). So I wonder if your model approach is somehow simplistic (I am not a modeller, so please excuse me!), does your model consider changes in salinity and temperature and how they affect the CO2 chemistry (TA for example), and even more, we know that the Revelle factor increases as pCO2 increases, making the waters less able to store CANT. I know it is complicated but the options in the model GLO-TA as in the global ocean, Med: mean TA equal to MedSEa values and VAR: salinity variations taken into account although interesting, could go a little bit further. What happens to the VAR option if including temperature & salinity increase and the feedback in the CO2 system? Maybe using the temporal change in the buffer factors (as defined in Egleston et al. but formulated correctly in Alvarez et al 2014) could help to calculate the change in the CO2 system.

Of course, our model is a simplification, by definition. However, we do indeed account for physical changes (temperature and salinity increases) and the Med Sea’s rapid ventilation of deep waters. Our physical model is driven by reanalysis data over roughly the last 50 years. Thus, we force the model with observed winds, heat fluxes, and water fluxes (evaporation minus precipitation) during that time. The modelled Med Sea also has more rapid ventilation of deep waters in our model of the Med Sea (relative to the global ocean), although it is still too weak, based on CFC-12 evaluation, as we point out in the manuscript.

For carbonate chemistry, we used the equations and constants recommended for best practices to derive our perturbation approach. With this approach our model certainly does account for the increase in the Revelle factor (reduced buffer capacity) as atmospheric CO$_2$
increases. There is no need for us to use the buffer factors from [Egleston et al. (2010)](https://doi.org/10.1007/s11356-010-0563-5) for the model simulations. The effects of increases in temperature, salinity, and CO$_2$ are all included in our model. We shall try to make this clearer in the revised manuscript.

2) Section 2.2.2 Anthropogenic carbon. I am sorry but I do not get the message from here. The driver is the pCO$_2$ atmospheric increase, $\delta$pCO$_2$ ocean is calculated from the only tracer that is carried in the model $\delta$C$_T$ (page 6470, lines 14-15) using Eq. 12 & 13. So why do you calculate $\delta$pCO$_2$ ocean?, is it needed in the model for something additional?. I do understand that $\delta$C$_T$ is calculated as the difference between the preindustrial value and the new one in time $x$ as a function of pCO$_2$ air in time $x$, TA, temperature and salinity (page 6471). And in the VAR simulation TA is calculated from Eq 11, in the other two is constant. SO I do not get why do you need $\delta$pCO$_2$ ocean and the empirical Eq. 13.

We must calculate oceanic $\delta$pCO$_2$ from $\delta$C$_T$ because we need the former to compute the air-sea flux of anthropogenic CO$_2$ (see equation 5) and only the latter is transported as a passive tracer in the model. That is, in our model the oceanic $\delta$pCO$_2$ is not the same as the atmospheric $\delta$pCO$_2$, unlike in equilibrium calculations that assume that the two are equal. The two must be different for there to be an air-sea flux of anthropogenic CO$_2$, both in the model and in the real ocean. Our equation 13 is actually the 3 equations for the coefficients that are needed to compute $\delta$pCO$_2$ from $\delta$C$_T$ in equation 12 (for the VAR simulation). Without these relationships we could not compute the air-sea flux of anthropogenic CO$_2$. We did explain this in the Discussion paper, but we will try to clarify further in the revised manuscript.

3) Section 2.3 Looping.
Sorry again but I am afraid that only modellers would understand this section. It could be nice to explain for lay people what means “run off-line, looping through the circulation fields...”.

In the revised manuscript, we will improve this section to be more understandable to non-modelers, in particular to better explain the offline approach and the looping. Offline means that first a simulation is made with the general circulation model (circulation model only), and then those simulated circulation fields are used later to drive other simulations that
include additional passive tracers such as $C_T$. Offline simulations are done for computational efficiency. They allow us to read in precomputed transport fields instead of recomputing them, which is very costly. They also allow us to make sensitivity tests (e.g., our simulations GLO, MED, and VAR) that use exactly the same circulation fields each time.

4) Section 2.4 $\delta$pH.
For surface or deep waters you would need to clarify if $\delta$pH refers to in situ pH or to pH is referred to any temperature, pH is mostly temperature dependent, but also pressure. I understand that the pH decrease in the water column is calculated for in situ temperature and pressure. But I think it needs to be clearly stated.

In the revised manuscript, we will clarify that we always refer to in situ pH. This is standard practice for modellers. We will also mention the pH depends on temperature and pressure.

5) Section 3.2 Air-sea flux.
Please make clear that you refer to CANT air-sea fluxes and the way they are calculated: do you calculate the storage (inventory), the transport across the Strait and then the air-sea is derived from them, or the other way, the air-sea CANT flux and storage are calculated from the model and the transport across the Strait is derived from them.

In the revised manuscript, we will make it clearer that the text always refer to anthropogenic carbon for concentrations, fluxes and transport. We will also further clarify how things are calculated. In short, we directly simulate the air-sea flux of anthropogenic CO$_2$ and the build up of anthropogenic $C_T$. Inventories are calculated as vertical integrals of the latter. Lateral fluxes of anthropogenic carbon at the Strait of Gibraltar are computed from the model’s advective fields and its simulated anthropogenic $C_T$. We have verified that the modeled storage of anthropogenic carbon (basin-wide inventory) is equal to the air-sea flux of anthropogenic carbon plus the net lateral transport across the Strait of Gibraltar. That is, the model conserves mass.
6) Section 3.3 Budget.
I understand in Fig. 8 that the light blue solid curve (inventory) is the sum of the green solid one (air-sea flux) plus the Gibraltar transport (solid purple). But I do not understand Fig. 9, what is the light blue dashed line (total storage) here?. I would plot the rate of change of the storage with time and the % contribution to it of the air-sea flux and the Gibraltar transport.

In the legend to Fig. 9, we will clarify (1) that the dashed purple line is the percent of total \( \delta C_T \) that outflows at the Strait of Gibraltar and (2) that total storage (light blue dashed line) is the percent of total \( \delta C_T \) that has entered Mediterranean Sea that remains in the Mediterranean Sea (total inflow minus Gibraltar outflow). The reviewer makes an interesting suggestion to plot instead of the cumulative change, the annual rate of change of the storage with time along with its contribution to the air-sea flux and Gibraltar transport. We will make this plot, and if it does indeed seem clearer, we’ll include it in the revised manuscript.

7) Section 3.6 \( \delta pH \).
It might be interesting to present the GLO results just to show that the MedSea is particular, but presenting the MED and VAR results as well it is a bit blurring. The consequence of smaller pH changes in warm waters with a higher TA is a direct consequence of the CO\(_2\) chemistry, eastern MedSea waters have the lowest DIC/TA ratio and consequently are more resistant to changes due to a DIC increase due to air-sea CO\(_2\) exchange (DIC increase, TA constant). This is shown in Alvarez et al. (2014).

If we understand the first criticism correctly, the reviewer suggests that we show results only for the GLO simulation and either the MED or VAR results. We do not agree. We must discuss results from all three simulations in order to demonstrate the sensitivity of the pH change to alkalinity and to quantify the extent to which spatial variability of alkalinity matters.

Referee #1 is correct to point out that higher \( A_T \) implies a smaller rate of change of pH with respect to the CO\(_2\) increase (\( \partial pH/\partial pCO_2 \)). However, the difference is small as discussed below. Moreover, others have suggested just the opposite, that the Med Sea’s higher alkalinity implies a higher rate of acidification (Touratier and Goyet, 2011).

In the revised manuscript, we will present additional analyses to adress this concern more quantitatively. As a start, we will show recently completed equilibrium calculations of
\[ \partial [\text{H}^+] / \partial pCO_2 \]. For more details, see our answers in section 11, Fig. 1 in this response. These calculations were made using the corrected equations from Egleston et al. (2010), made available as a new routine (buffesm) in the seacarb package by Orr (2011). They demonstrate that \( \partial [\text{H}^+] / \partial pCO_2 \) is only 8% lower in the eastern basin at its maximum \( A_T (2650 \ \mu\text{molkg}^{-1}) \) relative to the western basin’s minimum \( A_T (2380 \ \mu\text{molkg}^{-1}) \). Slightly less than the western minimum is the global ocean’s average alkalinity of 2300 \( \mu\text{molkg}^{-1} \). These equilibrium rates will also be compared to those computed from model output.

In addition, we will focus on the change in \([\text{H}^+]\). The model’s average simulated anthropogenic increase (1800–2001) in \([\text{H}^+]\) is only 1% less in the eastern relative to the western basin (VAR simulation in Table 1 below). One might expect then that the corresponding pH reduction would also be slightly less in the east, but it actually turns out to be slightly more (by 0.0004 units). That apparent discrepancy is really just due to taking differences on a log scale. Absolute differences in pH actually reflect a relative change in \([\text{H}^+]\); they depend on the initial state, which also differs between east and west. In any case, the difference is small, requiring 4 digits after the decimal to detect it.

The revised manuscript will further clarify the relationship between the rate of acidification and alkalinity. It will demonstrate quantitatively the extent to which the Mediterranean’s acidification rate is less than the global ocean average.

I think is very simplistic the last phrase in this section. If the pH change is so similar with any model simulation why bother to perform them. I do not think is identical, I do think that the spatial variations matter. But I would also ask if the yearly temporal changes are comparable to the seasonal changes?.

From the context, it appears that the Referee is not actually referring to the last sentence in this section but the last sentence in the 3rd to last paragraph (p. 6486, lines 21–24): “Although the higher alkalinity of the Mediterranean Sea enhances its anthropogenic carbon content by 10%, the anthropogenic reduction in surface pH is not significantly different from that for typical surface waters of the global ocean.” In the revised manuscript, we will change that sentence to, “The Mediterranean Sea’s higher alkalinity, relative to the global-ocean average, enhances
its anthropogenic carbon content by 10% while reducing its average anthropogenic change in surface acidity ([H\(^{+}\)]) by 8%. However, the corresponding pH changes differ by only 0.001 unit, an artefact of taking differences on a log scale.”

Regarding the seasonal cycle, we prefer to leave that to future work, particularly because seasonal variations may largely be dominated by the cycle of natural CO\(_2\), which we do not model.

8) Section 4.1 \(\delta C_T\) in the MedSea.
I am not a TTD expert but I miss some details about the TTD setting in Schneider et al. (2010), although also discussed in this paper, the \(\Delta/\Gamma\) ratio matters to calculate CANT. This ratio needs to be commented regarding the 2010 paper and the settings in the model.

In the revised manuscript, we will clarify what was done for the TTD approach. In particular, we will state that for consistency we have used exactly the same approach and settings as elaborated in \cite{Schneider2010}. That allows a rigorous comparison of TTD \(\delta C_T\) estimates from CFC-12 measurements and model results. Both studies used \(\Delta/\Gamma = 1\), which is appropriate for the interior ocean \cite{Waugh2004}.

9) Section 4.2 Transfer across the Strait of Gibraltar
Page 6481, lines 26-27: I totally disagree with this statement, in the global ocean the transport of CANT matters a lot, and there is a wealth of reference dealing with this point. This section is too long for the final conclusion achieved, it might be good to reduce the information given with numbers.

We do not understand why the Referee disagrees with the cited sentence (p. 6487, lines 26-27): “Unlike the global ocean where outside input of anthropogenic carbon comes only from the atmosphere, in the Mediterranean Sea there is also lateral input and output of anthropogenic carbon via the Strait of Gibraltar.” We think this is obvious even without having made any simulation. Perhaps, the Referee is referring to another sentence? In any case, we certainly agree with her that the transport of \(\delta C_T\) matters a great deal, both in the global ocean and in the Mediterranean Sea; we never say otherwise. Our point on the source of the anthropogenic
carbon is important though. Whereas for the global ocean, all the anthropogenic carbon inventory comes from the air-sea CO₂ flux, in the Mediterranean Sea, 25% of the inventory comes from net transport across the Strait of Gibraltar. As for the length of this section, we will do our best to shorten it in the revised manuscript following the reviewer’s recommendations.

10) Section 4.3 Sensitivity to TA
As commented previously, using the better resolution of the M84/3 2011 data to constrain TA and the information given in other papers for the contribution of riverine TA would improve the model results. I think that discussing the GLO results is trivial. This section needs to be reduced.

We have already addressed the Referee’s first remark in detail in previous responses. For the second remark, we do not understand why the Referee thinks that the GLO results are trivial. We think GLO is critical as a reference having the same total alkalinity everywhere as the mean for the global ocean. Only by comparison with the GLO simulation can we demonstrate how much the total alkalinity matters in terms of basin-wide uptake of anthropogenic carbon. We do not think that the results for the GLO simulation could have been guessed ahead of time, e.g., that its basin-integrated air-sea flux would be 25% lower than in the other 2 simulations, while its anthropogenic carbon inventory would be 9% less. For these reasons, we do not intend to reduce the length of this subsection, which takes up only 3.5 short paragraphs.

11) Section 4.4 Change in pH.
Page 6486, line 2-4: sorry to say, but your sensitivity test do not demonstrate anything, the direct consequence of the low DIC/TA ratio in the eastern MedSea is the lower change in pH (due to air-sea CO₂ exchange) compared to waters with a higher DIC/TA ratio, this is shown in Alvarez et al with the 2011 data, but is a direct consequence of the CO₂ chemistry, anybody could simulate this using DIC, TA, Temp and salinity from the MedSea.

If the referee failed to see the interest of our sensitivity tests, then we failed in communicating it. In the revised manuscript, we will take on this challenge while relying on a new, more targeted analysis of how the acidification rate is affected by total alkalinity as well as other key factors,
temperature, salinity, and the air-sea disequilibrium. In the sentence referred to by Referee #1, we stated that “the higher total alkalinity of the Mediterranean Sea does not result in a greater anthropogenic reduction in surface pH.” We admit that they are not exactly identical but they are very close. In the revised manuscript, we will be more quantitative and discuss the change in \( H^+ \) as well as pH. For the latter, basin-wide means in our 3 simulations are identical to 2 decimal places (as listed in a new Table, given below as Table 1).

Our enhanced assessment will clarify precisely how much the rate of acidification \( \partial[H^+] / \partial pCO_2 \) of the Mediterranean Sea differs because of its higher alkalinity. For simplicity, we will first show equilibrium calculations of \( \partial[H^+] / \partial pCO_2 \) using analytical equations of Egleston et al. (2010) as corrected by Orr (2011), as detailed in his contribution of the ‘buffesm’ routine of the seacarb carbonate system software package. A new figure will be shown with \( \partial[H^+] / \partial pCO_2 \) that was calculated by varying alkalinity from the minimum observed in the western basin (2380 \( \mu \)mol kg\(^{-1}\)) to the maximum observed in the western basin (2650 \( \mu \)mol kg\(^{-1}\)) and assuming equilibrium with atmospheric CO\(_2\). Temperature and salinity were held at the minimum values observed in the western basin during summer.

The Mediterranean’s west-to-east increase in alkalinity alone reduces \( \partial[H^+] / \partial pCO_2 \) by 8% (see new figure below, referred to here as Fig. 1). Then after including the west-to-east temperature increase (6\( ^\circ \)C during summer) the \( \partial[H^+] / \partial pCO_2 \) is reduced by another 0.5% (i.e., for the east relative to the west). But the temperature reduction in \( \partial[H^+] / \partial pCO_2 \) is compensated by the west-to-east increase in salinity (3 units on the practical salinity scale) during summer. For comparison, there is a 2% decrease in \( \partial[H^+] / \partial pCO_2 \) as atmospheric xCO\(_2\) increases from 280 to 385 ppm and another 4% decrease when atmospheric xCO\(_2\) increases further to 850 ppm.

The model’s surface acidification rates are slightly less intense, because it does not make the simplification that atmospheric and oceanic \( pCO_2 \) are identical (i.e., in equilibrium). Another new figure shown below (Fig. 2 in this response) shows the model’s average simulated \( \partial[H^+] / \partial pCO_2 \) per band of longitude (meridional mean) both in 1800 and in 2001 for each of the 3 simulations. It also shows the corresponding change in \([H^+]\) (nmol kg\(^{-1}\)). The acidification rate is 8% lower in MED (\(~17.5\; \text{pmol kg}^{-1}\; \mu \text{atm}^{-1}\) in 2001) than in GLO (\(~19.1\; \text{pmol kg}^{-1}\; \mu \text{atm}^{-1}\) in 2001). In VAR, the \( \partial[H^+] / \partial pCO_2 \) decreases by 8% in 2001 when moving from
west to east (from $\sim 18.5$ to $\sim 17$ pmol kg$^{-1}$ µatm$^{-1}$). That modeled west-to-east gradient is much like that found with the thermodynamic calculations, but curves are displaced downwards by 0.3 units.

The higher alkalinity of the Mediterranean Sea, relative to the global ocean, reduces its anthropogenic change in acidity ([H$^+$]) by 9% on average, but the average change in the eastern basin is only 1% lower than that in the western basin (Table 1 below). The latter is less even than estimated by the equilibrium calculations. The Referee was right to emphasize that there are differences in rates of acidification due to alkalinity. In the revised manuscript, we will demonstrate that the differences are small.

Referee #1’s final point that anyone could determine the effect of alkalinity on the acidification rate should be nuanced. Certainly almost anyone could make equilibrium calculations, but few have. Perhaps only two studies have touched on the issue with respect to the Mediterranean Sea (Orr, 2011; Alvarez et al., 2014). We are the first to discuss model simulations in the Mediterranean Sea, which do not assume air-sea equilibrium and take into account other physical factors that equilibrium calculations cannot. Moreover, opposite conclusions from others (Touratier and Goyet, 2011) point to a general lack of understanding surrounding this issue. We hope that our revised manuscript will help close the debate.

References


Table 1. Average changes in pH and $[H^+]$ between 1800 and 2001 for the three simulations for the Mediterranean Sea and its western and eastern basins.

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<th>$\delta$pH</th>
<th>$\delta[H^+]$ (nmol kg$^{-1}$)</th>
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<tr>
<td></td>
<td>West</td>
<td>East</td>
</tr>
<tr>
<td>GLO</td>
<td>-0.0851</td>
<td>-0.0849</td>
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<tr>
<td>MED</td>
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<td>-0.0848</td>
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<td>VAR</td>
<td>-0.0833</td>
<td>-0.0837</td>
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Figure 1. Acidification rate ($\partial[H^+]/\partial pCO_2$, in pmol kg$^{-1}$ µatm$^{-1}$) as a function of alkalinity varied over the observed Mediterranean range (2380 to 2650 µmol kg$^{-1}$) for 3 different atmospheric xCO$_2$ levels in 1765 (280 ppm, solid light-blue line), 2008 (385 ppm, solid green line) and 2100 (850 ppm, solid purple line). Also shown are lines for 2008 to illustrate the effects of also varying temperature (dashed orange) and temperature and salinity (dotted blue) over the observed west-to-east range.
Figure 2. Meridional mean of the acidification rate $\partial[H^+]/\partial pCO_2$ in pmol kg$^{-1}$ $\mu$atm$^{-1}$) in 1800 (dashed orange) and in 2001 (dashed-dotted green) in the Mediterranean Sea along with the corresponding [H$^+$] change between 1800 and 2001 in nmol kg$^{-1}$ (solid light-blue). Meridional means are taken from all grid cells with salinities above 32, thus avoiding bias from river mouths.