

Re: “A 1-D examination of decadal air–sea re-equilibration induced ocean surface anthropogenic CO₂ accumulation: present status, changes from 1960s to 2000s, and future scenarios” by Zhai and Zhao (Biogeosciences Discuss., 11, 11509–11532, 2014)

We thank the three referees for their comments and constructive suggestion. All of them have been incorporated in the modified MS.

Point-by-point responses have been made in the supplement.

Enclosure: revision statement

Response to comments by the anonymous referee #1 (BGD, 11, C5721–C5722, 2014)

I like many parts of this manuscript. The conclusions and methodology are broadly correct, but the manner of presentation is so awkward as to greatly diminish the usefulness of the paper.

[Response: We thank the referee for his positive comment. In the modified MS, we have reorganized the paper so as to make it clearer.](#)

Basically it begins with an inappropriate Introduction of a very general nature. But on reading this through I find it might be much better presented as a step forward in a classic series of papers in which ocean scientists have periodically reviewed (re-discovered?) the ocean chemical buffer factor. This is many ways quite a beautiful history, and it seems to be updated about once every decade – so the time for this is ripe. It would help the reader if it was presented in this way. A casual history might find a time line of continuous improvement from Callendar (1938) who recognized alkalinity as a control but did not appreciate the buffer factor, through the 1957 Revelle and 1960 Bolin papers, the work of Dyrssen and Sillen in 1967, the extraordinary efforts of Broecker and Takahashi in the early 1970s and the paper of Whitfield in 1974, the update by Sundquist and colleagues etc etc. Seen in this way the work here is a step forward in a classic series – with each decades improvement overlaid on others.

[Response: In the modified MS, we have modified the Introduction accordingly. In the new Introduction, we have presented the historical review of chemical buffering capacity. Thanks the referee for his constructive suggestion.](#)

Here the novelty is the very careful use of the newly reported mapped surface fields. The authors have obviously put a lot of work into dissecting and assimilating the now large array of surface mapped data.

[Response: We thank the referee for his positive comment.](#)

They point to the small discrepancy between competing estimates of ocean CO₂ uptake rates, and they refer these back to fundamental property of (rediscovered?) a changing buffer factor. It makes sense. But the argument is so badly presented that the message is lost.

[Response: Oceanic anthropogenic CO₂ uptake is driven by multiple mechanisms. We only use those earlier estimations as reference values, so as to show that the decadal air–sea re-equilibration induced ocean surface anthropogenic CO₂ accumulation serve as a non-negligible component of oceanic anthropogenic CO₂ sink.](#)

The manuscript is so full of notation and jargon as to lose the non-specialist the paper should be aimed at. The endless repetition of “DIC/xCO₂air” is particularly grating.

Response: In the modified MS, we change those unnecessary notations into words.

For details I can't see exactly what is meant by lines 26-28 on page 9.

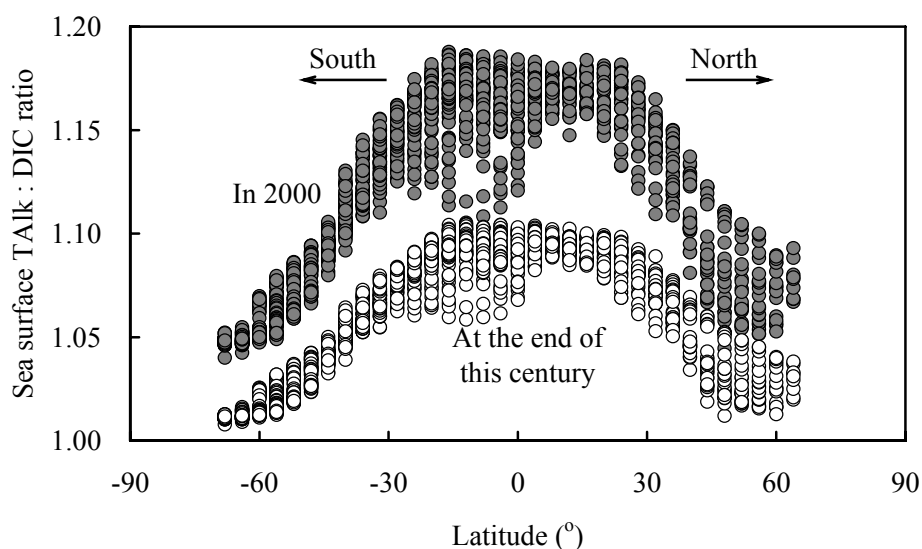
Response: In the modified MS, this sentence has been changed into “Considering another global mean air–sea CO₂ exchange time of ~5 years adopted by earlier box model researchers (e.g. Craig, 1957; Bolin and Eriksson, 1959), our global mean $\tau(\text{CO}_2)$ value of 302 days reasonably suggested that the wintertime mixed layer had a time window of 60 days every year to serve as a gateway between the atmosphere and the ocean interior.”

And on page 14, lines 11-12 the comment seems odd given the large efforts of the CMIP teams.

Response: We have removed the odd sentence on original page 13 lines 11-12.

For the Figures I find Figure 3 puzzling, but Figure 4, although simple, is a classical update on a problem now at least 40 years old and still of interest and too little understood by those outside the ocean chemistry world.

Response: We have modified Figure 3 as below.



Response to comments by the Referee W.-J. Cai (BGD, 11, C6193–C6194, 2014)

I first read Zhai and Zhao manuscript five weeks ago. After much struggling through it, I concluded that this is a quite informative writing on an old but quite interesting topic. I felt the authors made a good progress along the line of previous works using recently available surface mapping results of pCO₂. I also believed the technical approaches are sounds (I had a few email exchanges with the lead author on technical details). But I hesitated to write my recommendations on what path they should take to improve this paper. I now read the other referrer's suggestion and believe that is a good one to make this paper a combination of a mini review of historical contribution (literature), recent context (OA research made it even more important and interesting) and progresses, and their own new contribution.

Response: We thank the referee for his positive comment and constructive suggestion. In the modified MS, we have modified the Introduction accordingly.

Also, they should strive to make it flow better and easier to read.

Response: Done.

Finally, getting a professional English editorial service is highly recommended.

Response: Sure, we will ask a native English speaker to help us polish the English.

Response to comments by the anonymous referee #3 (BGD, 11, C6824–C6827, 2014)

This paper considers how the surface ocean carbon system might have varied over the last few decades in response to the anthropogenic CO₂ rise, using a combination of published observational products. Unfortunately, I must say that I struggled with this paper. First, I struggled to understand what exactly the authors had done. Second, I struggled to see how this calculation is a useful step forward.

Response: In the modified MS, we have reorganized the paper so as to make it clearer.

If I understand correctly, the calculation takes all required values as \uparrow present-day climatologies, and varies only the atmospheric pCO₂ over the time period at hand. The variable atmospheric pCO₂ enters the calculation as the global base value to which the 2-dimensional Takahashi year 2000 delta-pCO₂ is added. Thus, the 2d spatial climatology of Takahashi is held constant over time, and the values at each grid cell increase in step with the global atmospheric pCO₂.

Response: The referee's interpretation is correct. In the modified MS, we have clearly presented our assumption and methodology.

If my interpretation of the method is correct, I am not convinced that it is useful. That's not to say it isn't useful - but the paper does not clearly make the case. It would be helpful to explain better at the introduction, and also emphasize in the conclusion just why the results are valuable. Is the idea to better understand the carbon cycle? Is it to provide an observational constraint against which to test numerical models? Is it to gauge the impacts of ocean acidification? What is the real advance here beyond the Broecker et al. (1979) view?

Response: In the modified MS, we have reorganized the Introduction. The new Introduction focuses on the role of chemical buffering capacity in the oceanic CO₂ sink. And we changed the conclusion part into "Summary and implications", so as to explain why the results are valuable.

Is the idea to better understand the carbon cycle? Yes. This is the first try in recent 20 years to re-assess the role of chemical buffering capacity in the oceanic CO₂ sink. Our results show that the air-sea CO₂ re-equilibration led to a decadal anthropogenic CO₂ accumulation rate of 0.40 Pg C yr⁻¹ within the ocean surface, accounting for a non-negligible component of the recent oceanic anthropogenic CO₂ sink. It is worthy to note that compilation of field-measured air-sea CO₂ disequilibrium dataset shows a net air to sea CO₂ flux value in open oceans of only 1.6±0.9 Pg C yr⁻¹ for a reference year 2000 (Takahashi et al., 2009). Even if considering the coastal CO₂ sink, 0.2 to 0.4 Pg C yr⁻¹, the "best" estimate of the air-sea CO₂ disequilibrium induced flux across the global sea surface is still at a level of 2.0±0.6 Pg C yr⁻¹ (Wanninkhof et al., 2013), which is 0.2 to 0.5 Pg C yr⁻¹ lower than those well-documented oceanic

anthropogenic CO₂ sink results based on inorganic carbon measurements and tracer-based separation techniques. Our results suggested that the air–sea CO₂ re-equilibration induced anthropogenic CO₂ storage within the ocean surface reasonably closed the earlier gap between the tracer-based oceanic anthropogenic CO₂ sink estimation and the air–sea CO₂ flux compilation.

Is it to provide an observational constraint against which to test numerical models? Yes. The two US JGOFS time series study sites, i.e. the Hawaii Ocean Time series (HOT) and the Bermuda Atlantic Time-series Study (BATS), were used as checking values. Using our method, the wintertime DIC increasing rates were expected to be 1.14 μmol kg⁻¹ yr⁻¹ (HOT) and 1.20 to 1.28 μmol kg⁻¹ yr⁻¹ (BATS). Both were comparable to the field-measured increasing rates of sea surface salinity normalized DIC, i.e. 1.2 ± 0.1 μmol kg⁻¹ yr⁻¹ at HOT from 1988 to 2002 (Keeling et al., 2004) and 1.08 ± 0.06 μmol kg⁻¹ yr⁻¹ at BATS from 1983 to 2011 (Bates et al., 2012).

Is it to gauge the impacts of ocean acidification? Not exactly. Both of ocean acidification and the chemical buffering capacity decline are induced by the anthropogenic CO₂ accumulation within the ocean surface. They have the same cause. Therefore they work together.

What is the real advance here beyond the Broecker et al. (1979) view?

Response: Broecker et al. (1979) present their comprehensive results. The most important is they and Sundquist et al. (1979) together define Revelle factor as a homogeneous buffering factor for the first time. As for the issue of air–sea re-equilibration induced anthropogenic CO₂ sink, their analyses are nonobjective, presumably due to the insufficient knowledge about climatological TALK distributions and vertical mixing within the ocean surface until 1990s.

In this study, however, we attempted to link sea surface DIC change with the atmospheric CO₂ rise, using the potentials of wintertime DIC to rise after re-equilibration with the elevated atmospheric CO₂ mole fraction. It makes sense in a decadal period. Therefore, we have made progress as compared with earlier literatures.

If we are considering the importance for ocean carbon uptake, the mixed layer is most important as the gateway between the atmosphere and the ocean. The carbon contained directly in the mixed layer is a small amount of the total oceanic uptake, and the results here do not seem to make a significant change in our quantification of this uptake. Besides, the mixed layer depth is highly seasonal, changing by hundreds of metres at high latitudes. One might ask, why does it matter how much carbon is contained in the mixed layer? Again, maybe there is a good reason we should know this - but if so, I'm not sure what it is, and the paper has not pointed it out to me.

Response: Partially agreed. The anthropogenic CO₂ storage within the ocean surface

is a part of the total oceanic sink. Therefore the estimation of this CO₂ storage can not change the quantification of the total oceanic sink for anthropogenic CO₂. However, it is meaningful to identifying a component of >10% of the oceanic CO₂ sink. In the modified MS, we have point out that the earlier gap between the tracer-based oceanic anthropogenic CO₂ sink estimation and the air–sea CO₂ flux compilation has been closed, due to our estimation of anthropogenic CO₂ storage within the ocean surface (see above).

I hope these comments will help the authors to focus their work towards a product that will be useful to the community. I also offer a few additional, more specific comments below.

Response: Thanks for the critical comments and constructive suggestions. The revised MS has thoroughly taken your comments and suggestions into consideration.

p 11511: This sentence does not make sense: ‘The surface ocean uptake of anthropogenic CO₂ is just the case.’ Also, ‘This effect, chemical buffering capacity: : :’ is confusing, in that the chemical buffering capacity itself has not been introduced.

Response: The 1st sentence has been removed, while the 2nd sentence has been changed into “This ratio, traditionally named as Revelle factor...”.

R_{equ} is not well defined. Given that this is of central importance, it should be carefully defined.

Response: In the modified MS, we distinguish between the air–sea re-equilibration induced anthropogenic CO₂ accumulation rate at a unit area (*r_{equ}*) and the decadal air–sea re-equilibration induced anthropogenic CO₂ accumulation rate within the global ocean surface (*R_{equ}*). So the related statements and discussion flow better.

I’m not sure what is meant by the ‘eloquent definition’ of RF.

Response: We have deleted this unnecessary adjective.

I don’t follow what happens from the second to the third step here, please elaborate:

$$\delta \text{DIC} / \delta x \text{CO}_{\text{air}} = \delta \text{DIC} / \delta p \text{CO}_2 \hat{A}^{\circ} \text{u}(\text{P} \square \text{pH O}) = \text{DIC} / p \text{CO}_2 / \text{RF} \hat{A}^{\circ} \text{u}(\text{P} \square \text{pH O})$$

Response: Done.

To ..., we rewrote the definition of Revelle factor as:

$$\delta \text{DIC} / \delta p \text{CO}_2 = \text{DIC} / p \text{CO}_2 / \text{RF} \tag{1},$$

where prefix δ means a differential change, RF is Revelle factor. However, $p\text{CO}_2 = x\text{CO}_2 \cdot (P - p\text{H}_2\text{O})$, where $x\text{CO}_2$ means atmospheric CO_2 mole fraction in dry air, P is the atmospheric pressure at sea level, $p\text{H}_2\text{O}$ is saturated water vapor pressure. Ignoring the possible changes in atmospheric pressure and saturated water vapor pressure in those decades under study, the ratio of the potential sea surface DIC change to the atmospheric CO_2 change can be practically estimated as:

$$\begin{aligned} \delta\text{DIC}/\delta x\text{CO}_2 &= \delta\text{DIC}/\delta p\text{CO}_2 \cdot (P - p\text{H}_2\text{O}) \\ &= \text{DIC}/p\text{CO}_2/\text{RF} \cdot (P - p\text{H}_2\text{O}) \end{aligned} \quad (2).$$

This part of the method needs to be much better explained: ‘To illuminate the atmospheric forcing on the ocean surface carbonate system, we defined “steady-state sea surface $p\text{CO}_2$ ” in a given decade by scaling Takahashi et al. (2009) data (for a reference year 2000) to the change in $x\text{CO}_2$ from the corresponding time period.’ How scaled? Do you mean you assumed the $\text{D}p\text{CO}_2$ of Takahashi, i.e. the surface disequilibrium, was constant over time, so that the $p\text{CO}_2$ at all points varies directly with global CO_2 ?

Response: The unclear sentence has been changed into “To illuminate the atmospheric forcing on the ocean surface carbonate system, we defined ‘steady-state sea surface $p\text{CO}_2$ ’ in a given decade by assuming the sea surface disequilibrium of CO_2 was constant over time. Therefore we can scale Takahashi et al. (2009) data (for a reference year 2000) to the change in atmospheric CO_2 mole fraction from the corresponding time period.”

I don’t like the idea of looking at local relationships between surface ocean DIC change and the atmospheric conditions immediately above the same grid cell. The air-sea exchange timescale of carbon is long compared to the circulation rate. As a result, the DIC at a given point in the mixed layer has a lot to do with where that water was before, and little to do with where it is right now.

Response: In the modified MS, we have reminded readers that “any possible interaction between the neighboring grid boxes was ignored”.

The methodology is a hodge-podge that doesn’t obviously account for the most important things. For example, windspeeds vary by a large amount, and piston velocities along with them. Global wind fields are available.

Response: In the modified MS, the global wind speed data were applied in the air–sea re-equilibration time (τ) examination.

The term ‘potential’ first appears in section 2.3 It needs to be defined, since it’s not clear what it is.

Response: Done.

This is not well justified: ‘if the wintertime MLD was deeper than 100 m at any grid box, we replaced it by 100 m, as this is the approximate MLD to be fully ventilated in a decade’. The mixed layer is the mixed layer, isn’t it? Why cut it off at 100 m? There may be a good reason for this, but since I don’t really understand what we learn from Requ, I don’t know how it should be calculated.

Response: In the modified MS, we do not cut the mixed layer at 100 m. This is because we find the high-latitude air-sea exchange time of CO₂ within the wintertime mixed layer is not very long for a decade, after considering the global wind speed field data.

I can’t follow the last 2 paragraphs of section 2.3.

Response: Polished.

In general, the English needs improvement, and the writing is very dense.

Response: We do the best to improve the English.

Some sentences include details that do not help. For example, this sentence is unnecessary: ‘During the past five decades, decadal average of xCO_{air} rises from 320 ± 3 ppm in 1960s to 331 ± 4ppm in 1970s, to 345 ± 5ppm in 1980s, to 360 ± 5ppm in 1990s, and to 379 ± 7ppm in 2000s, based on the Mauna Loa station data released by NOAA/ESRL at <http://www.esrl.noaa.gov/gmd/ccgg/trends/>.’

Response: Deleted.

Is the title appropriate? It seems like a 2-D examination to me.

Response: We have changed the title into “Decadal air-sea re-equilibration induced anthropogenic CO₂ accumulation within the ocean surface and the chemical buffering capacity decline: from 1960s to 2000s and the future scenario”.

Since “any possible interaction between the neighboring grid boxes was ignored”, this work is still a highly simplified 1-D examination.

References

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