

Reviewer 1.def. December, 8, 2017.

Interactive comment on “Increase of dissolved inorganic carbon and decrease of pH in near surface waters of the Mediterranean Sea during the past two decades” by Liliane Merlivat et al.

Anonymous Referee #1

Received and published: 13 August 2017

The paper by Merlivat et al. provides a description of carbonate chemistry in two close fixed station located in the Ligurian Sea (northwestern Mediterranean Sea). By combining time series data of CO₂ fugacity with alkalinity derived estimations, they reported an increase of dissolved inorganic carbon and decrease of pH in near surface waters during the past two decades. This issue is of particular interest to the referee and I think that the authors have a very nice data set to exploit. However, I think the analysis is somewhat incomplete, and I finished the paper wanted a more in-depth analysis and discussion. I encourage the authors to further expand their work because at this stage their hypothesis are not well supported. The manuscript could be published in Biogeosciences after a major revision in order to clarify some aspects as indicated below.

Major Comments

My major reservation about this work is the difference between the measured fCO₂ at the sea surface (fCO₂sea) and the fCO₂ derived from atmospheric xCO₂ concentration (fCO₂air). In 2013-2015 the sea surface mean annual fCO₂ calculated at 18.25_C (the mean annual in situ temperature) was larger than the fCO₂air derived from atmospheric data at the same temperature. This result is quite strange, because it means a CO₂ outgassing from the sea surface to the atmosphere on annual average, which is in contrast with respect to the ongoing ocean acidification process and the general net anthropogenic CO₂ uptake measured in the Mediterranean Sea by different research.

In 2013-2015 I would expect an equilibrium between the fCO₂sea and fCO₂air, or a slightly higher value in the fCO₂air, as it was detected in the 1995-1997. How the authors can explain this issue?

In the 2 periods, 1995-1997 and 2013-2015, the CO₂ annual flux is directed from the atmosphere to the sea in both cases, although the annual average of fCO₂ in surface seawater

in 2013-2015 is higher than atmospheric $f\text{CO}_2$. This is due to higher wind speed in autumn and winter when the surface water is undersaturated. This is well illustrated in the figure in the attached file (Figure flux.pdf) for the time period 2013-2015. In the upper figure, the three thin lines indicate $f\text{CO}_2_{\text{atm}}$.

The mean annual CO_2 flux is equal to $-0.45 \text{ mol.m}^{-2}.\text{yr}^{-1}$ using the exchange coefficient of [Wanninkhof, 2014].

They suggested the contribution of the Atlantic Ocean as a source of anthropogenic carbon, but I do not understand how the Atlantic surface waters can be relatively enriched in anthropogenic carbon.

[Huertas *et al.*, 2009] conducted a sampling program at eight fixed stations in the Strait of Gibraltar to study natural and anthropogenic carbon exchange between the Atlantic Ocean and the Mediterranean Sea. Their results show that Atlantic water has a higher concentration of anthropogenic carbon than Mediterranean water. A decreasing vertical gradient of Cant in the water column is observed, the upper layers being enriched in Cant (Figures 5 and 6).

Moreover, this is in contrast with the end of the discussion where the authors say that (P13L331) “The Mediterranean Sea is actually able to absorb more anthropogenic CO_2 per unit area”.

As stated in the text, surface waters of the Mediterranean basin have a relatively low Revelle factor, close to 10, due to a high alkalinity and a high temperature and therefore have a relatively high uptake capacity for Cant.

Maybe there are other causes which could explain the $f\text{CO}_2$ increase at the sea surface observed in 2013-2015, such as a stronger and deeper winter vertical mixing with CO_2 enriched LIW.

The reviewer is right. A strong interannual variability of winter convection events between the two studied periods has been observed and must be taken into account to interpret the total temporal change of the computed increase of DIC. This is detailed in paragraph 4.3, lines 323

-329.

Finally, additional information about the water mass exchange throughout the Strait of Gibraltar and its temporal variation are needed.

This is analyzed and discussed in [Huertas *et al.*, 2009], see for instance figure 7. See also [Schneider *et al.*, 2010], table 2.

These can be found in the recent review of Jordà *et al.* (2017) which may provide more insights for this work.

The authors found a DIC increase larger than expected from equilibrium with atmospheric CO₂. They hypothesized a ~15% contribution of the Atlantic Ocean as a source of anthropogenic carbon to the Mediterranean Sea through the strait of Gibraltar. I think that the analysis presented in the manuscript are not sufficient to support such hypothesis and the authors should provide a lot more analysis and discussions.

This is detailed in the paragraph 4.3.

Moreover, the Mediterranean Sea overturning circulation and the sites of dense water formation could play a very important role in the sequestration of anthropogenic CO₂ and in the ocean acidification of the Mediterranean Sea. I think that the authors should read the recent papers of Touratier *et al.* (2016), Ingrosso *et al.* (2017), and Krasakopoulou *et al.* (2017), who estimated the anthropogenic CO₂ in the Gulf of Lion, Adriatic Sea, and the Aegean Sea respectively.

Certainly the reasons why the Mediterranean Sea water column stores large amounts of anthropogenic CO₂ are due to the fast deep water formation processes combined with surface water having high potential to take up CO₂ due to a relatively low Revelle factor.

The authors try to assess the influence of physical and biological process on the seasonal and inter-annual variation of fCO₂. To do this, they used a simple analysis of the change of fCO₂@13 (fCO₂ normalized to the constant temperature of 13°C) as a function of SST, which is not sufficient to achieve the scope. I suggest to quantify (1) the air-sea CO₂ exchange and (2) the thermal/not-thermal contributions on the fCO₂ variation with the

method of Takahashi et al. (2002). In this way the authors could clarify how fCO₂ seasonal variation is affected by physical (i.e. temperature, mixing, and air-sea CO₂ exchange) and biological processes (i.e. photosynthesis, respiration, and calcification).

The objective of our paper is to compare the time change of surface fCO₂ measurements made at 2 very close locations, Dyfamed and Boussole, at an interval of 18 years. The processes that govern the distribution of fCO₂ at the annual scale at the same site have been analyzed in detail in a publication entitled “Processes controlling annual variations in the partial pressure of CO₂ in surface waters of the central northwestern Mediterranean Sea (Dyfamed site)[*Begovic and Copin-Montegut, 2002*]. For instance, the figure 8 in this paper is a good illustration of the relative importance of individual processes which govern the distribution of DIC over an annual cycle. For this reason, we decided not to repeat this well-argued description which is already published.

Specific Comments

P4L93: If the authors followed the standard operational procedures, the reference of Dickson et al. (2007) could be added to Edmond (1970).

The reference to Edmond (1970) is line 102.

P5L126: I propose to consider here the the method of Takahashi et al. (2002) and to present the temporal variation of the thermal and not-thermal fCO₂ as differences (dfCO₂) with respect to the February, chosen as reference month because it usually presents the lowest temperature and the minimum biological activity.

We have chosen to estimate the difference between the values of the thermal component fCO₂@13 two decades apart according to the temperature (14 temperature steps of 1°) and not to the time. This approach is more quantitative than a comparison of monthly values because we know that key processes which control the fCO₂@13 distribution such as the beginning of the bloom depend more directly on a narrow temperature threshold (13-14 °) while it may vary up to one month.

P5L128: The “remineralization” is a biological activity. Please modify/clarify the sentence.

This has been done (line 139).

P5L130: Do the authors have oxygen data? The examination of the O₂/DIC or AOU (apparent oxygen utilization)/DIC ratio would provide useful information about the influence of biological activity to the observed fCO₂ variation. Also satellite data of Chloro-Phyll phyll a concentration may help, which nowadays are easy to get

See our comment above before Specific Comments.

P6L134: “The contribution of air-sea exchange is not significant”. In order to support this sentence, please can the authors calculate the air-sea CO₂ flux and estimate the real influence of this process?

This has been done, lines 146-148.

P6L150: Levantine Intermediate Water (LIW) originates in the Eastern Mediterranean and takes years to reach the Ligurian Sea. Due to the organic matter remineralization processes, the LIW presents low dissolved oxygen concentration and high CO₂ levels (Álvarez et al., 2014), even higher than then the atmospheric levels. Taking into account these considerations, in the present study, the increase of total dissolved inorganic carbon observed in 2013-2015 can be related to a stronger and deeper winter vertical mixing with CO₂ enriched LIW?

The reviewer is right. A strong interannual variability of winter convection events between the two studied periods has been observed and must be taken into account to interpret the total temporal change of the computed increase of DIC. This is detailed in paragraph 4.3, lines 323-329.

As reported by Alvarez et al. (2014), the LIW during its westward flows can increase DIC and lower pHT of different Mediterranean basin.

P7L197: “mixing with enriched deep waters” please substitute with “mixing with CO₂-enriched deep waters”. This may support the hypothesis of a general DIC increase generated by mixing with LIW, but further analysis and more discussions are needed.

P8L199: During summer, due to the high sea surface temperature, the CO₂ flux from the sea to the atmosphere could also play an important role. Please consider also this process in

addition to the biological drawdown of carbon.

See our comment above before Specific Comments

P9L223: “Changes of seawater carbonate chemistry in surface waters”. This section needs some modification/clarification. L223-227 seems more appropriate for the Material and methods.

In Material and methods, we consider the DIC and Alk analysis of the seawater samples taken at Boussole during the servicing cruises to the mooring. In the section 3.4, we consider the derived values of DIC and pH from the analysis of the 2 time series of $f\text{CO}_2$.

L229-234: DIC and pH are derived parameters. They are calculated from total alkalinity and $f\text{CO}_2$. Due to this reason, the $f\text{CO}_2$ -DIC and $f\text{CO}_2$ -pH may not have sense and the near perfect R^2 is not significant. Please, can the authors clarify this issue?

This has been changed. We just compute DIC and pH as suggested.

P9L229: pHT refers to the pH on the total scale. But the authors calculated the pH on the seawater scale (P9L228) which is conventionally denoted as pH_{sws}. Please substitute in all the manuscript/figures the pHT with pH_{sws}.

We compute pH on the seawater scale. We delete T. We indicate in the text that the change of pH is computed at the mean in situ temperature 18.25°C

P11L259: Any references which can support that Atlantic surfacewaters are relatively enriched in anthropogenic carbon and why?

See [Huertas *et al.*, 2009].

Even if the Atlantic surface water could be enriched in CO_2 , I do not think that it could preserve this property. An air-sea equilibrium, mixing, and biological processes may happen during the long time that Atlantic surface water spent to reach the Ligurian Sea from the Gibraltar Strait.

The depth of the surface water layer of the Atlantic entering the Mediterranean Sea through the Strait of Gibraltar is close to 200 meters. It would take a few months to reach the Dyfamed zone assuming a lower estimate of the average current close to 10 cm / s on its route along the Algerian coast and then northwards [Millot, 1999]. This indicates that CO₂-enriched Atlantic water may retain its signature during this relatively short period of time.

P11L270-272: More discussion and references are needed to support this sentence.

This was not correct. As indicated earlier, and illustrated in the figure, although the annual average of fCO₂ in surface sea water was higher than atmospheric fCO₂, the annual flux was directed from the atmosphere to the sea.

P13L335: More appropriate and recent references are Touratier et al. (2016), Ingrosso et al. (2017), and Krasakopoulou et al. (2017), who estimated the anthropogenic CO₂ in the three dense water formation area of the Mediterranean Sea.

We believe that the 2 references cited [Schneider et al., 2010] and [Palmiéri et al., 2015] give the relevant information in relation to the western basin of the Mediterranean Sea which is studied in our paper.

Technical comments

I suggest to improve the general quality of the figures.

P11L286: “P=0,0749” Substitute the coma with point.

This has been done.

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Interactive comment on Biogeosciences Discuss., <https://doi.org/10.5194/bg-2017-284>, 2017.

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