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Biogeosciences Discussions

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

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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? 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. 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 CO2 per unit area". Maybe there are other causes which could explain the fCO2 increase at the sea surface observed in 2013-2015, such as a stronger and deeper winter vertical mixing with CO2 enriched LIW. Finally, additional information about the water mass exchange throughout the Strait of Gibraltar and its temporal variation are needed. 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 hypnotized 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. 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.

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).

Specific Comments

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

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.

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

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 a concentration may help, which nowadays are easy to get.

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?

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? 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.

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. L229-234: DIC and pH are derived parameters. They are calculated from total alkalinity and fCO2. Due to this reason, the fCO2-DIC and fCO2-pH may not have sense and the near perfect R2 is not significant. Please, can the authors clarify this issue?

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 pHsws. Please

substitute in all the manuscript/figures the pHT with pHsws.

P11L259: Any references which can support that Atlantic surface waters are relatively enriched in anthropogenic carbon and why? Even if the Atlantic surface water could be enriched in CO2, 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.

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

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.

Technical comments

I suggest to improve the general quality of the figures.

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

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