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.

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Received and published: 7 December 2017

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 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 is higher than atmospheric fCO2. This is due to higher wind speed in autumn 2 and winter when the surface water is undersaturated. This is well illustrated in the figure in 36 the attached file (Figure flux.pdf) for the time period 2013-2015. In the upper figure, the three 37 thin lines indicate fCO2 atm. The mean annual CO2 flux is equal to -0.45 mol.m-2.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 42 anthropogenic carbon. [Huertas et al., 2009] conducted a sampling program at eight fixed stations in the Strait of 44 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 "The Mediterranean Sea is actually able to absorb more anthropogenic CO2 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 CO2 increase at the sea surface observed in 2013-2015, such as 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. 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.

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 81 water having high potential to take up Cant due to a relatively low Revelle factor. The authors try to assess the influence of physical and biological processes on the seasonal and inter-annual variation of fCO2. To do this, they used a simple analysis of the change of fCO2 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 at two very close locations, Dyfamed and Boussole, at an interval of 18 years. The 92 processes that govern the distribution of fCO2 at the annual scale at the same site have been 93 analyzed in detail in a publication entitled "Processes controlling annual variations in the 94 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. The reference to Edmond (1970) is line 102. The reference to Edmond (1970) is line 102. The reference to Edmond (1970) is line 102. The reference to Edmond (1970) is line 102. The reference to Edmond (1970) is line 102.
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 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 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. 114 P5L128: The “remineralization” is a biological activity. Please modify/clarify the sentence. 115 This has been done (line 139). 116 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 CO2 variation. Also satellite data of Chlorophyll concentration may help, which nowadays is easy to get. 120 See our comment above (lines 90-98 in this text). 121 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? 124 This has been done, lines 146-148. 125 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 the atmospheric levels. Taking into account these considerations, in the present study, the increase of total inorganic carbon observed in 2013-2015 can be related to a stronger and deeper winter vertical mixing with CO2 enriched LIW? 131 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 133 temporal change of the computed increase of DIC. This is detailed in paragraph 4.3, lines 323-329. 135 As reported by Alvarez et al. (2014), the LIW during its westward flows can increase DIC and lower pH of different Mediterranean basin. 137 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. 140 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. 143 See our comment above (lines 90-98 in this text). 144 P9L223: “Changes of seawater carbonate chemistry in surface waters”. This section needs some modification/clarification. 147 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 fCO2. 150 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? 153 This has been changed. We just compute DIC and pH as suggested. 154 P9L229: pH refers to the pH on the total scale. But the authors calculated the pH on the seawater scale (P9L228) which is conventionally denoted as pHsw. Please substitute in all 156 the manuscript/figures the pH with pHsw. 157 We compute pH on the seawater scale. We delete T. We indicate in the text that the change of 158 pH is computed at the mean in situ temperature 18.25°C. 159 P11L259: Any references which can support that Atlantic surfacewaters are relatively enriched in anthropogenic carbon and why? 161 See [Huertas et al., 2009]. 162 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 Strait of Gibraltar. 166 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
Fig. 1.