

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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1 Reviewer 1 1 .def.docx-December, 7, 2017. 2 Interactive comment on “Increase of dissolved inorganic carbon and decrease of pH in near 3 surface waters of the Mediterranean Sea during the past two decades” by Liliane Merlivat et 4 al. 5 6 Anonymous Referee #1 7 Received and published: 13 August 2017 8 9 The paper by Merlivat et al. provides a description of carbonate chemistry in two close fixed 10 station located in the Ligurian Sea (northwestern Mediterranean Sea). By combining time 11 series data of CO₂ fugacity with alkalinity derived estimations, they reported an increase of 12 dissolved inorganic carbon and decrease of pH in near surface

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waters during the past two 13 decades. This issue is of particular interest to the referee and I think that the authors have a 14 very nice data set to exploit. However, I think the analysis is somewhat incomplete, and I 15 finished the paper wanted a more in-depth analysis and discussion. I encourage the authors to 16 further expand their work because at this stage their hypothesis are not well supported. The 17 manuscript could be published in Biogeosciences after a major revision in order to clarify 18 some aspects as indicated below. 19 20 Major Comments 21 My major reservation about this work is the difference between the measured $f\text{CO}_2$ at the sea 22 surface ($f\text{CO}_{2\text{sea}}$) and the $f\text{CO}_2$ derived from atmospheric $x\text{CO}_2$ concentration ($f\text{CO}_{2\text{air}}$). In 23 2013-2015 the sea surface mean annual $f\text{CO}_2$ calculated at 18.25_C (the mean annual in situ 24 temperature) was larger than the $f\text{CO}_{2\text{air}}$ derived from atmospheric data at the same 25 temperature. This result is quite strange, because it means a CO_2 outgassing from the sea 26 surface to the atmosphere on annual average, which is in contrast with respect to the ongoing 27 ocean acidification process and the general net anthropogenic CO_2 uptake measured in the 28 Mediterranean Sea by different research. 29 In 2013-2015 I would expect an equilibrium between the $f\text{CO}_{2\text{sea}}$ and $f\text{CO}_{2\text{air}}$, or a slightly 30 higher value in the $f\text{CO}_{2\text{air}}$, as it was detected in the 1995-1997. How the authors can explain 31 this issue? 32 In the 2 periods, 1995-1997 and 2013-2015, the CO_2 annual flux is directed from the 33 atmosphere to the sea in both cases, although the annual average of $f\text{CO}_2$ in surface seawater 34 in 2013-2015 is higher than atmospheric $f\text{CO}_2$. This is due to higher wind speed in autumn 2 and winter when the surface water is undersaturated. This is well illustrated 35 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 $f\text{CO}_2$ atm. 38 The mean annual CO_2 flux is equal to $-0.45 \text{ mol.m}^{-2}\text{.yr}^{-1}$ using the exchange coefficient of 39 [Wanninkhof, 2014]. 40 They suggested the contribution of the Atlantic Ocean as a source of anthropogenic carbon, 41 but I do not understand how the Atlantic surface waters can be relatively enriched in 42 anthropogenic carbon. 43 [Huertas et al., 2009] conducted a sampling program at eight fixed stations in the Strait of 44 Gibraltar

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to study natural and anthropogenic carbon exchange between the Atlantic Ocean and 45 the Mediterranean Sea. Their results show that Atlantic water has a higher concentration of 46 anthropogenic carbon than Mediterranean water. A decreasing vertical gradient of Cant in the 47 water column is observed, the upper layers being enriched in Cant (Figures 5 and 6). 48 Moreover, this is in contrast with the end of the discussion where the authors saythat 49 (P13L331) “The Mediterranean Sea is actually able to absorb more anthropogenic CO₂ per 50 unit area”. 51 As stated in the text, surface waters of the Mediterranean basin have a relatively low Revelle 52 factor, close to 10, due to a high alkalinity and a high temperature and therefore have a 53 relatively high uptake capacity for Cant. 54 Maybe there are other causes which could explain the fCO₂ increase at the sea surface 55 observed in 2013-2015, such as a stronger and deeper winter vertical mixing with CO₂ 56 enriched LIW. 57 The reviewer is right. A strong interannual variability of winter convection events between 58 the two studied periods has been observed and must be taken into account to interpret the total 59 temporal change of the computed increase of DIC. This is detailed in paragraph 4.3, lines 323 60 -329. 61 Finally, additional information about the water mass exchange throughout the Strait of 62 Gibraltar and its temporal variation are needed. 63 This is analyzed and discussed in [Huertas et al., 2009], see for instance figure 7. See also 64 [Schneider et al., 2010], table 2. 65 These can be found in the recent review of Jordà et al. (2017) which may provide more 66 insights for this work. 67 The authors found a DIC increase larger than expected from equilibrium with atmospheric 3 CO₂. They hypnotized a _15% contribution of the Atlantic 68 Ocean as a source of 69 anthropogenic carbon to the Mediterranean Sea through the strait of Gibraltar. I think that the 70 analysis presented in the manuscript are not sufficient to support such hypothesis and the 71 authors should provide a lot more analysis and discussions. 72 This is detailed in the paragraph 4.3. 73 Moreover, the Mediterranean Sea overturning circulation and the sites of dense water 74 formation could play a very important role in the sequestration of anthropogenic CO₂ and in 75 the ocean acidification of the Mediterranean Sea.I think that the authors should

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read the recent 76 papers of Touratier et al. (2016), Inghosso et al. (2017), and Krasakopoulou et al. (2017), who 77 estimated the anthropogenic CO₂ in the Gulf of Lion, Adriatic Sea, and the Aegean Sea 78 respectively. 79 Certainly the reasons why the Mediterranean Sea water column stores large amounts of 80 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. 82 The authors try to assess the influence of physical and biological process on the seasonal and 83 inter-annual variation of fCO₂. To do this, they used a simple analysis of the change of 84 fCO₂@13 (fCO₂ normalized to the constant temperature of 13_C) as a function of SST, 85 which is not sufficient to achieve the scope. I suggest to quantify (1) the air-sea CO₂ 86 exchange and (2) the thermal/not-thermal contributions on the fCO₂ variation with the 87 method of Takahashi et al. (2002). In this way the authors could clarify how fCO₂ seasonal 88 variation is affected by physical (i.e. temperature, mixing, and air-sea CO₂ exchange) and 89 biological processes (i.e. photosynthesis, respiration, and calcification). 90 The objective of our paper is to compare the time change of surface fCO₂ measurements 91 made at 2 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 95 (Dyfamed site)[Begovic and Copin-Montegut, 2002]. For instance, the figure 8 in this paper 96 is a good illustration of the relative importance of individual processes which govern the 97 distribution of DIC over an annual cycle. For this reason, we decided not to repeat this well98 argued description which is already published. 99 100 Specific Comments 101 P4L93: If the authors followed the standard operational procedures, the reference of Dickson 4 102 et al. (2007) could be added to Edmond (1970). 103 The reference to Edmond (1970) is line 102. 104 P5L126: I propose to consider here the the method of Takahashi et al. (2002) and to present 105 the temporal variation of the thermal and not-thermal fCO₂ as differences (dfCO₂) with 106 respect to the February, chosen

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as reference month because it usually presents the lowest 107 temperature and the minimum biological activity. 108 We have chosen to estimate the difference between the values of the thermal component 109 $fCO_2@13$ two decades apart according to the temperature (14 temperature steps of 1°) and 110 not to the time. This approach is more quantitative than a comparison of monthly values 111 because we know that key processes which control the $fCO_2@13$ distribution such as the 112 beginning of the bloom depend more directly on a narrow temperature threshold ($13-14^\circ$) 113 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 O_2/DIC or AOU 117 (apparent oxygen utilization)/ DIC ratio would provide useful information about the influence 118 of biological activity to the observed fCO_2 variation. Also satellite data of Chloro-Phyll phyll 119 a concentration may help, which nowadays are 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 122 sentence, please can the authors calculate the air-sea CO_2 flux and estimate the real influence 123 of this process? 124 This has been done, lines 146-148. 125 P6L150: Levantine Intermediate Water (LIW) originates in the Eastern Mediterranean and 126 takes years to reach the Ligurian Sea. Due to the organic matter remineralization processes, 127 the LIW presents low dissolved oxygen concentration and high CO_2 levels (Álvarez et al., 128 2014), even higher than then the atmospheric levels. Taking into account these considerations, 129 in the present study, the increase of total dissolved inorganic carbon observed in 2013-2015 130 can be related to a stronger and deeper winter vertical mixing with CO_2 enriched LIW? 131 The reviewer is right. A strong interannual variability of winter convection events between 132 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 323 134 -329. 135 As reported by Alvarez et al. (2014), the LIW during its westward flows can increase DIC and 5 lower pHT 136 of different Mediterranean basin. 137 P7L197:

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“mixing with enriched deep waters” please substitute with “mixing with CO₂- 138 enriched deep waters”. This may support the hypothesis of a general DIC increase generated 139 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 141 to the atmosphere could also play an important role. Please consider also this process in 142 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 145 some modification/clarification. L223-227 seems more appropriate for the Material and 146 methods. 147 In Material and methods, we consider the DIC and Alk analysis of the seawater samples 148 taken at Boussole during the servicing cruises to the mooring. In the section 3.4, we consider 149 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 151 fCO₂. Due to this reason, the fCO₂-DIC and fCO₂-pH may not have sense and the near 152 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: pHT refers to the pH on the total scale. But the authors calculated the pH on the 155 seawater scale (P9L228) which is conventionally denoted as pH_{sws}. Please substitute in all 156 the manuscript/figures the pHT with pH_{sws}. 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 160 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 163 preserve this property. An air-sea equilibrium, mixing, and biological processes may happen 164 during the long time that Atlantic surface water spent to reach the Ligurian Sea from the 165 Gibraltar Strait. 166 The depth of the surface water layer of the Atlantic entering the Mediterranean Sea through 167 the Strait of Gibraltar is close to 200 meters. It would take a few months to reach the

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168 Dyfamed zone assuming a lower estimate of the average current close to 10 cm / s on its route 169 along the Algerian coast and then northwards [Millot, 1999]. This indicates that CO₂-enriched 6 Atlantic water may retain its signature during this 170 relatively short period of time. 171 P11L270-272: More discussion and references are needed to support this sentence. 172 This was not correct. As indicated earlier, and illustrated in the figure, although the annual 173 average of fCO₂ in surface sea water was higher than atmospheric fCO₂, the annual flux was 174 directed from the atmosphere to the sea. 175 P13L335: More appropriate and recent references are Touratier et al. (2016), Ingrosso et al. 176 (2017), and Krasakopoulou et al. (2017), who estimated the anthropogenic CO₂ in the three 177 dense water formation area of the Mediterranean Sea. 178 We believe that the 2 references cited [Schneider et al., 2010] and [Palmiéri et al., 2015] give 179 the relevant information in relation to the western basin of the Mediterranean Sea which is 180 studied in our paper. 181 182 Technical comments 183 I suggest to improve the general quality of the figures. 184 P11L286: “P=0,0749” Substitute the coma with point. This has been done. 185 References 186 Álvarez, M., Sanleón-Bartolomé, H., Tanhua, T., Mintrop, L., Luchetta, A., Cantoni, C., 187 Schroeder, K., Civitarese, G., 2014. The CO₂ system in the Mediterranean Sea: a basin wide 188 perspective. *Ocean Sci.* 10, 69–92. 189 Carter, B. R., N. L. Williams, A. R. Gray, and R. A. Feely. 2016. Locally interpolated 190 alkalinity regression for global alkalinity estimation. *Limnol. Oceanogr. Methods* 14: 268– 191 277. doi:10.1002/lom3.10087 192 Dickson, A.G., Sabine, C.L., Christian, J.R., 2007. Guide to best practices for ocean CO₂ 193 measurements. *PICES Spec. Publ.* 3, 191. 194 Ingrosso, G., Bensi, M., Cardin, V., Giani, M., 2017. Anthropogenic CO₂ in a dense water 195 formation area of the Mediterranean Sea. *Deep-Sea Research Part I* 123, 118– 128. 196 doi:10.1016/j.dsr.2017.04.004 197 Jordà, G., Schuckmann, Von, K., Josey, S.A., Caniaux, G., García-Lafuente, J., Sammartino, 198 S., Ozsoy, E., Polcher, J., Notarstefano, G., Poulain, P.M., Adloff, F., Salat, J., Naranjo, C., 199 Schroeder, K., Chiggiato, J., Sannino, G., Macías, D., 2017. The Mediterranean Sea heat and 200 mass budgets: Estimates, uncertainties and perspectives.

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Please also note the supplement to this comment:

<https://www.biogeosciences-discuss.net/bg-2017-284/bg-2017-284-AC3-supplement.pdf>

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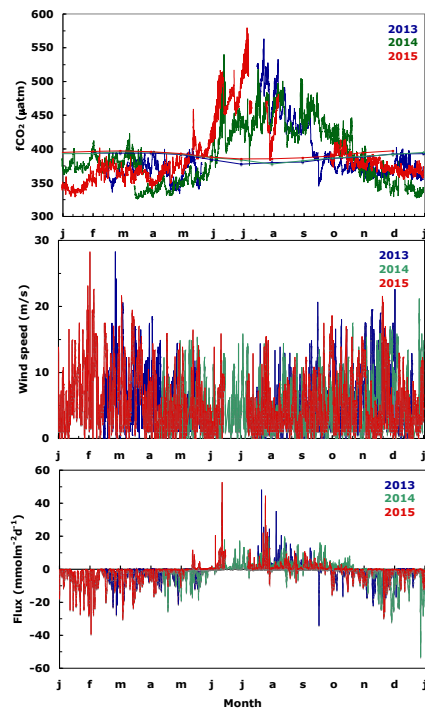
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6

Fig. 1.

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