

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.

Liliane Merlivat et al.

merlivat@locean-ipsl.upmc.fr

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Reviewer 2.def.docx- December, 5, 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 #2 Received and published: 22 September 2017

In this manuscript, Merlivat et al. report on measurements of $f\text{CO}_2$ during two 3-year windows whose midpoints are 18 years apart with samples taken adjacent locations in the Mediterranean Sea. They then combine those measurements with total alkalinity derived from measured temperature and salinity to compute DIC and pH. Because

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their derived DIC increase is larger than expected from equilibrium with atmospheric CO₂, the authors invoke lateral transport of anthropogenic DIC from the Atlantic to the Mediterranean Sea to explain the difference.

GENERAL COMMENTS The authors report on quality measurements of fCO₂, the fruit of decades of investment to develop and deploy the CARIOCA buoys with fCO₂ sensors. They use the same measurement system for all measurements, thus allowing an assessment of the total change in ocean fCO₂ between the 2 time periods that seems as precise as can be hoped for. Yet despite the quality of the measurements, my impression is that the uncertainties are underestimated when the authors discuss temporal changes in measured fCO₂ as well as derived DIC and pH. This impression comes partly from the authors' choice to represent uncertainties as the standard error of the mean rather than the standard deviation. Their estimated uncertainties for the difference between these two time periods is usually much smaller than the best measurement precision. For more about my concerns on the uncertainty analysis of the authors, please see the detailed comments below, e.g., those labeled line 214, lines 243-248, line 296, and line 320. We bring details under these comments. An even greater concern is that the authors assume that the total temporal change is entirely anthropogenically driven. They do not consider the potential contribution from natural variability (see detailed comments below for the section commenting on 'lines 44-46:') 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. . Because of these two concerns, it appears to me that the manuscript may well require in-depth revisions before it is acceptable for publication.

DETAILED COMMENTS lines 44-46: This statement from the authors in the introduction is an important one, making the point that there is large natural variability. Why then do they neglect to consider that natural decadal scale variability may explain part of the change between 1995-1997 and 2013-2017. In the North Atlantic, for instance

it has been shown that because of decadal variability it requires 25 years for the long-term trend to emerge (McKinley et al, 2011). In the North Pacific, about half of the change in near surface ocean pH over a 15-year period has been ascribed to natural (non-anthropogenic) contributions (Byrne et al., 2010). In the Southern Ocean, early studies suggested a weakening of the Southern Ocean CO₂ uptake, but more recent work with 30-year perspective indicates a tendency in the opposite direction, with such oscillations being ascribed in part to natural variability (Lanschutzer, 2015). In contrast to these studies, the authors do not consider any contribution of natural decadal variability in their interpretation, assigning the measured and estimated changes entirely to an anthropogenically forced trend. The change between the 2 points in time, even if they represent 3-year averages as in this study by Merlivat et al., are also likely to be affected by natural variability. This point is now discussed in paragraph 4.3 lines 53-55: - please add "over extended periods" after air-water interface – please delete "related to the absorption of increasing atmospheric CO₂ concentration" or nuance the message so as not to neglect natural variability. This has been done. lines 58-59: - please delete the commas just after "temperature" and just after "salinity" as these confuse the listing, making it appear longer than it is. You may also want to add parentheses around 'T' and 'S', although I don't think that is necessary. This has been done. lines 76-77: - Can you provide references to support your statement that the Ligurian current isolates the two stations from coastal inputs. I would expect that eddies and jets would allow some transfer of heat, salt, momentum, and chemical species from coastal waters to the open Mediterranean Sea, even if that transfer is not occurring immediately adjacent to the two sampling sites. This has been well documented in Antoine et al, 2008, Heimburger et al, 2013 in addition to the work of Millot, 1999. - You could strengthen your case that the 2 stations (BOUSSOLE and DYFAMED) sample the same water mass by showing carbonate system measurements as well as T and S taken at the same time at both stations. line 83: change "They" to "Both" This has been done. lines 96-98: - add "K1 and K2" before "dissociation constants" - Why do the authors choose to use the K1 and K2 from Dickson and Millero (1987) even though the first author of the paper,

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when asked, suggests that there is a mistake in those formulations? I think it would be better to use K1 and K2 from Lueker et al. (2000), which is recommended for best practices (Dickson et al., 2007). We have kept the dissociation constants of Mehrbach refitted by Dickson and Millero [Dickson and Millero, 1987; Mehrbach et al., 1973] in order to remain consistent with the work previously published on Dyfamed [Begovic and Copin-Montegut, 2002; Copin-Montegut and Begovic, 2002] as one goal of our work was to compare data measured in close locations 18 years apart. However, we have checked that the computed DIC and pH changes deduced from a given change of fCO₂ is identical when we consider one or the other set of constants. line 106: This sentence could be ambiguous. Are you referring to the standard deviation of the all 56 samples? Please clarify. This has been done. line 110: The authors use the term "fCO₂@13" before it has been defined. Would it not be simpler just to delete "and fCO₂@13" and get to the details later. This has been done. lines 120-121: The fCO₂ is also a function of total dissolved inorganic phosphorus and silicon, when computed from DIC and total alkalinity, although in the oligotrophic surface waters of the Med Sea those nutrient concentrations are negligible and do not contribute significantly. We have modified the sentence. line 123: Did Takahashi et al. (1993) study the Med Sea? If not, how do you make the connection. The reference to Takahashi (1993) should not have been at that place. It has been deleted. line 130: change "decay of" to "decline in" This has been done. line 131: You could improve sentence flow by adding add "the ensuing" before "increase. This has been done. lines 134-135: The authors should provide evidence for their statement that the contribution of the air-sea flux is insignificant. This is well discussed for the years 1998-2000 in Begovic and Copin-Montegut ,2002 .For the period 2013-2015, the air –sea flux is equal to -0.45mmolm⁻²d⁻¹, a value close to what was observed in previous years. This is indicated in the manuscript. line 140: change "15th to 26th" to "15 to 26". This has been done. line 142: The meaning of "Likewise" is not clear. Please modify sentence to clarify your meaning. This has been done . line 201 (211): The word "monotonous" means "boring" in English, perhaps not what was intended. I would suggest to use "monotonic" instead. OK. This has been done.

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line 214: We have rewritten this part lines 237 to 244. We hope it is clearer now. - By "standard error" I presume that the authors are using the 'standard error of the mean', the latter 3 words which should be added to make it clearer to readers. We should have written "The mean value of $\text{dfCO}_2@13$ is equal to $33.17 \mu\text{atm}$ with a standard error of the mean equal to $1.68 \mu\text{atm}$ ". In the original manuscript, we had computed the standard error of the mean equal to $6.29/\sqrt{14}=1.68 \mu\text{atm}$, the standard deviation of the 14 values of $\text{dfCO}_2@13$ being equal to $6.29 \mu\text{atm}$. The standard deviation (SD) is a measure of variability. The standard error of the mean depends on both the standard deviation and the sample size. I have several problems with the authors' choice to use the standard error of the mean (SE) in this case. We agree with the reviewer that the error estimate in the previous version was confused as we did not separate accuracy and precision. In the new version, we consider the analytical accuracy of each sensor ($2 \mu\text{atm}$), as derived from the error on each sensor calibration and which has been confirmed experimentally by ship comparisons. This is now detailed section 2.2 and in lines 237 to 244. * First it gives the wrong impression that the uncertainty of these calculations is small ($1.7 \mu\text{atm}$), even lower than the precision of individual fCO_2 measurements ($3 \mu\text{atm}$). Because the SE is the standard deviation divided by the square root of N, it is nearly 5 times smaller than the standard deviation in this case ($N=24$, Table 1). * Second, the result for the SE will also depend on the authors' arbitrary choice for the scale. * Third, even if the SE were appropriate, I do not understand how the authors get $N=24$ for the 'daily scale' mentioned in Table 1. This was a mistake. We intended to make subsampling but dividing N by 24 was not correct. It has been deleted. * Fourth, The use of SE in the right hand portion of Table 1 is at least visually inconsistent with the use of the standard deviation for each of the time periods shown in the left and center portions of the same table. I would strongly recommend that the authors simply use the standard deviation at least in Table 1. This has been done. If the authors insist on using SE, I would ask that they also provide the standard deviation in addition to the SE and that they statistically justify the use of the SE while explaining their choices in detail (e.g., $N=24$). There have been comments in scientific

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journals about the misuse of SE being a common practice. The SE could perhaps be used correctly here if well justified, but it can also mislead readers. line 215: The text says that "fCO₂@13 is evenly distributed *in* the whole range of temperature". I am not sure I understand. It is seen in Table 1 that fCO₂@13 varies from 19 to 45. Please clarify this sentence. We have modified the sentence and write "The distribution of values around the mean seems random and indicates no trend". line 217: Change "2 last decades" to "last two decades". This has been done. lines 228: You say that pH is on the seawater scale but later you use pHT, meaning it is on the total scale. Please clarify. 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 line 231: The text says, "We used these sensitivity factors to compute the increase in DIC, ..." It is not clear why you need these sensitivity factors. Can you not simply compute DIC and pH for both time periods then take the difference? This has been changed. We just compute DIC and pH as suggested. line 232: The numbers for the increase in DIC are given with too many significant figures. We think it is coherent regarding the annual data reported for surface time series like for instance in [Bates et al., 2014]. Table 2: The numbers for dfCO₂ and dDIC are given with 4 significant figures, much too much. The number of significant figures given in the paper is often too many. The authors should carefully go over the reported numbers and reduce to a justifiable number of significant figures in every case. We keep two significant figures for the annual change data being coherent with numbers reported for surface time series like for instance in [Bates et al., 2014]. lines 243-248: - Please inform the reader what the error bars are reporting, standard deviation or standard error of the mean. There is insufficient information about how 'atmospheric fCO₂' was calculated from atmospheric xCO₂. Did the authors make a humidity correction, which can change numbers by a few percent? Nothing along those lines was mentioned. How much of a difference would there be if the authors did not assume that the atmospheric pressure is 1 atm. Did they make the xCO₂-to fCO₂ conversion on a monthly basis and then take an annual average? Currently it seems they are making only an annual-mean calculation. Would results

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differ? – fCO₂ atm was computed as:

with x CO₂ molar fraction of CO₂ in the atmosphere, p_{H_2O} at 18.25°C equal to 21 mb, P equal to 1013 mb, and f , factor to convert partial pressure to fugacity, equal to 0.9966. Then: $fCO_2 = 0.976 \times CO_2$. For a sensitivity test, as a meteorological buoy was in place close to the mooring during the 2013-2015 period, we have made the same exercise taking into account the monthly distribution of x , p_{H_2O} and P . We get the same factor to convert xCO_2 in fCO_2 as when considering annual values. The mean annual value of fCO_2 μatm is computed as follows considering monthly values of xCO_2 : 1995-1997: $fCO_2 mean = 355.3 \mu atm$, $N=36$, $SD=5.0$, $SE=0.8$. 2013-2015: $fCO_2 mean = 389.6 \mu atm$, $N=36$, $SD=5.5$, $SE=0.9$. We then calculate: $dfCO_2 = 34.3 \pm 2.3 \mu atm$ with $SE=1.2$.

The error estimate appears to be too small for the change in fCO_2 at the sea surface at 18.25 C. It is smaller than the measurement precision for individual fCO_2 measurements. - My overall impression is that the authors may well be underestimating the uncertainties, especially concerning the change in oceanic fCO_2 between 1995-1997 and 2013-2015. Even if estimates of $fCO_2 ocn$ for each of those 3-year periods can be made to within 3 μatm , the 2-sigma error bars for oceanic and atmospheric fCO_2 would overlap. Furthermore, there has been no discussion of potential systematic errors nor their potential for evolution over time. line 253 : Such numbers should be given to at most one decimal point. We have made changes. lines 290-291: - Delete "It is thus interesting to notice that". - Change "impact significantly" to "significantly affect". This has been done. line 296: I find that the error bar of $\pm 1.3 \mu mol/kg$ for the temporal change in DIC to be much too small. It is less than half of the measurement precision quoted by the authors. These estimates are given to 4 significant figures when indeed it is not really justified to report them to better than 2 significant figures. The same holds for the numbers reported on line 298. Changes have been made. line 320: The uncertainty given for the annual average change in pH over the 18-year period is very small (0.0001) compared to estimates from other sites (around 0.0006). How do you explain this? Once again, it seems related to your use of SE instead of the standard

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deviation. The SE is misleading. Our number (0.0001) is very comparable to other data reported in the literature. For instance, Bates et al (2014) in the analysis of 7 pH time series indicate standard error changes of pH of 0.0001 for the BATS and HOT sites and 0.0002 for ESTOC lines 337-338: Please provide support for this final sentence. We have added the value of the Revelle factor close to 10 and deleted the last sentence. line 343: The authors need to bring up long-term (decadal) variability which is not addressed in this manuscript because sampling occurred only over two 3-year windows and because a longer time series beyond 18 years may well be necessary. We have modified the sentence. line 348: The model study from Palmieri et al does not suggest a 15% contribution but rather a 25% contribution. OK Furthermore that model-based estimate is based on the anthropogenic carbon inventory in the Med Sea not on an estimated surface concentration of anthropogenic DIC. The relationship between the surface concentration and the vertical integral of the concentration (inventory) may not be one to one, and the difference between the two should be distinguished in this study. It is exact that vertical profiles of anthropogenic carbon in the Med Sea indicate higher concentration of anthropogenic carbon in the upper part of the water column (Huertás et al, 2009, Schneider et al, 2010). However both studies establish that there is a net flux of anthropogenic carbon from the Atlantic towards the Mediterranean basin. (Schneider et al, 2010) propose that it may represent about 10% of the total inventory of C_{ant} in the whole basin. We have corrected the sentence in our text.

Global changes: - Please make global changes so that there is always a space between all numbers and their units, e.g., 5 μatm , not 5 μatm (line 98) and "3 m and 10 m" instead of "3m and 10m" (line 146). Corrections have been made.. - Please be consistent in your use of the abbreviation to represent total dissolved inorganic carbon. Sometimes you use DIC; other times you use TCO₂. Actually, I would prefer to see the more modern abbreviation of CT, with T given as a subscript. For consistency, I would further recommend to use AT (with T also subscripted) for total alkalinity. We have deleted TCO₂. We use DIC and Alk - Often citations in the text are provided with the wrong format. For example on lines 126-127 it says "using the equation of [Takahashi et

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al., 1993]". The square brackets are misplaced. If you are using the LaTeX template with BibTeX for Biogeosciences, this problem is easily fixed (use `\citet` instead of `\citep`). We will check carefully in the manuscript. REFERENCES Byrne, R. H., Mecking, S., Feely, R. A., & Liu, X. (2010). Direct observations of basin-wide acidification of the North Pacific Ocean. *Geophysical Research Letters*, 37(2). Dickson, A. G., Sabine, C. L., and Christian, J. R.: Guide to best practices for ocean CO₂ measurements, PICES Special Publication 3, 191 pp., 2007. Landschützer, P., N. Gruber, F. Alexander Haumann, C. Rödenbeck, D. C. E. Bakker, S. van Heuven, Mario Hoppema, N. Metzl, C. Sweeney, T. Takahashi, B. Tilbrook, R. Wanninkhof (2015). The reinvigoration of the Southern Ocean carbon sink. *Science*, 349(6253), 1221-1224. McKinley, G. A., Fay, A. R., Takahashi, T., & Metzl, N. (2011). Convergence of atmospheric and North Atlantic carbon dioxide trends on multidecadal timescales. *Nature Geoscience*, 4(9), 606. Interactive comment on Biogeosciences Discuss., <https://doi.org/10.5194/bg-2017-284>, 2017.

Bates, N., Y. Astor, M. Church, K. Currie, J. Dore, M. Gonaález-Dávila, L. Lorenzoni, F. Muller-Karger, J. Olafsson, and M. Santa-Casiano (2014), A Time-Series View of Changing Ocean Chemistry Due to Ocean Uptake of Anthropogenic CO₂ and Ocean Acidification, *Oceanography*, 27(1), 126-141. Begovic, M., and C. Copin-Montegut (2002), Processes controlling annual variations in the partial pressure of fCO₂ in surface waters of the central northwestern Mediterranean sea (Dyfamed site), *Deep-Sea Research II*, 49, 2031-2047. Copin-Montegut, C., and M. Begovic (2002), Distributions of carbonate properties and oxygen along the water column (0–2000 m) in the central part of the NW Mediterranean Sea (Dyfamed site): influence of winter vertical mixing on air–sea CO₂ and O₂ exchanges, *Deep-Sea Research II* 49, 2049-2066. Dickson, A. G., and F. J. Millero (1987), A comparison of the equilibrium constants for the dissociation of carbonic acid in seawater media, *Deep Sea Research Part A. Oceanographic Research Papers*, 34(10), 1733-1743. Mehrbach, C., C. H. Culberson, J. E. Hawley, and R. M. Pytkowicz (1973), Measurement of the apparent dissociation constants of carbonic acid in seawater at atmospheric pressure, *Limnol*

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Oceanogr, 18(6), 897-907.

Please also note the supplement to this comment:

<https://www.biogeosciences-discuss.net/bg-2017-284/bg-2017-284-AC1-supplement.pdf>

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