Second 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

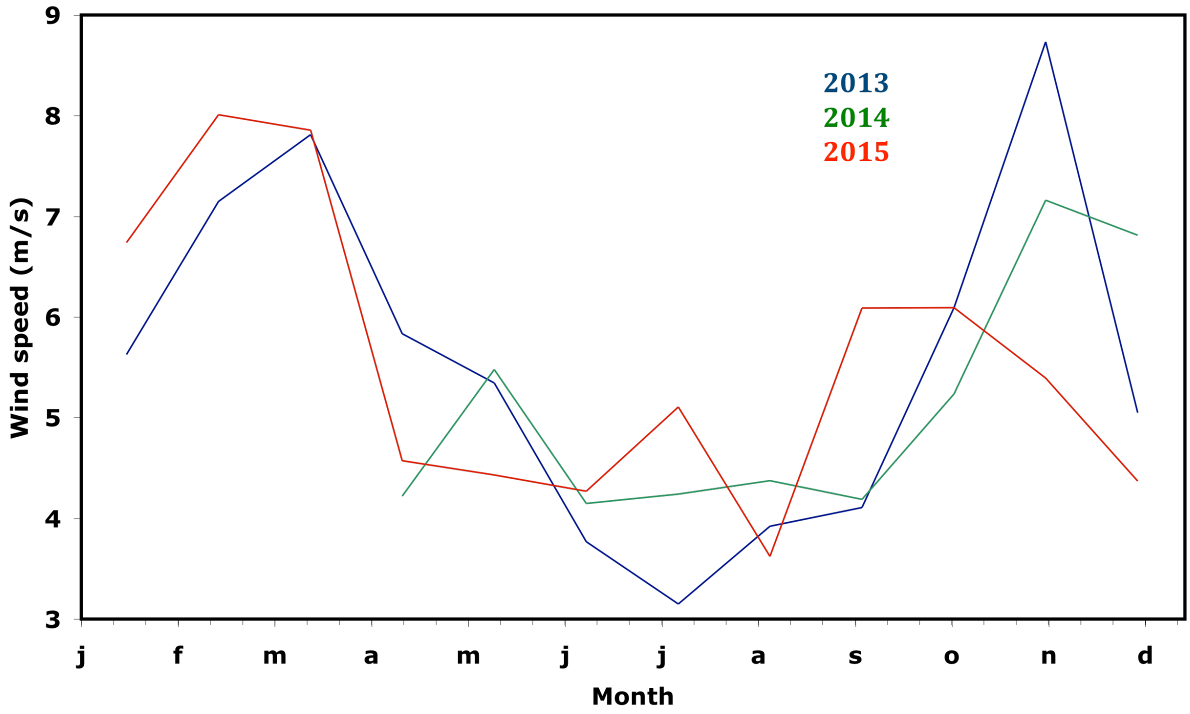
**Major Comments**

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 CO2 in surface seawater in 2013-2015 is higher than atmospheric fCO2. This is due to higher wind speed in autumn and winter when the surface water is undersaturated. This is well illustrated in the figure below for the time period 2013-2015. In the upper figure, the three thin lines indicate fCO2 atm.

This could be a good explanation, but it must be supported by a statistical analysis of the data. Is there a significant statistical difference in the wind speed between winter/spring/summer/autumn? From the figure proposed, the wind speed seems more or less the same during the different month.

On the figure below, we see that during the period May-September, the monthly values of the wind speed are almost 2 times lower than during the other months.



The mean annual CO2 flux is equal to -0.45 mol .m$^{-2}$.yr$^{-1}$ using the exchange coefficient of [Wanninkhof, 2014].

How was calculated the mean annual CO2 flux? If this is the average of the daily CO2 flux, it is also necessary to report the standard deviation. Please clarify.

It is calculated as the mean of individual hourly values of the product of the gas exchange coefficient and the atmosphere-sea $fCO_2$ gradient. We are not sure to understand why the reviewer asks for the standard deviation which is necessary large because of the seasonality of both terms, the wind speed and $fCO_2$ at the sea surface.

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).

My doubts remain. Since Cant cannot be measured directly, as it cannot be chemically discriminated from the bulk of dissolved inorganic carbon, different approaches for its indirect estimation have been developed. All the proposed approach do not give good results in the surface layer, due to the effect of the biological activity and the strong dynamic of this portion of the water column. For these reasons usually the the surface waters (0-200m) is not considered in the estimation of Cant. Touratier et al. (2012) strongly criticized Huertas et al., 2009 to calculate the Cant in the surface layer, and Palmieri et al. (2015) also reported Cant calculation of the surface layer. So, is the Atlantic Ocean a sink or a source of Can respect to the Mediterranean Sea? At the moment we do not have clear scientific evidence to answer at this question.

We added in 4.2.2. the conclusion of the paper by Flecha et al. [2012]. In this study, 3 observational methods using 3 different back calculation techniques for the $C_{ant}$ concentration assessment were used to calculate the anthropogenic carbon inventory in the Gulf of Cadiz. The authors also conclude that there is a net import of $C_{ant}$ from the Atlantic towards the Mediterranean Sea. We have written lines 371-378:

« The concentration of oceanic anthropogenic carbon, $C_{ant}$, is not a directly measurable quantity. To estimate it, several empirical methods have been developed. Flecha et al.[2012] computed the anthropogenic carbon inventory in the Gulf of Cadiz. They used observations made during a cruise in October 2008 throughout the oceanic area covered by the Gulf of Cadiz and the Strait of Gibraltar to estimate $C_{ant}$ with 3 methods: $\Delta C^*$ [*Gruber et al.*, 1996] ,TrOCA [*F Touratier and Goyet*, 2004; *F. Touratier et al.*, 2007] , $\varphi C_T^0$ [*Vazquez-Rodriguez et al.*, 2009]. In the 3 cases, their results indicate a net import of $C_{ant}$ from the Atlantic towards the Mediterranean through Gibraltar. »

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”.

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.

The answer is not pertinent to may question. I try to be more clear. How the Atlantic Ocean can be a source of the Can if (as the authors say P13L331) "The Mediterranean Sea is actually able to absorb more anthropogenic CO2 per unit area"?

In the strait of Gibraltar, Atlantic waters flow eastward to the Mediterranean Sea located in the upper layers of the water column while the westward Mediterranean outflow occupies the deeper part. In the shallower depth, the Atlantic waters are enriched in anthropogenic $CO_2$ as they have been recently in contact with the atmosphere while the deep Mediterranean waters have not been in interaction with the atmosphere since a long time period.

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.

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.

In this revised version of the manuscript, we expanded the discussion on the potential effect of natural variability. We wrote, lines 348-369:
"**4.2.1** Natural variability

Time series of mixed layer depth, MLD, show a strong variability in winter at interannual scale. During the two periods, 1995-1997 and 2013-2015, the winter MLD never exceeded 220 m, whereas values over 300 m were observed in 1999 and especially in February and March 2006 with values close to 2000 m [Coppola et al., 2016; Pasqueron de Fommervault et al., 2015]. These episodes of strong and deep vertical mixing must have entrained DIC rich LIW in the surface waters. This could be causing an increase in DIC between the 1995-1997 and 2013-2015 periods. Monthly surface samples collected at the Dyfamed time series station between 1998 and 2013 indicate an increasing DIC trend of 1.35 µmol $kg^{-1}$ $yr^{-1}$. This value is known with great uncertainty ($r^2 = 0.05$) because of the large seasonal variability displayed in the monthly samples [*Gemayel et al.*, 2015]. Nevertheless, this value is closer to the trend we calculated between the two periods, 1993-1995 and 2013-2015 (1.40 µmol $kg^{-1}$ $yr^{-1}$) than to the trend inferred from the atmospheric increase (1.15 µmol $kg^{-1}$ $yr^{-1}$). On DYFAMED time series, we find no evidence that the strong increase in MLD observed during winters 1999 and especially 2006 resulted in a further increase in DIC.

The monthly cruises of the Dyfamed time-series study have also been analyzed in order to investigate the hydrological changes and some biological consequences over the period 1995-2007 [*Marty and Chiavérini*, 2010]. These authors show that extreme convective mixing events such as recorded in 1999 and 2006 are responsible of large increases in nutrient content in surface layers and conclude that the biological productivity is increasing especially during the 2003-2006 period, which could lead to a larger consumption of carbon, i.e. a decrease of DIC. "

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 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.

This is detailed in the paragraph 4.3.

Why the author do not consider the recent review of Jordà et al. (2017) about the water mass exchange in the Strait of Gibraltar?

In their article, Jorda et al review various estimates and uncertainties regarding the heat and mass flow across the Strait of Gibraltar. They update and analyze data from existing literature and indicate possible directions for improving methodological and observational methods to estimate the heat and mass content of the Mediterranean Sea. We do not think it is necessary to add this reference to our article

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 Cant due to a relatively low Revelle factor.

Ok, but why the author do not want to consider and to cite these recent papers which estimate the Cant in Mediterranean Sea? Touratier et al. (2016) also estimate the Cant in an area very close respect to the DYFAMED site.

Cant estimates in the Mediterranean Sea differ greatly from one method to another. Some critics of the TROCA back calculation technique are put forward more specifically for its application in the Mediterranean Sea. We do not want to enter this debate (Yool et al, 2010, Schneider et al., 2010, Palmieri et al., 2015).

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 CO 2 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.

Where is the reference of Dickson et al. (2007)? Did the authors follow the standard operational procedures?

The standard procedures have been applied . We have added the reference Dickson et al. (2007).

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.

Do the authors have oxygen data? I do not found answer to this question.

We do not have oxygen data.

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.

No reply to this comment

In our revised manuscript, we added a paragraph (4.2.1 Natural variability, lines 348-369) to evaluate the impact of natural variability as an increase in vertical mixing that could have entrained a larger mixing with LIW enriched in DIC. We noted that, with existing available data in the literature, we found no significant signature of an increase in DIC between the 2 time periods, 1995-1997 and 2013-2015.

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

I do not understand why the author do not consider the influence of the CO2 flux from the sea to the atmosphere.

Our computations consider the budget of annual DIC in the mixed layer. They are independent of the seasonal variation of the flux.

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 fCO2.

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?

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

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

You should substitute in all the manuscript/figures the pHT with pHsws. Not only delete T. Only pH is not correct and ambiguous.

We use $\mathrm{pH}_{\mathrm{sws}}$ in the manuscript

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

See [Huertas et al., 2009].

In the same paper the TrOCA approach measured a greater Cant in the Mediterranean waters.

See our previous comment p.6

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.

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 seawater 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.

This has not been done. The figures are the same.

We reworked the figures. We hope it will be more satisfying.

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

This has been done.

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Palmiéri, J., J. C. Orr, J. C. Dutay, K. Béranger, A. Schneider, J. Beuvier, and S. Somot (2015), Simulated anthropogenic CO2 storage and acidification of the Mediterranean Sea,Biogeosciences, 12(3), 781:802.

Schneider, A., T. Tanhua, A. Körtzinger, and D. W. R. Wallace (2010), High anthropogenic carbon content in the eastern Mediterranean, Journal of Geophysical Research, 115(C12).

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We do not quote this paper as it has not been accepted for publication in Biogeosciences and the reviews available in BGD are severe.

Second 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

## MAJOR CONCERNS:

In my previous review of the submitted manuscript from Merlivat et al., I mentioned two general concerns that led me to recommend that in-depth revisions were needed. First, uncertainties appeared underestimated and poorly described, and second natural variablity was ignored as a possible explanation for some of the change seen between the two 3-year periods.

In the revised manuscript, the authors have tried to clarify their text in regards to my first concern. Yet the discussion of these results, appears unclear, imprecise, and does not offer a clear statistical demonstration that the differences between the two time periods are significant. More detailed concerns about the generally poor description of uncertainty analyses are provided below in the comments concerning lines 108-109, 241-246, 254-255, and 275-276.

We bring details under these comments. We have modified the section 4 “Discussion” which is now organized as follows:

4.1 Time change of surface alkalinity

4.2 Drivers of the temporal change of DIC in surface waters

4.2.1 Natural variability

4.2.2 Anthropogenic carbon exchange through the Strait of Gibraltar

4.3 Long term trends in surface DIC and pH

As for my second major concern, the authors response is unsatisfactory. Although this concern is mentioned briefly in the Introduction, the authors have just cut and paste an entire sentence from my Review, word for word. The same concern is mentioned briefly in the Abstract, Discussion, and Conclusion. Much more text is devoted to the explanation of anthropogenic change rather natural decadal variability.

We have added more details in the paragraph 4.2.1 " Natural variability"

Overall, I am disappointed with the authors responses to both of my previous major concerns. Substantial improvements would still be needed to clarify these points to a satisfactory level before I could recommend that the manuscript would be publishable.

DETAILS:

lines 51-53: Change
The quantitative estimation of anthropogenic CO2 storage in the
Mediterranean Sea based on experimental data is very inaccurate, of the order of a factor two [Huertas et al., 2009; Touratier and Goyet2009] " to
"Estimates of anthropogenic storage in the in the Mediterranean Sea differ by about a factor of two [Huertas et al., 2009; Touratier and Goyet, 2009] "

This has been done.

lines 56-57: "[McKinley et al, 2011]" is repeated 5 times. This sentence is plagiarized from my review.

This has been corrected.

lines 58-59: Suggest changing of time is a way to detect a possible trend in DIC." to "iIs useful to assess trends and variability of DIC."

This has been corrected.

line 62: change "very close" to "nearby" or "adjacent".

This has been done.

line 86: delete "depth"

This has been done.

line 96: Incorrect format in sentence for citation.

This has been corrected.

line 101: change "meters" to "m"

This has been changed.

lines 108-109: Errors on fCO2 calculated from DIC and Alk, each having uncertainties of about 3 umol/kg, is about 5% based on results from Dickson (2010, Table 1.6). For a base value of fCO2=400 uatm, that would imply that the uncertainty in calculated fCO2 from Merlivat et al. is +/- 20 uatm. This is four times larger than the estimate quoted by the authors based on the paper from Millero et al. (2007). The authors need to mention this more recent study and the much higher uncertainty in calculated fCO2 that is implied from that.

Table 1.6 of Dickson (Acidification_Handbook_EU.,2010) refers to overall uncertainty on measurements performed using various techniques and coming from uncertainties on dissociation constants. As stated on page 37 the marine chemistry community rarely considers such combined uncertainty, because marine scientists usually consider measurements performed using a single technique, a single set of equilibrium constants, and are then interested in a precision estimate. This is our case, as measurements performed during the two time periods were performed using the same instrument type and the processing was made using the same dissociation constants. If a systematic error occurs, it will not significantly affect the changes estimated between the two time periods. Hence, we keep the error estimate according to (Millero 2007). It is also important to notice that in a recent study, Alvarez et al. (2014) recommend to use the dissociation constants of Mehrbach et al. (1973) refitted by Dickson and Millero(1987) in the Mediteranean Sea.

We have not added the reference to Dickson (2010) because of the reasons explained above. We have added a reference to Alvarez et al. (2014).

line 138: change this last effect should be negligible" to “the effect of nutrients may be neglected".

This has been corrected.

line 150: change "meters" to "m".

This has been changed.

line 236: delete It is interesting to note that

This has been corrected.

Table 1: Over the final 2 columns it is marked "Temporal trend". Actually this is not a trend (change per unit time) but just the difference between the 2 periods.

We have written "Temporal change".

lines 241-246: Confusing explanation of the uncertainties in the estimates of the difference dfCO213. just because there are 3 CARIOCA sensors and each is supposed to have an accuracy of +/-2 uatm does not mean that the accuracy of the estimate (presumably the time average) for each period is 2/(3)^0.5. The standard deviation of the measurements in each time period is much larger (7 to 28 uatm). The standard deviation of the difference is much larger still. The authors are not clear about what they are referring to exactly when they say that the accuracy on the difference is estimated to be 1.6 uatm." They may be referring to the standard error of the mean, but they do not say so explicitly. In any case, judging from the numbers in Table 1, the last 2 columns suggest that the difference between the 2 time periods is not always even significant. The authors would need to provide a significance test to show that the means of the two time periods actually differ significantly.

We have modified and rewritten this part as follows:

"We have estimated the uncertainties in the estimates of the difference dfCO$_2$@13 with 2 methods. Firstly, the arithmetic mean of dfCO$_2$@13 is equal to 33.17µatm, with a standard deviation, SD, and standard error, SE, respectively equal to 6.29 µatm and 1.68 µatm. A 95% confidence interval is thereby achieved within 1.96 SE, i.e 3.29 µatm. A second approach consists of computing a weighted average of the mean of dfCO$_2$@13. In this case, mean weighted value of dfCO$_2$@13 over the whole range of temperature is estimated, the weights being equal to the variance of dfCO$_2$@13 in each temperature step. It is equal to 32.70 µatm. The weighted SD, and the associated SE, of the 14 data points are respectively equal to 4.85 µatm and 1.30 µatm. A 95% confidence interval is achieved within 2.54 µatm. The difference between the two mean dfCO$_2$@13 estimates is 0.47 µatm, well below SE. In the following, we have chosen the former method which produces a more conservative estimate."

We hope that it is clearer.

lines 254-255: The authors do not provide enough detail on how they made their calculations for the changes in DIC and pH and the corresponding uncertainties. Are they using mean values of fCO213 and their for the two time periods? Are they using the standard error of the mean for the uncertainty? Without substantially more detail, I am left with the impression that they are underestimating the uncertainties. The uncertainties they do provide for the differences in DIC and pH are much smaller than the measurement uncertainties.

We indicate how we made the calculations for the change in DIC and pH. We have written (lines 281-285):

“The error on dfCO2@13 ,+/-3.3µatm, has been propagated to compute the uncertainty on dDIC and dp$H_{SWS}$. This makes the implicit assumption that there is no systematic error on DIC and p$H_{SWS}$ derived from fCO2@13 between the two time periods; in particular, mean temperature and salinity remain the same (section 3.2). This is further discussed in section 4.1.”

lines 275-276: change the corresponding amount of anthropogenic carbon taken up from the atmosphere in order to maintain a chemical equilibrium at the sea surface would be equal"

to

the corresponding change in surface DIC, assuming air-sea equiliibrium, would be would be

This has been changed

It is unsure that these annual mean calculations are adequate since it has been shown previously that the air-sea flux of anthropogenic carbon varies seasonally. This doubt is further supported by the authors own statements in their lines 291-297.

Our computations consider the annual budget of DIC in the mixed layer. They are independent of the seasonal variation of the air-sea flux of anthropogenic $CO_2$.

line 332 : improper format for citation

line 333 : improper format for citation

line 339 : improper format for citation

line 345: improper format for both citations.

We have made the corrections in the 3 cases.

line 355: The authors still use the symbol "pH_T", unlike what they say in their response to my previous comments.

This has been corrected.

line 356: improper format for citation.

line 360: improper format for citation.

line 364: improper format for citation.

We have made the corrections in the 4 cases.

Section 4.4: The discussion of changes in pH is inadequate. It does not consider that the change in pH depends not only on the change in

line 354-370: Section 4.4

This subsection appears particularly weak. It is descriptive but offers no real discussion. Why is the magnitude of the change of pH in the Mediterranean Sea more than the global ocean average. Is that difference significant? Why is it more than in the Iceland Sea but less than in the Irminger Sea. The authors have made no effort to discuss the causes of these differences. The last sentence only talks about the change in anthropogenic carbon, but that is not so clearly related to the change in pH since the alkalinity in the Mediterranean Sea is higher than at the other sites that are mentioned. Thus anthropogenic DIC increase there should be higher there although the pH change may be similar to that for the global ocean (Palmieri et al., 2015). But changes in pH are confusing because of the log scale. An absolute change in pH actually represents a relative change in H+.

This subsection has been deeply modified. The magnitude of the change of pH in the Mediterranean Sea does not differ significantly from the global ocean average. This is now clearly written. We have modified the title of the section “The signal of acidification” into “ Long term trends in surface DIC and pH” (lines 368-400). The section 4.3 has been rewritten.
We hope it is clearer now.

# Increase of dissolved inorganic carbon and decrease of pH in near surface waters of the Mediterranean Sea during the past two decades

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## Abstract

Two three-year-long time series of hourly measurements of the fugacity of $CO_2$ ($fCO_2$) in the upper 10m of the surface layer of the northwestern Mediterranean Sea have been recorded by CARIOCA sensors almost two decades apart, in 1995-1997 and 2013-2015. By combining them with alkalinity derived from measured temperature and salinity, we calculate changes of pH and dissolved inorganic carbon (DIC). DIC increased in surface seawater by ~ 25 µmol $kg^{-1}$ and $fCO_2$ by 40 µatm, whereas seawater pH decreased by ~ 0.04 (0.0022 $yr^{-1}$). The DIC increase is about 15% larger than expected from equilibrium with atmospheric $CO_2$. This could result from natural variability, e.g. the increase between the two periods in the frequency and intensity of winter convection events. Likewise, it could be the signature of the contribution of the Atlantic Ocean as a source of anthropogenic carbon to the Mediterranean Sea through the strait of Gibraltar. Under this assumption, we estimate that the part of DIC accumulated over the last 18 years represents ~30% of the total change of anthropogenic

carbon since the beginning of the industrial period.

## 1 Introduction

The concentration of atmospheric carbon dioxide ($CO_2$) has been increasing rapidly over the 20th century and, as a result, the concentration of dissolved inorganic carbon (DIC) in the near surface ocean increases, which drives a decrease in pH in order to maintain a chemical equilibrium. These changes have complex direct and indirect impacts on marine organisms and ecosystems [*Gattuso and Hansson*, 2011]. Empirical methods to estimate the anthropogenic $CO_2$ penetration in the ocean since the industrial revolution have improved over the past few decades [*Chen and Millero*, 1979; *Gruber et al.*, 1996]; [*Sabine et al.*, 2008]; [*F Touratier and Goyet*, 2004; 2009; *Woosley et al.*, 2016]. As the concentration of anthropogenic carbon, $C_{ant}$, cannot be distinguished from the natural background of DIC through total DIC measurements, these methods are based on the analysis of different chemical properties of the water column. Direct estimates of the anthropogenic $CO_2$ absorption in the sea surface layers are difficult owing to the large natural variability driven by physical and biological phenomena. [*Bates et al.*, 2014] have extracted the trend from the large variability, based on analysis of a long time series (monthly or seasonal sampling). For the global surface ocean, [*Lauvset et al.*, 2015] have used the Surface Ocean $CO_2$ Atlas (SOCAT) database [*Bakker et al.*, 2014] combined with an interpolation method. Estimates of anthropogenic storage in the Mediterranean Sea differ by about a factor of two [*Huertas et al.*, 2009; *F Touratier and Goyet*, 2009]. In addition to the anthropogenic signal, oceanic DIC can also be the signature of a strong interannual variability. In the North Atlantic, for instance, McKinley et al. [2011] has shown that the long term trend emerges after more than 25 years because of natural variability.

A high frequency sampling of the seawater carbon chemistry at the air-water interface over extended periods of time is useful to assess trends and variability of DIC. In this paper we analyze two three-year time series of hourly fugacity of $CO_2$, $fCO_2$, measured with autonomous CARIOCA sensors [*Copin-Montégut et al.*, 2004; *Merlivat and Brault*, 1995] in 1995-1997 and 2013-2015, at two nearby locations in the northwestern Mediterranean Sea (Fig. 1). Using measured $fCO_2$, temperature (T) and salinity (S), we derive the other variables of the carbonate system (pH and DIC). The experimental setting is first described, and the recent data obtained over the 2013-2015 period are presented. Combined with the 1995-1997 measurements previously published [*Hood and Merlivat*, 2001], we estimate the decrease of pH and the increase of DIC. The results are discussed with respect to the contributions of the exchange with atmospheric $CO_2$, to the possible impact of vertical mixing and to recent estimates of the transport of anthropogenic carbon from the Atlantic Ocean over a 18 years period.

## 2 Material and methods

### **2.1**-The BOUSSOLE and DYFAMED sites

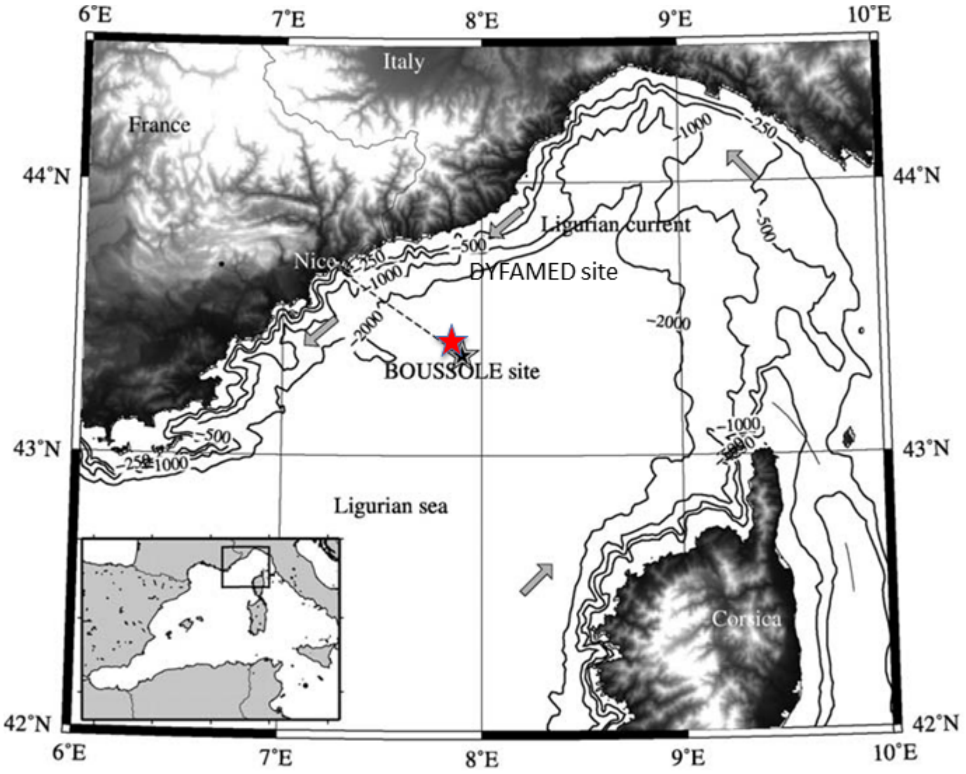

Fig.1. The area of the northwestern Mediterranean Sea showing the southern coast of France, the Island of Corsica, the main current branches (gray arrows), and the location of the DYFAMED site (43°25'N, 7°52'E, red star) and the BOUSSOLE buoy (43°22'N, 7°54'E, black star) in the Ligurian Sea.

Data collection was carried out at the BOUSSOLE site (43°22'N, 7°54'E) in 2013-2015 [*Antoine et al.*, 2008; *Antoine. and others*, 2006] and at the DYFAMED site (43°25'N, 7°52'E) in 1995-1997 [*J.C. Marty et al.*, 2002]. These sites are 3 nautical miles apart, both located in the Ligurian Sea, one of the basins of the northwestern Mediterranean Sea (Fig.1).

The water depth is of ~2400 m. The prevailing ocean currents are usually weak (<20 cm $s^{-1}$), because these sites are in the central area of the cyclonic circulation that characterizes the Ligurian Sea. The two sites surrounded by the permanent geostrophic Ligurian frontal jet flow are protected from coastal inputs [*Antoine et al.*, 2008; *Heimbürger et al.*, 2013; *Millot*, 1999]. Monthly cruises are carried out at the same location .

**2.2**- Analytical methods

At DYFAMED, $fCO_2$ measurements at 2 m were provided by an anchored floating buoy fitted with a CARIOCA sensor. At BOUSSOLE, measurements were carried out from a mooring normally dedicated to radiometry and optical measurements, and onto which two CARIOCA sensors were installed. Both monitored $fCO_2$ hourly at 3 and 10 m depth (although only one of the two depths was equipped with a functional sensor at some periods); S and T were monitored at the same two depths using a Seabird SBE 37-SM MicroCat instrument. The CARIOCA sensors were adapted to work under pressure in the water column. They were swapped about every 6 months, with serviced and calibrated instruments replacing those having been previously deployed. The accuracy of CARIOCA $fCO_2$ measurements by the spectrophotometric method based on the optical absorbance of a solution thymol blue diluted in seawater is estimated at 2 µatm during both periods. Hood and Merlivat [2001] have reported agreement between $fCO_2$ measured by CARIOCA buoys, similar to the one deployed at DYFAMED, with ship based measurements, during a number of field programs, with an accuracy of 2 µatm and a precision of 5 µatm .

At Boussole, newly designed $fCO_2$ sensors have been calibrated using in situ seawater samples taken at 5 and 10 m depth during the monthly servicing cruises to the mooring. The total alkalinity, Alk, and DIC of the samples were determined by potentiometric titration using a closed cell according to the method developed by [*Edmond*, 1970]. Certified Reference Materials (CRMs) supplied by Dr. A.G. Dickson (Scripps Institution of Oceanography, San Diego, USA) were used for calibration [*Dickson et al.*, 2007]. The accuracy is estimated at 3 µmol $kg^{-1}$ for both DIC and Alk. $fCO_2$ is calculated using the dissociation constants of Mehrbach refitted by Dickson and Millero [*Dickson and Millero*, 1987; *Mehrbach et al.*, 1973] as recommended by Alvarez et al.[2014] for the Mediterranean Sea. Error on $fCO_2$ derived from an individual sample is expected to be on the order of 5 µatm [*Millero*, 2007]. About 8 samples have been used to calibrate each CARIOCA sensor so that the error on the absolute calibration of each $fCO_2$ CARIOCA sensor, is estimated at 1.8 µatm. In addition, we observe that the standard deviation of the difference between the

CARIOCA $fCO_2$ and $fCO_2$ computed with the monthly discrete samples (Fig. 2b) is equal to 4.4 µatm, consistent with the expected precision on CARIOCA $fCO_2$ of 5 µatm. Alk and S of the 56 samples taken at BOUSSOLE are linearly correlated according the following relationship :

$$\text{Alk } (\mu\text{mol kg}^{-1}) = 87.647 \text{ S} - 785.5 \qquad (1)$$

The standard deviation of the Alk data around the regression line is equal to 4.4 µmol $kg^{-1}$ ($r^2$=0.89).

## 3 Results

### **3.1** The BOUSSOLE mooring (2013-2015) time series

Temperature and $fCO_2$ were measured from February 2013 to February 2016. All seasons were well represented, with missing data only in May-July 2013. For some periods, simultaneous measurements were made at 3 and 10 m depth (Fig. 2, a, b, c).

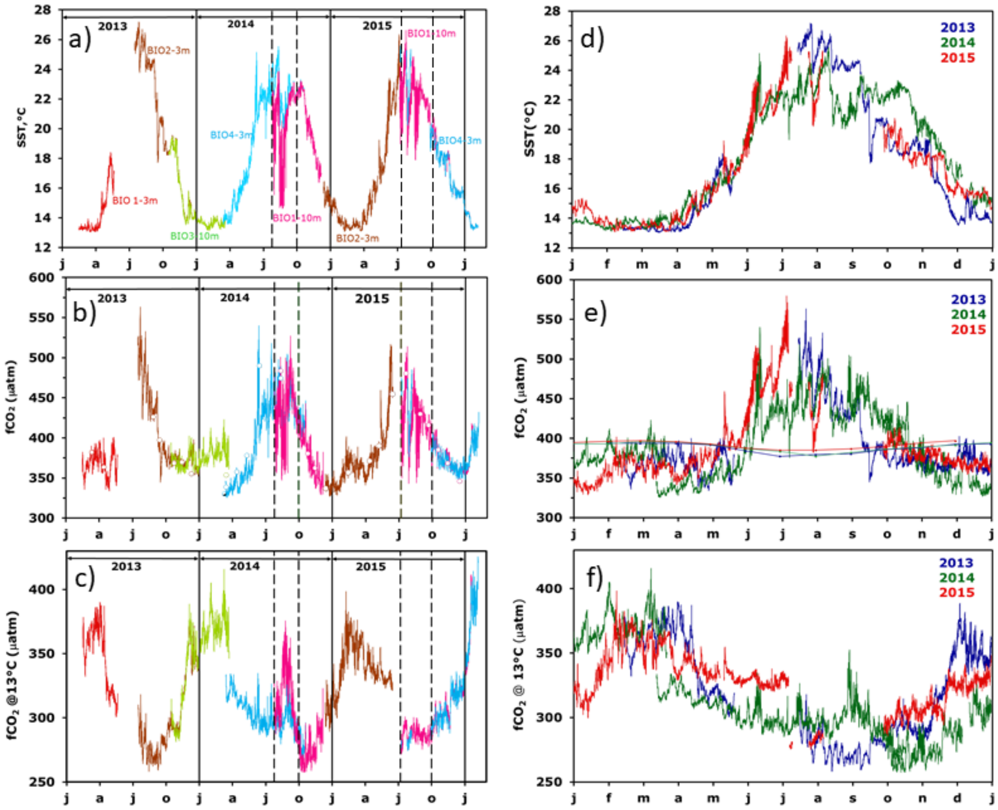

Fig.2. Interannual variability of CARIOCA data: a) T, b) $fCO_2$, c) $fCO_2$@13. The dotted lines indicate the period affected by stratification and internal waves (July, 26 th to October 1st, 2014 and July, 8 th to October 1st, 2015). On 2(b), the open circles correspond to fCO2 data derived from DIC and alkalinity measurements of samples taken at 5 and 10 m. (d), (e), (f),

seasonal variability. On 2(e), the thin lines indicate $fCO_{2atm}$. Note that the color code on (d), (e), (f) is different from (a), (b), (c).

The range of temperature (Fig. 2a) extends from 13°C in winter up to 27°C in summer, followed by progressive cooling in fall. The coldest temperature, 13°C, results from the winter vertical mixing with the deeper Levantine Intermediate Water, LIW, marked by extrema in temperature and salinity [*Copin-Montegut and Begovic*, 2002]. Temperature provides the main control of the seasonality of $fCO_2$, from 350 µatm to more than 550 µatm in summer 2013 (Fig. 2b). The fugacity of $CO_2$ in seawater is a function of temperature, DIC, alkalinity, salinity and dissolved nutrients. In the oligotrophic surface waters of the Mediterranean Sea, the effect of nutrients may be neglected. Temperature and DIC have the strongest influences. By normalizing $fCO_2$ to a constant temperature, the thermodynamic effect can be removed and changes in $fCO_2$ resulting from changes in DIC can be more easily identified. Figure 2c shows the variability of $fCO_2$ normalized to the constant temperature of 13°C, ($fCO_2$@13), using the equation of [*Takahashi et al.*, 1993]. The underlying processes that govern the seasonal variability of $fCO_2$@13 are successively winter mixing, biological activity (organic matter formation and remineralization) and deepening of mixed layer in fall [*Begovic and Copin-Montegut*, 2002; *Hood and Merlivat*, 2001]. Biology accounts for the decline in $fCO_2$@13 observed from March-April to late summer; the ensuing increase of surface $fCO_2$@13 is associated with the deepening of the mixed layer in the fall or convection in winter as the vertical distribution of $fCO_2$@13 at DYFAMED shows a maximum in the 50-150 m layer where a large remineralization of organic matter occurs, the productive layer being mostly between 0 and 40 m [*Copin-Montegut and Begovic*, 2002]. The contribution of air-sea exchange is not significant [*Begovic and Copin-Montegut*, 2002]. Over the period 2013-2015, the $CO_2$ air-sea flux from the atmosphere to the ocean surface is equal to -0.45 mol $m^{-2}$ $yr^{-1}$.

During summer 2014, large differences between measurements at 3 and 10 m were observed (Fig. 2, a, b, c between dashed lines). A detailed analysis of the temporal variability during that period underscores the role of inertial waves at the frequency of 17.4 hours that create the observed differences between the 2 depths of observations, the deeper waters being colder and enriched in $fCO_2$@13. T and $fCO_2$@13 variability is dominated by inertial waves. In particular, from 15 to 26 of August 2014, the difference in T between the two depths is as large as 7.6°C, and 5.1°C on average. $fCO_2$ decreases on average by 32.7 μatm leading to an increase of $fCO_2$@13 equal to 42.8 μatm.

The 2013-2015 seasonal and inter-annual variability of T, $fCO_2$ and $fCO_2$@13 is illustrated on Fig. 2, d, e, f. The larger interannual changes in temperature (Fig.2, d) are observed during summer, both at 3 m and 10 m depth, while over February and March, a constant value of 13°C is observed as the result of vertical mixing with the LIW. A very large inter-annual variability of $fCO_2$@13 is observed for T<14°C (Fig. 2,f). This is associated with the winter mixing at the mooring site, which is highly variable from year to year. Winter mixed-layer depth, MLD, varies between 50 and 160 m, at the top of the LIW over the 2013-2015 period [*Coppola et al.*, 2016]. The variable depth of the winter vertical mixing causes the difference in $fCO_2$@13 as $fCO_2$ increases with depth [*Copin-Montegut and Begovic*, 2002]. The deepening of MLD is driven by episodic and intense mixing processes characterized by a succession of events lasting several days, related to atmospheric forcing [*Antoine et al.*, 2008] which lead to increase in $fCO_2$@13. Figure 2,e illustrates the solubility control of the variability of $fCO_2$, as fCO2 increases when T increases. Another cause of inter-annual variability of $fCO_2$ for T~14°C is the timing of the spring increase of biological activity which differs by a month between years; for instance, it happened at the beginning of April in 2013, T~15-16°C and by mid March in 2014, T~14°C. Another cause is the deepening of the mixed layer due to the fall cooling which varies by a month between years.

### **3.2** Decadal changes of hydrography

#### **3.2.1** Sea surface temperature changes

Monthly mean values of temperature have been computed for the two three-year periods, 1995-1997 and 2013-2015. In 1995-1997, $fCO_2$ and T at 2 m were measured with CARIOCA sensors installed on a buoy at DYFAMED [*Hood and Merlivat*, 2001]. The mean annual temperature of hourly CARIOCA data is equal to 18.21°C. For 2013-2015, temperature measurements made on the BOUSSOLE mooring at 3 and 10 meters have been used. For the April to September time interval, there are only data at 3m depth. In addition, temperature data measured half hourly at 0.7 m at a nearby meteorological buoy (43°23'N, 7°50'E) (http://www.meteo.shom.fr/real-time/html/DYFAMED.html) have been used (Fig.3d). Mean annual temperature are equal to 18.29°C and 17.97°C respectively, based on the meteorological buoy and the BOUSSOLE mooring data. The two sets of data differ essentially during July and August, with the temperatures at 3 m being colder than at 0.7 m, indicating a thermal gradient between the two depths during summer. Therefore, for 2013-2015, we select the mean annual value computed with the meteorological buoy, 18.29°C, as better representing the sea surface. This value is very close to 18.21°C computed for 1995-1997. Then, no significant change of SST is found between the 2 decades, with a mean value equal to 18.25°C.

#### **3.2.2** Sea surface salinity changes

The mean value of salinity computed from 56 samples taken at BOUSSOLE in 2013-2015 is equal to 38.19+/-0.14. In 1998-1999, ship measurements of surface salinity were made during monthly cruises at the DYFAMED site [*Copin-Montégut et al.*, 2004]. The mean salinity of this set of 19 data is equal to 38.21+/-0.12. Thus, there is no significant salinity change between the two decades.

### **3.3** Decadal changes of $fCO_2$@13

#### **3.3.1** Time series of $fCO_2$@13 in 1995-1997 and 2013-2015

The two time series of high frequency data were analyzed in order to quantify the change of $fCO_2$@13 at the sea surface two decades apart. To account for the interannual seasonal variability as well as irregular sampling, we performed an analysis of the change of $fCO_2$@13 as a function of SST (Fig. 3, a and b). For the 2013-2015 data set, we excluded summer data measured at 10 m depth as they were not representative of the surface mixed layer due to a strong stratification. Much larger $fCO_2$@13 values are observed at low temperature than at high temperature, the decrease being similar for the two studied periods and strongly non linear. As described in section 3.1, large values at low temperature result from mixing with enriched deep waters during winter and low values for 26°C-28°C temperatures occur at the end of summer after biological drawdown of carbon. An increase of $fCO_2$@13 between the 2 periods is clearly highlighted for the whole range of temperature.

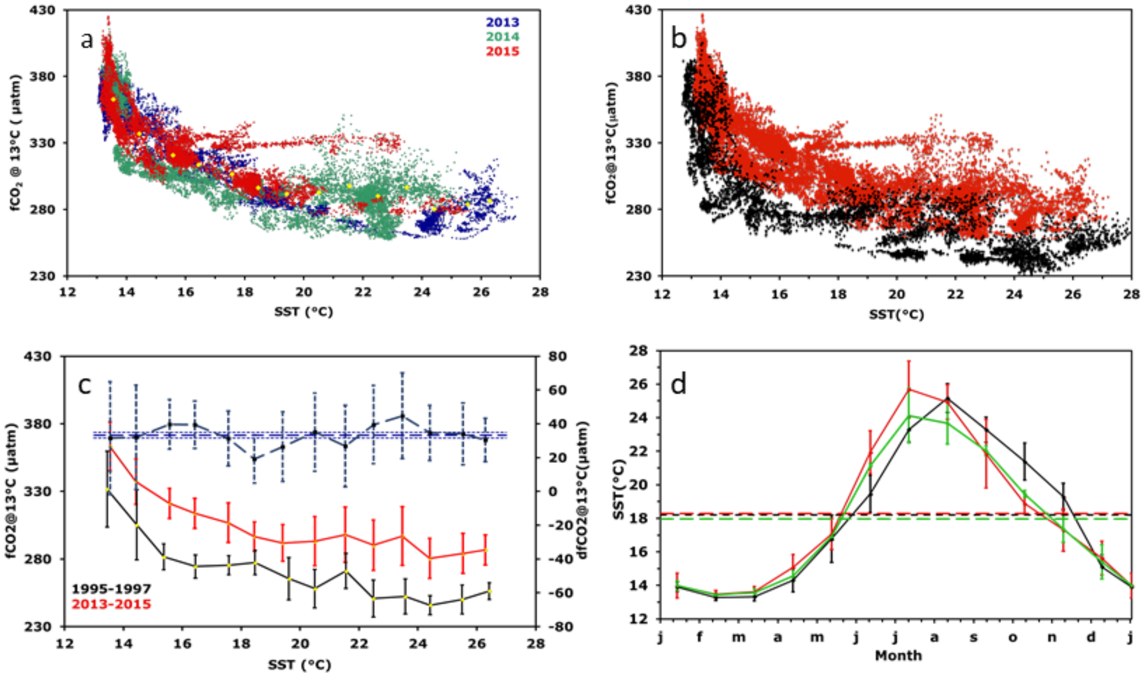

Fig.3. (a) fCO$_2$@13 as a function of temperature for hourly data in 2013, 2014 and 2015.The yellow dots indicate mean fCO$_2$@13 (b) as in (a) but for all hourly data in 1995-1997 (black) and in 2013-2015 (red) (c) As in (b), but for average values per 1°C interval (standard deviation as dotted line). The difference between the two periods is also displayed (dashed black curve; scale on the right axis). (d) Mean monthly sea surface temperature for 1993-1995 (black curve; CARIOCA sensors), 2013-2015 (green; CARIOCA sensors), 2013-2015 (red, meteorological buoy). Corresponding mean annual values are indicated by dotted lines.

### **3.3.2** Trend analysis and statistics

To quantify the change of fCO$_2$@13 between the two data sets, we proceed as follows: data are binned by 1°C temperature intervals, thereby removing any potential seasonal weighting, especially towards the 13-14°C winter months temperature. The measurements made in this temperature interval represent about 25% of the total number of data for both periods. For each of the fourteen 1°C step, the mean and standard deviation of hourly fCO$_2$@13 measurements are reported in Table 1 and on Fig. 3c.

| | Time interval 1995-1997 | | | Time interval 2013-2015 | | | | Temporal change | |
|---|---|---|---|---|---|---|---|---|---|
| T$^1$ °C | fCO2@13 µatm | N | standard deviation µatm | T$^1$ °C | fCO2@13 µatm | N | standard deviation µatm | dfCO2@13 µatm | standard deviation µatm |
| 13.45 | 331.58 | 1212 | 28.09 | 13.55 | 363.14 | 6869 | 18.07 | 31.56 | 33.40 |
| 14.45 | 305.28 | 495 | 26.02 | 14.43 | 337.16 | 3270 | 16.65 | 31.87 | 30.89 |
| 15.37 | 281.54 | 447 | 9.62 | 15.57 | 321.10 | 3112 | 11.09 | 39.56 | 14.68 |
| 16.44 | 274.43 | 182 | 8.53 | 16.42 | 313.79 | 1818 | 11.09 | 39.36 | 13.99 |
| 17.58 | 275.54 | 190 | 7.04 | 17.56 | 306.83 | 1528 | 14.65 | 31.29 | 16.25 |
| 18.47 | 277.34 | 300 | 9.04 | 18.45 | 296.57 | 2621 | 10.95 | 19.23 | 14.20 |
| 19.62 | 265.43 | 342 | 15.58 | 19.41 | 291.84 | 1406 | 13.45 | 26.40 | 20.59 |
| 20.50 | 258.08 | 529 | 14.15 | 20.50 | 293.16 | 1135 | 18.21 | 35.08 | 23.06 |
| 21.56 | 271.15 | 239 | 12.98 | 21.54 | 297.96 | 1200 | 20.41 | 26.82 | 24.19 |
| 22.49 | 250.75 | 742 | 13.66 | 22.49 | 290.27 | 2385 | 18.57 | 39.52 | 23.05 |
| 23.57 | 252.22 | 320 | 13.00 | 23.47 | 296.92 | 747 | 21.77 | 44.70 | 25.36 |
| 24.41 | 245.85 | 506 | 7.08 | 24.40 | 280.44 | 959 | 14.82 | 34.59 | 16.43 |
| 25.50 | 250.06 | 215 | 10.77 | 25.53 | 284.05 | 456 | 14.81 | 33.99 | 18.31 |
| 26.42 | 256.29 | 279 | 6.24 | 26.29 | 286.71 | 249 | 11.23 | 30.42 | 12.85 |

Table 1:

Distribution of temperature, fCO2@13, and increase dfCO2@13 data binned by 1°C temperature interval for the 2 periods 1995-1997 and 2013-2015.

The mean temperature within each 1° step differ for the two periods as the distribution of individual measurements are not identical.

For both data sets, a monotonic relationship between fCO$_2$@13 and T is observed with correlation coefficients respectively equal to -0.861 and -0.857. The difference in fCO2@13 between the two periods, dfCO2@13, is derived in each temperature step, as the difference between column 2 and 6 of Table 1. The variability of this difference is estimated as the quadratic mean of the standard deviation in each time series. Both values are reported in Table 1, column 9 and 10, and on Fig. 3c.

The distribution of dfCO$_2$@13 values around the mean seems random and indicates no trend dependency with SST (Fig. 3c). This suggests that the processes which control the seasonal variation of $fCO_2$@13 at the sea surface have not changed over the last two decades.

We have estimated the uncertainties in the estimates of the difference $dfCO_2$@13 with 2 methods. Firstly, the arithmetic mean of $dfCO_2$@13 is equal to 33.17µatm, with a standard deviation, SD, and standard error, SE, respectively equal to 6.29 µatm and 1.68 µatm. A 95% confidence interval is thereby achieved within 1.96 SE, i.e 3.29 µatm. A second approach consists of computing a weighted average of the mean of $dfCO_2$@13. In this case, mean weighted value of $dfCO_2$@13 over the whole range of temperature is estimated, the weights being equal to the variance of $dfCO_2$@13 in each temperature step. It is equal to 32.70 µatm. The weighted SD, and the associated SE, of the 14 data points are respectively equal to 4.85 µatm and 1.30 µatm. A 95% confidence interval is achieved within 2.54 µatm. The difference between the two mean $dfCO_2$@13 estimates is 0.47 µatm, well below SE. In the following, we have chosen the former method which produces a more conservative estimate.

### **3.4** Changes of seawater carbonate chemistry in surface waters

We estimated the DIC and pH changes related to the increase of $fCO_2$@13 measured at the sea surface 18 years apart, assuming a mean salinity equal to 38.2, a mean alkalinity equal to 2562.3 µmol $kg^{-1}$ following equation (1), and a mean in situ temperature, T, equal to 18.25°C. The dissociation constants of Mehrbach refitted by Dickson and Millero [*Dickson and Millero*, 1987; *Mehrbach et al.*, 1973] were used. pH is calculated on the seawater scale. The error on dfCO2@13 ,+/-3.3µatm, has been propagated to compute the uncertainty on dDIC and $dpH_{SWS}$. This makes the implicit assumption that there is no systematic error on DIC and $pH_{SWS}$ derived from fCO2@13 between the two time periods; in particular, mean temperature and salinity remain the same (section 3.2). This is further discussed in section 4.1.We compute an increase of DIC, dDIC, equal to 25.2+/-2.7 $\mu$ mol $kg^{-1}$ (1.40+/-0.15 $\mu$ mol $kg^{-1}yr^{-1}$) and the decrease of $pH_{SWS}$ , $dpH_{SWS}$ equal to -0.0397+/-0.0042 $pH_{SWS}$ unit (-0.0022+/-0.0002 $pH_{SWS}$ unit $yr^{-1}$) (Table 2).

| | d $fCO_2^*$ @ 13 µatm | d $fCO_2^*$ @ T µatm | d DIC$^*$ µmolkg$^{-1}$ | d $pH_{SWS}$*** pH unit | $dfCO_2$@T annual µatm $yr^{-1}$ | d DIC annual µmolkg$^{1}$yr$^{1}$ | d $pH_{SWS}$*** annual pH unit yr$^{1}$ |
|---|---|---|---|---|---|---|---|
| sea surface | 33.2 +/-3.3 | 41.4 +/-4.1 | 25.2 +/-2.7 | -0.0397 +/-0.0042 | 2.30 +/-0.23 | 1.40 +/-0.15 | -0.0022 +/-0.0002 |
| atmosphere Lampedusa data | | 34.3 +/-2.3 | **20.8 +/-1.3 | | 1.91 +/-0.13 | 1.15 +/-0.07 | |
| $dfCO_2@T_{air}/dfCO_2@T_{sea}$ | | 0.83 +/-0.10 | 0.83 +/-0.09 | | | | |

Table 2

Seasonally detrended long term and annual trends of seawater carbonate chemistry and atmosphere composition.

T, mean annual temperature equal to 18.25°C

*, change from 1995-1997 to 2013-2015.

**, dDIC $_{ant}$

*** $dpH_{SWS}$ computed at T

### 3.5 Changes in atmospheric and seawater $fCO_2$

The increase of atmospheric $fCO_2$ from 1995-1997 to 2013-2015 was computed from monthly atmospheric $xCO_2$ concentrations measured at the Lampedusa Island station (Italy) (35°31'N, 12°37'E) (http://ds.data.jma.go.jp/gmd/wdcgg/) (see equation 3 in [*Hood and Merlivat*, 2001]). Considering a mean annual in situ temperature equal to 18.25°C and an atmospheric pressure of 1 atm, we derived a mean atmospheric $fCO_2$ equal to 355.3+/-0.8 µatm for 1995-1997 and 389.6+/-0.9 µatm for 2013-2015, that is an increase of 34.3+/-2.3 µatm (95% confidence interval) (Table 2). At this temperature, the change of $fCO_2$ at the sea surface is 41.4+/-4.1 µatm. Thus the contribution of the increase in atmospheric $CO_2$ is responsible for 84+/-5 % of the increase of $fCO_2$ measured in the surface waters. With the same salinity and alkalinity as previously, the corresponding change in surface DIC, assuming air-sea equilibrium, would be 20.8+/- 1.3 µmol kg$^{-1}$ (Table 2).

## 4 Discussion

### 4.1 Time change of surface alkalinity

High frequency measurements of $fCO_2$ and temperature over 2 periods of 3 years, 2 decades apart, have allowed the computation of an increase of DIC equal to 25.1+/-2.3 µmol kg$^{-1}$ assuming no change of alkalinity. In the range of salinity of the BOUSSOLE samples, 37.9 to 38.5, the alkalinity values computed with Eq (1) are larger than those predicted by the relationship established for the DYFAMED site, with a mean difference equal to 10+/-2 µmol kg$^{-1}$ [*Copin-Montegut and Begovic*, 2002]. In both cases alkalinity measurements were made with a potentiometric method using certified reference material supplied by A.G. Dickson for calibration. It is difficult to identify the cause for a possible change of alkalinity between the 2 periods, 18 years apart, while no salinity change has been observed. At a coastal site 50 km away from DYFAMED, Kapsenberg et al. [2017] have measured an increase of alkalinity unrelated to salinity over the period from 2007 to 2015. They attribute it to changes in freshwater inputs from land. However, based on data from Coppola et al. [2016], alkalinity in the upper 50m at DYFAMED did not change significantly from 2007 through 2014 (3.204 µmol kg$^{-1}$, P=0.0794, $r^{*2}$=0.08). Thus, we cannot conclude on whether the difference observed at DYFAMED/BOUSSOLE between the two periods is real or an artifact of measurement techniques. As a sensitivity test, we compute the expected changes of DIC and pH from 1995-1997 to 2013-2015 for a mean alkalinity increase of 10 µmol kg$^{-1}$: we get annual changes, dDIC=+0.46 µmol kg$^{-1}$ yr$^{-1}$ and dpH=-0.0001 pH unit yr$^{-1}$, which are well below errors estimated in section 3.4. Hence, such a change in alkalinity does not significantly affect the increase of DIC and the decrease of pH shown in Table 2.

### **4.2** Drivers of the temporal change of DIC in surface waters

The increase in sea surface DIC from 1995-1997 to 2013-2015 is 25.2+/-2.7 µmol kg$^{-1}$ (Table 2). The expected contribution due to ocean uptake of anthropogenic $CO_2$ is 20.8+/-1.3 µmol kg$^{-1}$. The difference between these two values is significant. In order to interpret this difference, we examine potential changes that may result from interannual variability in local physical and biological processes or anthropogenic carbon invasion from lateral advection of Atlantic waters.

#### **4.2.1** Natural variability

Time series of mixed layer depth, MLD, show a strong variability in winter at interannual scale. During the two periods, 1995-1997 and 2013-2015, the winter MLD never exceeded 220 m, whereas values over 300 m were observed in 1999 and especially in February and March 2006 with values close to 2000 m [Coppola et al., 2016; Pasqueron de Fommervault et al., 2015]. These episodes of strong and deep vertical mixing must have entrained DIC rich

LIW in the surface waters. This could be causing an increase in DIC between the 1995-1997 and 2013-2015 periods. Monthly surface samples collected at the Dyfamed time series station between 1998 and 2013 indicate an increasing DIC trend of 1.35 µmol kg$^{-1}$ yr$^{-1}$. This value is known with great uncertainty ($r^2 = 0.05$) because of the large seasonal variability displayed in the monthly samples [*Gemayel et al.*, 2015]. Nevertheless, this value is closer to the trend we calculated between the two periods, 1993-1995 and 2013-2015 (1.40 µmol kg$^{-1}$ yr$^{-1}$) than to the trend inferred from the atmospheric increase (1.15 µmol kg$^{-1}$ yr$^{-1}$). On DYFAMED time series, we find no evidence that the strong increase in MLD observed during winters 1999 and especially 2006 resulted in a further increase in DIC.

The monthly cruises of the Dyfamed time-series study have also been analyzed in order to investigate the hydrological changes and some biological consequences over the period 1995-2007 [*J. C. Marty and Chiavérini*, 2010]. These authors show that extreme convective mixing events such as recorded in 1999 and 2006 are responsible of large increases in nutrient content in surface layers and conclude that the biological productivity is increasing especially during the 2003-2006 period, which could lead to a larger consumption of carbon, i.e. a decrease of DIC.

### **4.2.2** Anthropogenic carbon exchange through the Strait of Gibraltar.

The concentration of oceanic anthropogenic carbon, $C_{ant}$, is not a directly measurable quantity. To estimate it, several empirical methods have been developed. Flecha et al.[2012] computed the anthropogenic carbon inventory in the Gulf of Cadiz. They used observations made during a cruise in October 2008 throughout the oceanic area covered by the Gulf of Cadiz and the Strait of Gibraltar to estimate $C_{ant}$ with 3 methods: $\Delta C^*$ [*Gruber et al.*, 1996] ,TrOCA [*F Touratier and Goyet*, 2004; *F. Touratier et al.*, 2007] , $\varphi C_T^0$ [*Vazquez-Rodriguez et al.*, 2009]. In the 3 cases, their results indicate a net import of $C_{ant}$ from the Atlantic towards the Mediterranean through Gibraltar.

Schneider et al. [2010], using the transit time distribution method applied to a dataset of a Mediterranean cruise in 2001, estimated a net anthropogenic carbon flux across the Strait of Gibraltar into the Mediterranean Sea of 3.5 Tg C yr$^{-1}$. Over the whole period from 1850 to 2001, this contribution of $C_{ant}$ represents almost 10% of the total $C_{ant}$ inventory of the Mediterranean Sea. Accordingly, about 90% must have been taken directly by equilibrium with atmospheric $CO_2$. Based on a high-resolution regional model, Palmieri et al. [2015] computed the anthropogenic carbon storage in the Mediterranean basin. They concluded that 75% of the total storage of $C_{ant}$ in the whole basin comes from the atmosphere and 25% from net transport from the Atlantic through the Strait of Gibraltar. The findings of these two studies support our estimated change of DIC in excess of 17+/-10% over the direct contribution of air-sea exchange suggesting that it could result from the anthropogenic carbon input from the Atlantic Ocean towards the Mediterranean basin.

Huertas et al. [2009] and Schneider et al. [2010] report $DIC_{ant}$ surface concentrations respectively equal to 65-70 µmol $kg^{-1}$ at the Strait of Gibraltar in the years 2005-2007 and close to 65 µmol $kg^{-1}$ in the western basin in 2001. We extrapolate these figures to the year 2014, assuming a mean increase rate of DIC equal to 1.4 µmol $kg^{-1}yr^{-1}$ as previously computed (Table 2). Taking into account the increase of $DIC_{ant}$ equal to 25.2 µmol $kg^{-1}$ between 1995-1997 and 2013-2015, we would estimate that the contribution of the change of $DIC_{ant}$ over the last 18 years represents ~30% of the total change since the beginning of the industrial period (t>~1800).

## 4.3 Long term trends in surface DIC and pH

The annual changes of DIC and $pH_{SWS}$ calculated between 1995-1997 and 2013-2015 are respectively equal to 1.40 +/-0.15 µmol $kg^{-1}$ and -0.0022+/-0.0002. At the DYFAMED site, at 10 m, Marcellin Yao et al. [2016] studied the time variability of pH over 1995-2011, based on measurements of T, S, Alk and DIC sampled approximately once a month. They computed a mean annual decrease of -0.003 ± 0.001 pH units on the seawater scale that is not significantly different from our estimate. For the global surface ocean, Lauvset et al. [2015] have reported a mean rate of decrease of pH, -0.0018+/-0.0004 for 1991-2011. This value is also within the limits of uncertainty of the pH change computed in our study.

Bates et al. [2014] examined changes in surface seawater $CO_2$-carbonate chemistry at the locations of seven ocean $CO_2$ time series that have been gathering sustained observations from 15 to 30 years with monthly or seasonal sampling. Six stations are located in the Atlantic and Pacific oceans in a latitudinal band between 10° N and 68°N. The range of increasing and decreasing annual trends of DIC and pH extends from 0.93 +/-0.24 to 1.89 +/-0.45 µmol $kg^{-1}yr^{-1}$ and -0.0014+/-0.0005 to -0.0026+/-0.0006 respectively. The Revelle factor of surfaces waters vary from 9-10 in the low latitude to 12-15 in the subpolar time series sites, with higher Revelle factor values reflecting reduced capacity to absorb atmospheric $CO_2$. The data show that the increase of DIC is not only controlled by the buffer capacity of the water but compounding effects of changes in physical factors as strengthening of winter mixing or larger air-sea uptake, have also to be taken into account [*Olafson et al.*, 2010].

The increase of DIC computed at DYFAMED is rather in the upper range of values reported at the other time series. A low Revelle factor, close to 10, characterizes the Mediterranean

Sea because of its warm and high-alkalinity waters. Moreover, as the result of a relatively short deep water renewal time estimated to be 20-40 years in the western basin[*Schneider et al.*, 2010] , the waters of the Mediterranean Sea have a relatively high absorption capacity to absorb anthropogenic $CO_2$ from the atmosphere and transport it to depth.

The calculated decrease of pH in surface water at DYFAMED and in the global ocean are quite similar, despite the higher alkalinity of the Mediterranean Sea. Thermodynamic equilibrium calculations have highlighted the alkalinity effect on the Mediterranean anthropogenic acidification [*Palmiéri et al.*, 2015]. Their results show that, notwithstanding a higher total alkalinity, the average anthropogenic change in surface pH does not differ significantly from the global average ocean.

## 5 Conclusion

High-frequency ocean $fCO_2$ measurements made by CARIOCA sensors were sufficient to estimate trends in $fCO_2$, DIC and pH over a period of two decades, notwithstanding a considerable short-time and natural seasonal variability of these properties at the sea surface. We have estimated a large change of sea surface carbonate chemistry, an increase of DIC and a decrease of pH. The computed increase of DIC is larger than the change expected from chemical equilibrium with atmospheric $CO_2$.This could be the result of a strong interannual variability of the winter mixing as observed between the two periods 1993-1995 and 2013-2015. Likewise, our results support modeling work and analysis of vertical profiles measurements that suggest that the Atlantic Ocean contributes as a source of anthropogenic carbon towards the Mediterranean basin, close to 10% ([*Schneider et al.*, 2010] or 25% [*Palmiéri et al.*, 2015].

*Data availability*: Time series data from Dyfamed (19951997) are available in the SOCAT v3 database. Boussole data (2013-2015) will be available in SOCAT v6.

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Table 1:

Distribution of temperature, fCO$_2$@13, and increase dfCO$_2$@13 data binned by 1°C temperature interval for the 2 periods 1995-1997 and 2013-2015 .

The mean temperature within each 1° step differ for the two periods as the distribution of individual measurements are not identical.

| Time interval 1995-1997 | | | | Time interval 2013-2015 | | | | Temporal change | |
|---|---|---|---|---|---|---|---|---|---|
| T[1] °C | fCO2@13 µatm | N | standard deviation µatm | T[1] °C | fCO2@13 µatm | N | standard deviation µatm | dfCO2@13 µatm | standard deviation µatm |
| 13.45 | 331.58 | 1212 | 28.09 | 13.55 | 363.14 | 6869 | 18.07 | 31.56 | 33.40 |
| 14.45 | 305.28 | 495 | 26.02 | 14.43 | 337.16 | 3270 | 16.65 | 31.87 | 30.89 |
| 15.37 | 281.54 | 447 | 9.62 | 15.57 | 321.10 | 3112 | 11.09 | 39.56 | 14.68 |
| 16.44 | 274.43 | 182 | 8.53 | 16.42 | 313.79 | 1818 | 11.09 | 39.36 | 13.99 |
| 17.58 | 275.54 | 190 | 7.04 | 17.56 | 306.83 | 1528 | 14.65 | 31.29 | 16.25 |
| 18.47 | 277.34 | 300 | 9.04 | 18.45 | 296.57 | 2621 | 10.95 | 19.23 | 14.20 |
| 19.62 | 265.43 | 342 | 15.58 | 19.41 | 291.84 | 1406 | 13.45 | 26.40 | 20.59 |
| 20.50 | 258.08 | 529 | 14.15 | 20.50 | 293.16 | 1135 | 18.21 | 35.08 | 23.06 |
| 21.56 | 271.15 | 239 | 12.98 | 21.54 | 297.96 | 1200 | 20.41 | 26.82 | 24.19 |
| 22.49 | 250.75 | 742 | 13.66 | 22.49 | 290.27 | 2385 | 18.57 | 39.52 | 23.05 |
| 23.57 | 252.22 | 320 | 13.00 | 23.47 | 296.92 | 747 | 21.77 | 44.70 | 25.36 |
| 24.41 | 245.85 | 506 | 7.08 | 24.40 | 280.44 | 959 | 14.82 | 34.59 | 16.43 |
| 25.50 | 250.06 | 215 | 10.77 | 25.53 | 284.05 | 456 | 14.81 | 33.99 | 18.31 |
| 26.42 | 256.29 | 279 | 6.24 | 26.29 | 286.71 | 249 | 11.23 | 30.42 | 12.85 |

## Table 2

Seasonally detrended long term and annual trends of seawater carbonate chemistry and atmosphere composition.

T,mean annual temperature equal to 18.25°C

*, Change from 1995-1997 to 2013-2015.

**, $dDIC_{ant}$

***, $dpH_{SWS}$ computed at T

| | d $fCO_2^{*}$– @ 13 µatm | d $fCO_2^{*}$– @ T µatm | d $DIC^{*}$ µmolkg$^{-1}$ | d $pH_{SWS}$ *** pH unit | $dfCO_2$@T annual µatm yr$^{-1}$ | d DIC annual µmolkg$^{1}$yr$^{1}$ | d $pH_{SWS}$ *** annual pH unit yr$^{1}$ |
|---|---|---|---|---|---|---|---|
| sea surface | 33.2 +/-3.3 | 41.4 +/-4.1 | 25.2 +/-2.7 | -0.0397 +/-0.0042 | 2.30 +/-0.23 | 1.40 +/-0.15 | -0.0022 +/-0.0002 |
| atmosphere Lampedusa data | | 34.3 +/-2.3 | **20.8 +/-1.3 | | 1.91 +/-0.13 | 1.15 +/-0.07 | |
| $dfCO_2@T_{air}/dfCO_2@T_{sea}$ | | 0.83 +/-0.10 | 0.83 +/-0.09 | | | | |

Figure 1. The area of the northwestern Mediterranean Sea showing the southern coast of France, the Island of Corsica, the main current branches (gray arrows), and the location of the DYFAMED site (43°25’N, 7°52’E, red star) and the BOUSSOLE buoy (43°22’N, 7°54’E, black star) in the Ligurian Sea.

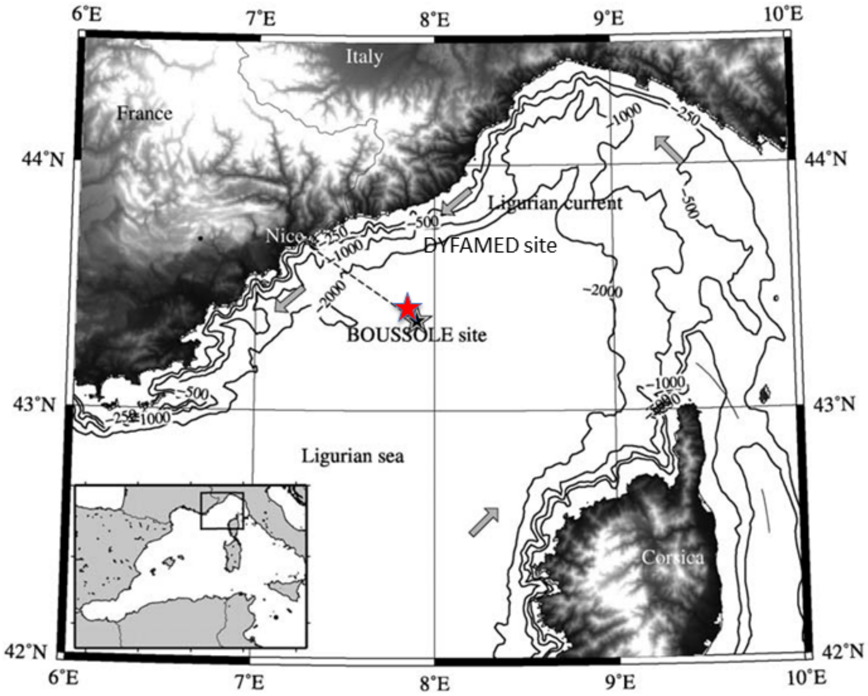

Figure 2. Interannual variability of CARIOCA data: a) T, b) fCO$_2$, c) fCO$_2$@13. The dotted lines indicate the period affected by stratification and internal waves (July, 26 th to October 1st, 2014 and July, 8 th to October 1st, 2015). On 2(b), the open circles correspond to fCO2 data derived from DIC and alkalinity measurements of samples taken at 5 and 10 m. (d), (e), (f), seasonal variability. On 2(e), the thin lines indicate fCO$_{2atm}$. Note that the color code on (d), (e), (f) is different from (a), (b), (c).

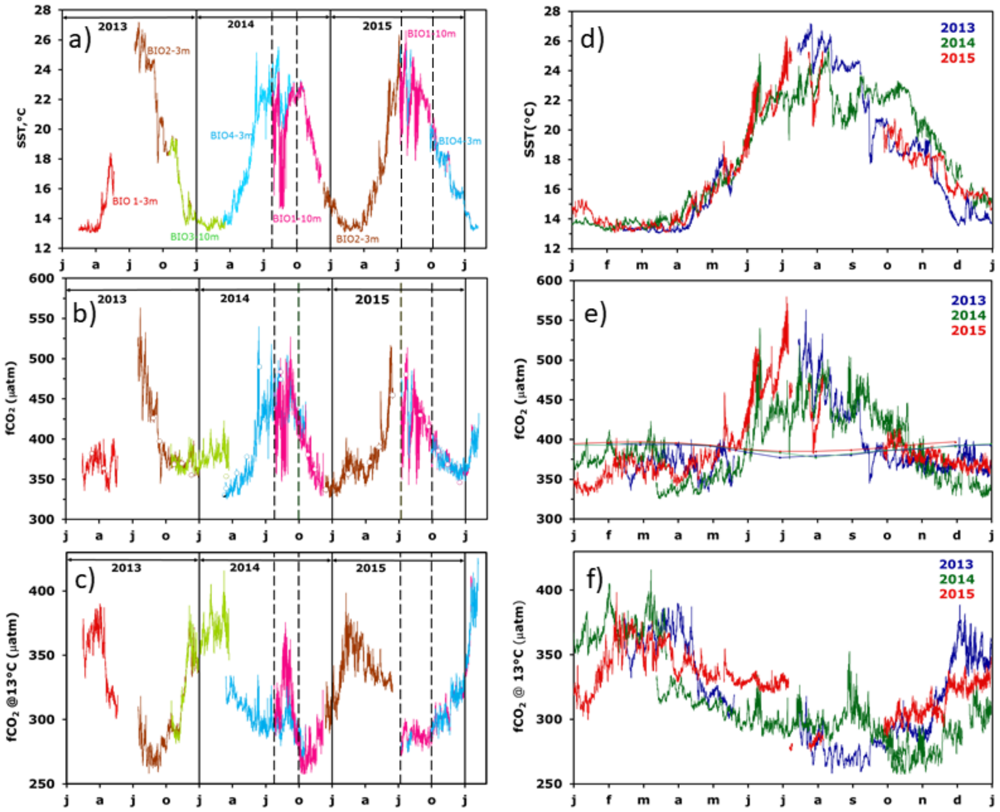

Figure 3. (a) fCO$_2$@13 as a function of temperature for hourly data in 2013, 2014 and 2015.The yellow dots indicate mean fCO$_2$@13 (b) as in (a) but for all hourly data in 1995-1997 (black) and in 2013-2015 (red) (c) As in (b), but for average values per 1°C interval (standard deviation as dotted line). The difference between the two periods is also displayed (dashed black curve; scale on the right axis). (d) Mean monthly sea surface temperature for 1993-1995 (black curve; CARIOCA sensors), 2013-2015 (green; CARIOCA sensors), 2013-2015 (red, meteorological buoy). Corresponding mean annual values are indicated by dotted lines.