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

Received and published: 13 August 2017

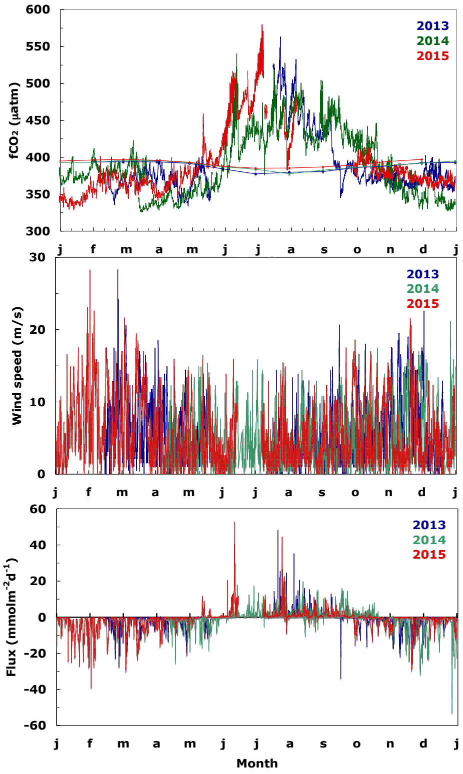
The paper by Merlivat et al. provides a description of carbonate chemistry in two close fixed station located in the Ligurian Sea (northwestern Mediterranean Sea). By combining time series data of CO2 fugacity with alkalinity derived estimations, they reported an increase of dissolved inorganic carbon and decrease of pH in near surface waters during the past two decades. This issue is of particular interest to the referee and I think that the authors have a very nice data set to exploit. However, I think the analysis is somewhat incomplete, and I finished the paper wanted a more in-depth analysis and discussion. I encourage the authors to further expand their work because at this stage their hypothesis are not well supported. The manuscript could be published in Biogeosciences after a major revision in order to clarify some aspects as indicated below.

Major Comments

My major reservation about this work is the difference between the measured fCO2 at the sea surface (fCO2sea) and the fCO2 derived from atmospheric xCO2 concentration (fCO2air). In 2013-2015 the sea surface mean annual fCO2 calculated at 18.25_C (the mean annual in situ temperature) was larger than the fCO2air derived from atmospheric data at the same temperature. This result is quite strange, because it means a CO2 outgassing from the sea surface to the atmosphere on annual average, which is in contrast with respect to the ongoing ocean acidification process and the general net anthropogenic CO2 uptake measured in the Mediterranean Sea by different research.

In 2013-2015 I would expect an equilibrium between the fCO2sea and fCO2air, or a slightly higher value in the fCO2air, as it was detected in the 1995-1997. How the authors can explain this issue?

In the 2 periods, 1995-1997 and 2013-2015, the CO_2 annual flux is directed from the atmosphere to the sea in both cases, although the annual average of fCO_2 in surface seawater in 2013-2015 is higher than atmospheric fCO_2. 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 fCO$_{2\,atm}$.



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The mean annual CO$_2$ flux is equal to -0.45 mol.m^{-2}.yr^{-1} using the exchange coefficient of [*Wanninkhof*, 2014].

They suggested the contribution of the Atlantic Ocean as a source of anthropogenic carbon, but I do not understand how the Atlantic surface waters can be relatively enriched in 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).

Moreover, this is in contrast with the end of the discussion where the authors saythat (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.

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.

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.

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 CO_2 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.

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 fCO_2 measurements made at 2 very close locations, Dyfamed and Boussole, at an interval of 18 years. The processes that govern the distribution of fCO_2 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.

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.

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.

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

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 fCO_2.

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

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

See [*Huertas et al.*, 2009].

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 CO_2-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 fCO_2 in surface seawater was higher than atmospheric fCO_2, 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.

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

This has been done.

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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 fCO2 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 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 investement to develop and deploy the CARIOCA buoys with fCO2 sensors. They use the same measurement system for all measurements, thus allowing an assessement 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 variabilty 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 weaking 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 anthrogenically 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 that it is. You may also want 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, 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 fCO_2 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 -0.45 mol $m^{-2}yr^{-1}$, 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.

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 $dfCO_2$@13 is equal to 33.17 µatm with a standard error of the mean equal to 1.68µatm. ».

In the original manuscript, we had computed the standard error of the mean equal to $6.29/\sqrt{14}=1.68$ µatm , the standard deviation of the 14 values of dfCO2@13 being equal to 6.29 µatm. 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 µatm), 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 µatm), even lower than the precision of individual fCO2 measurements (3 µatm). 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 stongly 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 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 differ? –

$fCO_{2\ atm}$was computed as:

$fCO_{2\ atm}= x\ CO_2\ (1-p_{H2O}/P_{atm})\ f$

with x CO_2 molar fraction of CO_2 in the atmosphere , p_{H2O} at 18.25°C equal to 21mb , P equal to 1013mb, and f, factor to convert partial pressure to fugacity, equal to 0.9966. Then:

$fCO_{2\ atm}= 0.976\ x\ CO_2$

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 exercice taking into account the monthly distribution of x, p_{H2O} 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_2mean=355.3 µatm,   N=36 , SD=5.0, SE=0.8.

2013-2015: fCO_2mean=389.6 µatm,   N=36 , SD=5.5, SE=0.9.

We then calculate:

$dfCO_2$ =34.3+/-2.3 µatm with SE=1.2.

The error estimate appears to be too small for the change in fCO2 at the sea surface at 18.25 C. It is smaller than the measurement precision for individual fCO2 measurements. - My overall impression is that the authors may well be underestimating the uncertainties, especially concerning the change in oceanic fCO2 between 1995-1997 and 2013-2015. Even if estimates of fCO2ocn for each of those 3-year periods can be made to within 3 µatm, the 2-sigma error bars for oceanic and atmospheric fCO2 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 +/-1.3 µmol/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 (aroung 0.0006). How do you explain this? Once again, it seems related to your use of SE instead of the standard 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 occured 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 dstinguished 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 or the water column (Huertas 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 Cant 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 5µatm (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 TCO_2.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 al., 1993]". The square brakets 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.

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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 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

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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 [*Millero*, 2007]. 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]; [*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. Constraints on the Mediterranean Sea's storage of anthropogenic CO_2 are limited, as the data based approaches disagree by more than a factor of two [*Huertas et al.*, 2009; *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 it has been shown that because of decadal variability it requires 25 years for the long-term trend to emerge [*McKinley et al.*, 2011][*McKinley et al.*, 2011][*McKinley et al.*, 2011][*McKinley et al.*, 2011].

A high frequency sampling of the seawater carbon chemistry at the air-water interface over extended periods of time is a way to detect a possible trend in 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 very close 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

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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.

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2 Material and methods

2.1-The BOUSSOLE and DYFAMED sites

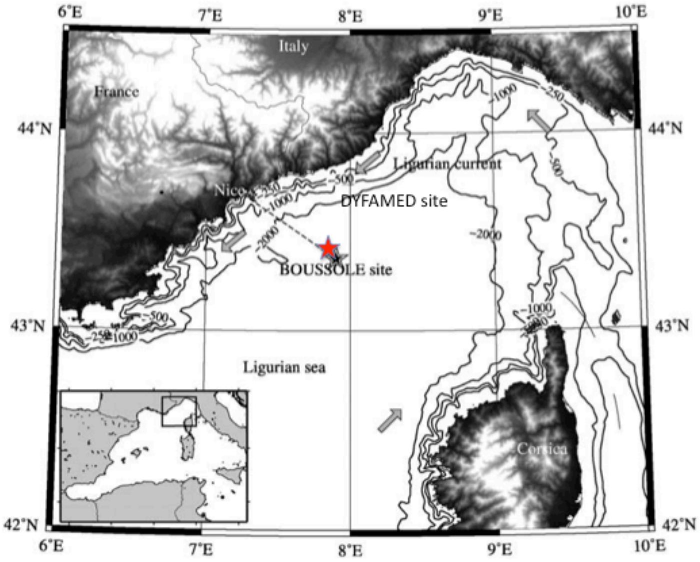

Fig. 1. The area of the northwestern Mediterranean Sea showing the southern coast of France, the island of Corsica, the main current branches (gray arrows), and the location of the DYFAMED site (red star) and the BOUSSOLE buoy (black star) in the Ligurian Sea.

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 [*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*,

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1999]. Monthly cruises are carried out at the same location.

2.2- Analytical methods

At DYFAMED, fCO_2 measurements at 2 m depth 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 meters 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 using the spectrophotometric method with thymol blue 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 meters depth during the monthly servicing cruises to the mooring. The samples were analyzed using potentiometric titration from the method developed by [*Edmond*, 1970] with a closed cell, and provides measurements of DIC, and total alkalinity, Alk. For calibration, Certified Reference Materials (CRMs) provided by Prof. A. Dickson (Scripps Institution of Oceanography, San Diego, USA) were used. 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]. 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 :

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

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

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3 Results

3.1 The BOUSSOLE mooring (2013-2015) time series

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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).

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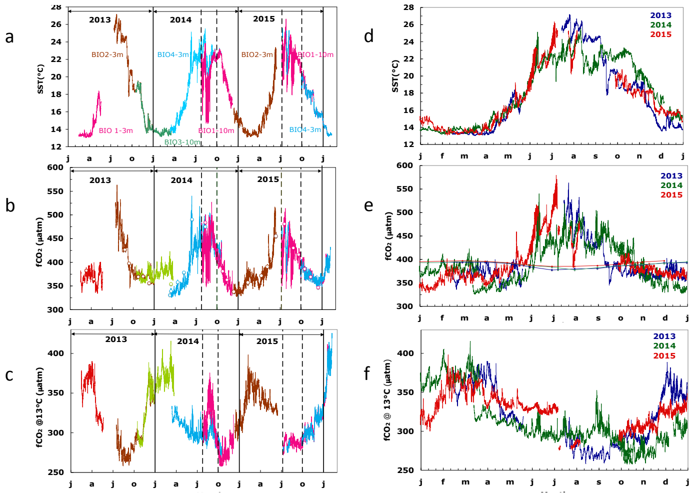

Fig.2. Interannual variability of CARIOCA data: a) T, b) fCO_2, c) fCO_2@13 The dotted lines indicate the period affected by stratification and internal waves (July, 26 th to October 1st, 2014 and July, 8 th to October 1st, 2015). On 2(b), the open circles correspond to fCO2 data derived from DIC and alkalinity measurements of samples taken at 5 and 10 meters. (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, this last effect should be negligible. Temperature and DIC have the strongest influences. By normalizing fCO_2 to a constant temperature, the thermodynamic

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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 meters 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

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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

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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.

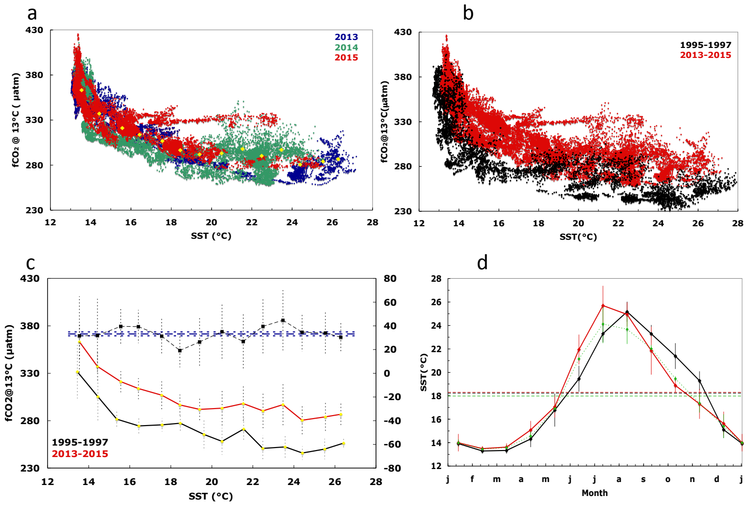

Fig.3. (a) fCO_2@13°C as a function of temperature for hourly data in 2013, 2014 and 2015.The yellow dots indicate mean fCO_2@13°C (b) as in (a) but for all hourly data in 1995-1997 (black) and in 2013-2015 (red) (c) As in (b), but for average values per 1°C interval (standard deviation as dotted line). 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

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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 trend	
T °C	fCO2@13 µatm	N	standard deviation µatm	T °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

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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.

It is interesting to note that the distribution of 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. The mean weighted value of dfCO2@13 over the whole range of temperature is estimated as the mean of dfCO2@13 in each temperature step weighted by the variance. It is equal to 32.7µatm. We estimate the accuracy on this value as follows. For each time interval, the mean fCO2@13 per temperature step has been derived from at least three independent CARIOCA sensors. Given that the accuracy on fCO_2 from each CARIOCA sensor is estimated at 2 µatm and that the calibrations of the three sensors are independent, the accuracy on fCO_2 averaged in each time interval is 2/√3=1.15 µatm. Hence the accuracy on the difference is estimated at 1.6 µatm.

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. We compute an increase of DIC, dDIC, equal to 24.8+/-1.3 µmol kg^{-1} (1.38+/-0.07 µmol $kg^{-1}yr^{-1}$) and the decrease of pH , dpH equal to -0.0390+/-0.0020 pH unit (-0.0022+/-0.0001 pH uniyr^{-1}) (Table 2).

	d fCO_2^* @ 13°C µatm	d fCO_2^* @ T µatm	d DIC^* µmolkg^{-1}	d pH * pH unit	dfCO_2@T annual µatm yr^{-1}	d DIC annual µmol$kg^1 yr^1$	d pH annual pH unit yr^1
sea surface	32.7 +/-1.6	40.8 +/-2.0	24.8 +/-1.3	-0.0390 +/-0.0020	2.27 +/-0.11	1.38 +/-0.07	-0.0022 +/-0.0001
atmosphere Lampedusa data		34.3 +/-1.2	**20.8 +/-0.8		1.91 +/-0.07		
dfCO_2@T_{air}/dfCO_2@T_{sea}		0.84 +/-0.05					

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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.

**, $dDIC_{ant}$

3.5 Changes in atmospheric and seawater fCO_2

The increase of atmospheric fCO_2 from 1995-1997 to 2013-2015 was computed from the 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 equal to 1 atm, we derived a mean atmospheric fCO_2 equal to 355.3+/-0.8 µatm and 389.6+/-0.9 µatm for 1995-1997 and 2013-2015, that is an increase equal to 34.3+/-1.2 µatm (Table 2). At this temperature, the change of fCO_2 at the sea surface is equal to 40.8+/-2.0 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. Assuming the same salinity and alkalinity as previously, 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 20.8+/- 0.8 µmol kg^{-1} (Table 2).

4 Discussion

4.1 fCO_2 at the air-sea interface

We have computed that 84% of the increase of $fCO_{2\ sea}$ in the northwestern Mediterranean, two decades apart, comes from the atmosphere. One implicit assumption is that any change in atmospheric fCO_2 immediately transfers as a change in the surface ocean fCO_2. In agreement with the circulation pattern of the basin [*Millot*, 1999], this increase of surface fCO_2 could follow two routes: in situ chemical equilibrium at the air-sea interface or winter mixing with DIC rich Levantine Intermediate water or surface waters of Atlantic origin, relatively enriched in anthropogenic carbon. Keeping in mind that the deep-water renewal time is estimated to be 20-40 years in the western basin, and given that the atmospheric increase was slower 20-40 years ago, our estimate of the atmospheric contribution to the ocean trend is likely an upper bound.

The mean values of fCO_2 computed at the mean annual SST, 18.25°C, computed with all the

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individual hourly fCO_2 measurements in 1995-1997 and 2013-2015 are respectively equal to 352.3 µatm and 400.2 µatm, while the corresponding atmospheric values are 355.3 µatm and 389.6 µatm respectively. The CO_2 annual flux is directed from the atmosphere to the sea in both cases, although the annual average of fCO_2 in surface seawater in 2013-2015 is higher than atmospheric fCO_2. This is due to higher wind speed in autumn and winter when the surface water is undersaturated (Fig.2, b).

4.2 Time change of surface alkalinity?

In the range of salinity of the BOUSSOLE samples, 37.9 to 38.5 psu, the alkalinity values computed with Eq (1) are larger than those predicted by the [*Copin-Montegut and Begovic*, 2002] relationship established for the DYFAMED site, with a mean difference equal to 10+/-2 µmol kg^{-1}. In both cases alkalinity measurements were made with a potentiometric method using certified reference material supplied by AG 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. However, as a sensitivity test, if 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}. Such a change in alkalinity does not significantly affect the decrease of pH shown in Table 2.

4.3 Anthropogenic carbon storage in surface waters

The increase of sea surface DIC from 1995-1997 to 2013-2015 is equal to 24.8+/-1.3 µmol kg^{-1} (Table 2). ($dDIC_{ant}$) predicted solely from chemical equilibrium of the sea surface with the atmosphere is equal to 20.8+/-0.8 µmol kg^{-1}. The ratio of these two terms is equal to 0.84+/-0.05. In order to interpret the additional contribution of DIC to that resulting from the local CO_2 air-sea exchange, we examine below two processes, respectively an increased mixing with deep waters and an anthropogenic carbon invasion.

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MLD time series 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 a cause for the observed increase of DIC measured between the two periods 1995 -1997 and 2013-2015.

As a result of a monitoring program in the Strait of Gibraltar, [*Huertas et al.*, 2009] calculated a net flux of C_{ant} from the Atlantic towards the Mediterranean basin. [*Schneider et al.*, 2010], using the transit time distribution method applied to a dataset from a cruise in the Mediterranean Sea in 2001, estimated that the input of C_{ant} through the Strait of Gibraltar from 1850 to 2001 accounts for almost 10% of the total C_{ant} inventory of the Mediterranean Sea, which means that ~90% must have been taken up directly from the atmosphere. Based on a high-resolution regional model, [*Palmiéri 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 across the Strait of Gibraltar. The findings of these two studies support the conclusion that computed change of DIC in excess of 16+/-5% over the direct contribution of air-sea exchange 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 1.38 µmol kg^{-1}yr^{-1} as previously computed (Table 2). Taking into account the increase of DIC_{ant} equal to 24.8 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).

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4.4 The signal of acidification

The annual decrease of pH_T calculated between 1995-1997 and 2013-2015 is equal to -0.0022+/-0.0001. At the DYFAMED site, at 10 m depth, [*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.

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[*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. The range of decreasing trends of pH extends from -0.0026+/-0.0006 unit yr^{-1} at the Irminger Sea time series site to -0.0014+/-0.0005 unit yr^{-1} at the Iceland Sea time series. For the global surface ocean, [*Lauvset et al.*, 2015] have reported a mean rate of decrease of -0.0018+/-0.0004 for 1991-2011.The decrease of pH computed here at DYFAMED is in the upper range of values compared to other time series. The Mediterranean Sea is actually able to absorb more anthropogenic CO_2 per unit area, first because of its higher total alkalinity that leads to a greater chemical capacity to take up anthropogenic CO_2 and, second, because deep waters are ventilated on relatively short timescales (30-40 years in the western basin), which allows deeper penetration of anthropogenic tracers [*Schneider et al.*, 2010], [*Palmiéri et al.*, 2015]. The lowering effect of high alkalinity on the Revelle factor, close to ten, implies a relatively high uptake capacity for anthropogenic carbon, C_{ant}.

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.

Acknowledgments

Seawater samples were analyzed for DIC and Alk by the SNAPO-CO_2 at LOCEAN in Paris. The CO_2Sys toolbox of [*Pierrot et al.*, 2006] has been used for the calculations of DIC and

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pH. The adaptation of CARIOCA sensors to high pressure has been supported by the BIO-optics and CARbon EXperiment (BIOCAREX) project, funded by the Agence Nationale de la Recherche (ANR,Paris). We are grateful for helpful comments from Gilles Reverdin on the manuscript. Many thanks to Laurent Coppola who kindly provided additional MLD data at Dyfamed.

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Figure caption and tables

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 meters. (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.

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.

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.

**, $dDIC_{ant}$

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