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 CO₂ (fCO₂) 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 fCO₂ 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 CO₂. 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
beginning of the industrial period.

1 Introduction

The concentration of atmospheric carbon dioxide (CO₂) 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 CO₂ 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_{ants}, 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 CO₂
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 CO₂ Atlas
(SOCAT) database [Bakker et al., 2014] combined with an interpolation method. Constraints
on the Mediterranean Sea’s storage of anthropogenic CO₂ 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 CO₂, fCO₂, 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 fCO₂, 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 CO₂, 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

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; Heimbüberger 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 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:

$$\text{Alk (µmol kg}^{-1}) = 87.647 \times \text{S} - 785.5$$

(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](image)

Fig. 2. Interannual variability of CARIOPCA data: a) T, b) fCO\(_2\), c) fCO\(_2\) from 13°C. The dotted lines indicate the period affected by stratification and internal waves (July 26\(^{th}\) to October 1\(^{st}\), 2014 and July 8\(^{th}\) to October 1\(^{st}\), 2015). On 2(b), the open circles correspond to fCO\(_2\) 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\(_{2\text{sys}}\) 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
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
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 fCO$_2$ 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 nonlinear. 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 two periods is clearly highlighted for the whole range of temperature.

![Fig.3](image)

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
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.

<table>
<thead>
<tr>
<th></th>
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<tr>
<td>T °C</td>
<td>fCO$_2$@13 μatm</td>
<td>N standard deviation μatm</td>
</tr>
<tr>
<td>14.45</td>
<td>305.28</td>
<td>495</td>
</tr>
<tr>
<td>15.37</td>
<td>281.54</td>
<td>447</td>
</tr>
<tr>
<td>16.44</td>
<td>274.43</td>
<td>182</td>
</tr>
<tr>
<td>17.58</td>
<td>275.54</td>
<td>190</td>
</tr>
<tr>
<td>18.47</td>
<td>277.34</td>
<td>300</td>
</tr>
<tr>
<td>19.62</td>
<td>265.43</td>
<td>342</td>
</tr>
<tr>
<td>20.50</td>
<td>258.08</td>
<td>529</td>
</tr>
<tr>
<td>21.56</td>
<td>271.15</td>
<td>239</td>
</tr>
<tr>
<td>22.49</td>
<td>250.75</td>
<td>742</td>
</tr>
<tr>
<td>23.57</td>
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<td>320</td>
</tr>
<tr>
<td>24.41</td>
<td>245.85</td>
<td>506</td>
</tr>
<tr>
<td>25.50</td>
<td>250.06</td>
<td>215</td>
</tr>
<tr>
<td>26.42</td>
<td>256.29</td>
<td>279</td>
</tr>
</tbody>
</table>

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°C 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 fCO$_2$@13 between the two periods, dfCO$_2$@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.

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 dfCO$_2$@13 over the whole range of temperature is estimated as the mean of dfCO$_2$@13 in each temperature step weighted by the variance. It is equal to 32.7 µatm. We estimate the accuracy on this value as follows. For each time interval, the mean fCO$_2$@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 $2/\sqrt{3}=1.15$ 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 unit yr$^{-1}$) (Table 2).

<table>
<thead>
<tr>
<th></th>
<th>d fCO$_2$@13°C</th>
<th>d fCO$_2$@T</th>
<th>d DIC</th>
<th>d pH</th>
<th>dfCO$_2$@T</th>
<th>d DIC</th>
<th>d pH</th>
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<tr>
<td></td>
<td>µatm</td>
<td>µatm</td>
<td>µmolkg$^{-1}$</td>
<td>pH unit</td>
<td>annual</td>
<td>µmolkg yr$^{-1}$</td>
<td>annual</td>
</tr>
<tr>
<td>sea surface</td>
<td>32.7 +/−1.6</td>
<td>40.8 +/-2.0</td>
<td>24.8 +/−1.3</td>
<td>-0.0390 +/−0.0020</td>
<td>2.27 +/−0.11</td>
<td>1.38 +/−0.07</td>
<td>-0.0022 +/−0.0001</td>
</tr>
<tr>
<td>atmosphere Lampedusa data</td>
<td>34.3 +/−1.2</td>
<td>**20.8 +/−0.8</td>
<td>1.91 +/−0.07</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>dfCO$<em>2$@T$</em>{air}$/dfCO$<em>2$@T$</em>{sea}$</td>
<td>0.84 +/−0.05</td>
<td></td>
<td></td>
<td></td>
<td></td>
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<td></td>
</tr>
</tbody>
</table>
Seasonally detrended long term and annual trends of seawater carbonate chemistry and atmosphere composition.

T\(_{\text{mean}}\) annual temperature equal to 18.25°C


**, \(d\text{DIC\_ant}\)

### 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/wdogg/](http://ds.data.jma.go.jp/gmd/wdogg/)) (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
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, $d$DIC=+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). $d$DIC$_{am}$ 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.
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\text{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\text{ant} through the Strait of Gibraltar from 1850 to 2001 accounts for almost 10% of the total C\text{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\text{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\text{ant} surface concentrations respectively equal to 65-70 µmol kg\textsuperscript{-1} at the strait of Gibraltar in the years 2005-2007 and close to 65 µmol kg\textsuperscript{-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\textsuperscript{-1}yr\textsuperscript{-1} as previously computed (Table 2). Taking into account the increase of DIC\text{ant} equal to 24.8 µmol kg\textsuperscript{-1} between 1995-1997 and 2013-2015, we would estimate that the contribution of the change of DIC\text{ant} over the last 18 years represents ~30% of the total change since the beginning of the industrial period (t>~1800).

4.4 The signal of acidification

The annual decrease of pH\text{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.
[Bates et al., 2014] examined changes in surface seawater CO₂-carbonate chemistry at the locations of seven ocean CO₂ 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 CO₂ per unit area, first because of its higher total alkalinity that leads to a greater chemical capacity to take up anthropogenic CO₂ 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], [Palmieri 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 fCO₂ measurements made by CARIOCA sensors were sufficient to estimate trends in fCO₂, 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 CO₂. 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% [Palmieri 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

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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 CARIUMCA data: a) T, b) $f_{CO_2}$, c) $f_{CO_2}@13$. The dotted lines indicate the period affected by stratification and internal waves (July, 26th to October 1st, 2014 and July, 8th to October 1st, 2015). On 2(b), the open circles correspond to $f_{CO2}$ 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 $f_{CO_2}^{atm}$. Note that the color code on (d), (e), (f) is different from (a), (b), (c).

Figure 3. (a) $f_{CO_2}@13$ as a function of temperature for hourly data in 2013, 2014 and 2015. The yellow dots indicate mean $f_{CO_2}@13$ (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; CARIUMCA sensors), 2013-2015 (green; CARIUMCA sensors), 2013-2015 (red, meteorological buoy). Corresponding mean annual values are indicated by dotted lines.

Table 1:
Distribution of temperature, $f_{CO_2}@13$, and increase $df_{CO_2}@13$ 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


**, dDIC ant