Biogeosciences Discuss., https://doi.org/10.5194/bg-2017-284
Manuscript under review for journal Biogeosciences
Discussion started: 6 July 2017




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

Liliane. Merlivat [a], Jacqueline. Boutin [a], David. Antoine [b,c], Laurence. Beaumont [d], Melek. Golbol [b], Vincenzo. Vellucci. [b]

[a] Sorbonne Universités (UPMC, Univ Paris 06)-CNRS-IRD-MNHN, LOCEAN Laboratory, F-75005 Paris, France
[b] Sorbonne Universités (UPMC, Univ Paris 06)-CNRS, LOV, Observatoire Océanologique, Villefranche-sur-Mer 06230, France
[c] Remote Sensing and Satellite Research Group, Department of Physics and Astronomy, Curtin University, Perth, WA 6845, Australia
[d] Division Technique INSU-CNRS, 92195 Meudon Cedex, France

Corresponding author: L. Merlivat (merlivat@locean.upmc.fr)

## 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 calculated 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 (0.0021 $yr^{-1}$). The DIC increase is larger than expected from equilibrium with atmospheric $CO_2$. This supports the hypothesis of a ~15% contribution of the Atlantic Ocean as a source of anthropogenic carbon to the Mediterranean Sea through the strait of Gibraltar. We estimate that the part of DIC accumulated over the last 18 years represents ~30% of the total change since the beginning of the industrial period.

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33 **1 Introduction**

34 The concentration of atmospheric carbon dioxide ($CO_2$) has been increasing rapidly over the
35 20$^{th}$ century and, as a result, the concentration of dissolved inorganic carbon (DIC) in the near
36 surface ocean increases, which drives a decrease in pH in order to maintain a chemical
37 equilibrium [*Millero*, 2007]. These changes have complex direct and indirect impacts on
38 marine organisms and ecosystems [*Gattuso and Hansson*, 2011]. Empirical methods to
39 estimate the anthropogenic $CO_2$ penetration in the ocean since the industrial revolution have
40 improved over the past few decades [*Chen and Millero*, 1979; *Gruber et al.*, 1996]; [*Sabine et*
41 *al.*, 2008]; [*Touratier and Goyet*, 2004; 2009; *Woosley et al.*, 2016]. As the concentration of
42 anthropogenic carbon, $C_{ant}$, cannot be distinguished from the natural background of DIC
43 through total DIC measurements, these methods are based on the analysis of different
44 chemical properties of the water column. Direct estimates of the anthropogenic $CO_2$
45 absorption in the sea surface layers are difficult owing to the large natural variability driven
46 by physical and biological phenomena. [*Bates et al.*, 2014] have extracted the trend from the
47 large variability, based on analysis of a long time series (monthly or seasonal sampling). For
48 the global surface ocean, **[***Lauvset et al.*, 2015] have used the Surface Ocean $CO_2$ Atlas
49 (SOCAT) database [*Bakker et al.*, 2014] combined with an interpolation method. Constraints
50 on the Mediterranean Sea's storage of anthropogenic $CO_2$ are limited, as the data based
51 approaches disagree by more than a factor of two [*Huertas et al.*, 2009; *Touratier and Goyet*,
52 2009].

53 A high frequency sampling of the seawater carbon chemistry at the air-water interface is a
54 way to detect a possible trend in DIC related to the absorption of increasing atmospheric $CO_2$
55 concentration. In this paper we analyzed two three-year time series of hourly fugacity of $CO_2$,
56 $fCO_2$, measured with autonomous CARIOCA sensors [*Copin-Montégut et al.*, 2004; *Merlivat*
57 *and Brault*, 1995] in 1995-1997 and 2013-2015, at two very close locations in the
58 northwestern Mediterranean Sea (Fig. 1). Using measured $fCO_2$, temperature, T, and salinity,
59 S, we derived the other variables of the carbonate system (pH and DIC). The experimental
60 setting is first described, and the recent data obtained over the 2013-2015 period are
61 presented. Combined with the 1995-1997 measurements previously published [*Hood and*
62 *Merlivat*, 2001], we estimated the decrease of pH and the increase of DIC. The results are
63 compared with the respective contributions of the exchange with atmospheric $CO_2$ and with

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recent estimates of the transport of anthropogenic carbon from the Atlantic Ocean over a 18 years period.

## 2 Material and methods

### 2.1-The BOUSSOLE and DYFAMED sites

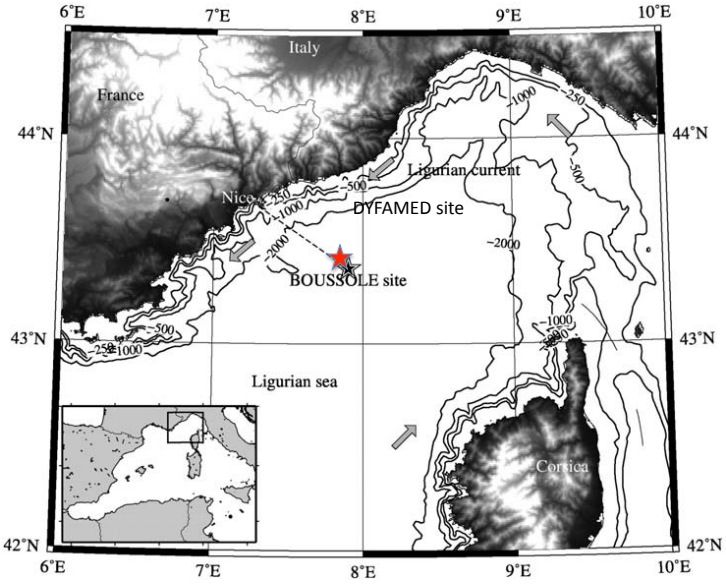


Fig. 1. The area of the northwestern Mediterranean Sea showing the southern coast of France, the island of Corsica, the main current branches (gray arrows), and the location of the DYFAMED site (red star) and the BOUSSOLE buoy (black star) in the Ligurian Sea.

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 [*Millot*, 1999]. The two sites are protected from coastal inputs by the Ligurian current. Monthly cruises are carried out at the same location.

### 2.2- Analytical methods

At DYFAMED, $fCO_2$ measurements at 2m 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. They 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. These 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 $fCO_2$ measurements using the spectrophotometric method with thymol blue is estimated at 3 µatm [*Copin-Montégut et al.*, 2004; *Hood and Merlivat*, 2001]. For *in situ* calibration of the newly designed $fCO_2$ sensors, seawater samples were taken at 5 and 10 meters depth during the monthly servicing cruises to the mooring and analyzed in terms of S, DIC, and total alkalinity, Alk. The samples were analyzed using potentiometric titration from the method developed by [*Edmond*, 1970] with a closed cell. 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 $TCO_2$ 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]. Its error is expected to be on the order of 5µatm [*Millero*, 2007] so that if the errors are fully random, the error on the mean of the 56 samples corresponding on the error on the absolute calibration of the sensor $fCO_2$, is 0.7µatm. In fact, the standard deviation of the difference between the $fCO_2$ sensor data and $fCO_2$ computed with the monthly discrete samples (Fig. 2b) is equal to 4.4 µatm, very consistent with the expected error on individual estimate. Alk and S of the 56 samples taken at BOUSSOLE are linearly correlated according the following relationship :

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

The standard deviation on predicted Alk is equal to 4.4 µmol $kg^{-1}$ ($r^2$=0.89).

## 3 Results

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

Temperature, $fCO_2$ and $fCO_2$@13 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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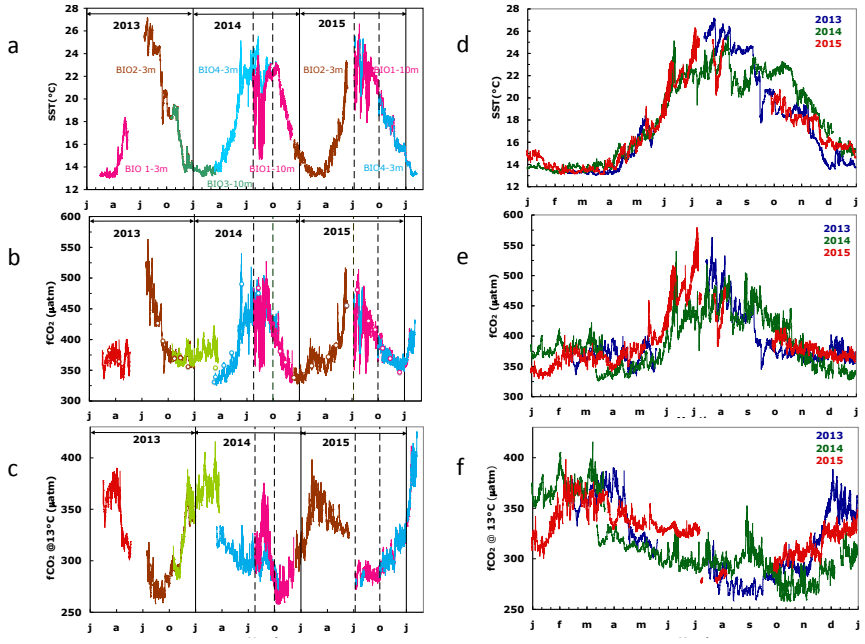


Fig.2. Interannual variability of CARIOCA data :a) T, b) $fCO_2$, c) $fCO_2$ at 13°C. The dotted lines indicate the period strongly affected by stratification and internal waves (July, 26 $^{th}$ to October 1$^{st}$, 2014 and July, 8 $^{th}$ to October 1$^{st}$, 2015). On 2(b), the open circles correspond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

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, and salinity. Among these, for the conditions encountered in the Mediterranean sea, temperature and DIC have the strongest influences, whereas changes in alkalinity and salinity have only minor effects [*Takahashi et al.*, 1993]. 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, remineralization and deepening of mixed layer in fall [*Begovic and Copin-Montegut*, 2002; *Hood and Merlivat*, 2001]. Biology accounts for the decay of $fCO_2$@13 observed from March-April to late summer;



131 increase of surface $fCO_2$@13 is associated with the deepening of the mixed layer in the fall or
132 convection in winter as the vertical distribution of $fCO_2$@13 at DYFAMED shows a
133 maximum in the 50-150 m layer where a large remineralization of organic matter occurs, the
134 productive layer being mostly between 0 and 40 m. The contribution of air-sea exchange is
135 not significant. During summer 2014, large differences between measurements at 3 and
136 10 meters were observed (Fig. 2, a, b, c between dashed lines). A detailed analysis of the
137 temporal variability during that period underscores the role of inertial waves at the
138 frequency of 17.4 hours that create the observed differences between the 2 depths of
139 observations, the deeper waters being colder and enriched in $fCO_2$@13. T and $fCO_2$@13
140 variability is dominated by inertial waves. In particular, from 15$^{th}$ to 26$^{th}$ of August
141 2014, the difference in T between the two depths is as large as 7.6°C, and 5.1°C on
142 average. Likewise, $fCO_2$ decreases on average by 32.7 μatm leading to an increase of
143 $fCO_2$@13 equal to 42.8 μatm.
144 The 2013-2015 seasonal and inter-annual variability of T, $fCO_2$ and $fCO_2$@13 is
145 illustrated on Fig. 2, d, e, f. The larger interannual changes in temperature (Fig.2, d) are
146 observed during summer, both at 3m and 10m depth, while over February and March, a
147 constant value of 13°C is observed as the result of vertical mixing with the LIW. A very
148 large inter-annual variability of $fCO_2$@13 is observed for T<14°C (Fig. 2,f). This is
149 associated with the winter mixing at the mooring site, which is highly variable from year
150 to year. Winter mixed-layer depth, MLD, varies between 30 and 200-300 m, at the top of
151 the LIW. The variable depth of the winter vertical mixing causes the difference in
152 $fCO_2$@13 as $fCO_2$ increases with depth [*Copin-Montegut and Begovic*, 2002]. The
153 deepening of MLD is driven by episodic and intense mixing processes characterized by a
154 succession of events lasting several days, related to atmospheric forcing [*Antoine et al.*,
155 2008] which lead to increase in $fCO_2$@13. Figure 2,e illustrates the solubility control of
156 the variability of $fCO_2$, as fCO2 increases when T increases. Another cause of inter-
157 annual variability of $fCO_2$ for T~14°C is the timing of the spring increase of biological
158 activity which differs by a month between years; for instance, it happened at the
159 beginning of April in 2013, T~15-16°C and by mid March in 2014, T~14°C. Another
160 cause is the deepening of the mixed layer due to the fall cooling which varies by a month
161 between years.
162
163 **3.2** Decadal changes of hydrography



164 **3.2.1** Sea surface temperature changes

165 Monthly mean values of temperature have been computed for the two three-year periods,
166 1995-1997 and 2013-2015. In 1995-1997, $fCO_2$ and T at 2m were measured with CARIOCA
167 sensors installed on a buoy at DYFAMED [*Hood and Merlivat*, 2001]. The mean annual
168 temperature of hourly CARIOCA data is equal to 18.21°C. For 2013-2015, temperature
169 measurements made on the BOUSSOLE mooring at 3 and 10 meters have been used. For the
170 April to September time interval, there are only data at 3m depth. In addition, temperature
171 data measured half hourly at 0.7 m at a nearby meteorological buoy (43°23'N, 7°50'E)
172 (http://www.meteo.shom.fr/real-time/html/DYFAMED.html) have been used (Fig.3d). Mean
173 annual temperature are equal to 18.29°C and 17.97°C respectively, based on the
174 meteorological buoy and the BOUSSOLE mooring data. The two sets of data differ
175 essentially during July and August, with the temperatures at 3m being colder than at 0.7m,
176 indicating a thermal gradient between the two depths during summer. Therefore, for 2013-
177 2015, we select the mean annual value computed with the meteorological buoy, 18.29°C, as
178 better representing the sea surface. This value is very close to 18.21°C computed for 1995-
179 1997. Then, no significant change of SST is found between the 2 decades, with a mean value
180 equal to 18.25°C.

181 **3.2.2** Sea surface salinity changes

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

187

188 **3.3** Decadal changes of $fCO_2$@13

189 **3.3.1** Time series of $fCO_2$@13 in 1995-1997 and 2013-2015

190 The two time series of high frequency data were analyzed in order to quantify the change of
191 $fCO_2$@13 at the sea surface two decades apart. To account for the interannual seasonal
192 variability as well as irregular sampling, we performed an analysis of the change of $fCO_2$@13
193 as a function of SST (Fig. 3, a and b). For the 2013-2015 data set, we excluded summer data
194 measured at 10 m depth as they were not representative of the surface mixed layer due to a
195 strong stratification. Much larger $fCO_2$@13 values are observed at low temperature than at
196 high temperature, the decrease being similar for the two studied periods and strongly non
197 linear. As described in section 3.1, large values at low temperature result from mixing with

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198 enriched deep waters during winter and low values for 26°C-28°C temperatures occur at the
199 end of summer after biological drawdown of carbon. An increase of $fCO_2$@13 between the 2
200 periods is clearly highlighted for the whole range of temperature. No interannual bias of the
201 observed data is displayed.

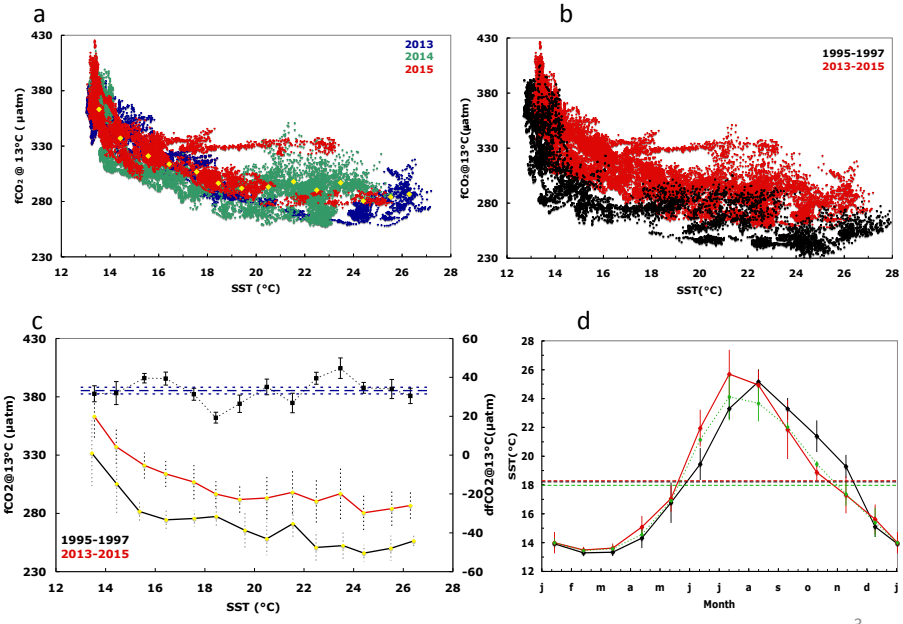


Fig.3. (a) $fCO_2$@13 as a function of temperature for hourly data in 2013, 2014 and 2015 (b) as in (a) but for all hourly data in 1995-1997 (black) and in 2013-2015 (red) (c) As in (b), but for average values per 1°C interval (standard deviation as dotted line). The difference between the two periods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

202
203
204 **3.3.2** Trend analysis and statistics
205 To quantify the change of $fCO_2$@13 between the two data sets, we proceeded as follows: data
206 were binned by 1°C temperature intervals, thereby removing any potential seasonal
207 weighting, especially towards the 13-14°C winter months temperature. The measurements
208 made in this temperature interval represent about 25% of the total number of data for both
209 periods. For each of the fourteen 1°C step, the mean, standard deviation of hourly $fCO_2$@13
210 measurements were computed (Table 1). For both data sets, a monotonous relationship
211 between $fCO_2$@13 and T is observed with correlation coefficients respectively equal to -
212 0.861 and -0.857 (Fig. 3c). The increase of $fCO_2$@13 between the two time series,
213 $dfCO_2$@13, was computed for each 1°C temperature interval. The mean value of $dfCO_2$@13

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214 is equal to 33.17 µatm with a standard error equal to 1.68µatm. It is interesting to note that
215 $dfCO_2@13$ is evenly distributed in the whole range of temperature (Fig. 3c), which
216 suggests that the processes which control the seasonal variation of $fCO_2@13$ at the sea
217 surface have not changed over the 2 last decades at the exception of the $CO_2$ air-sea flux .

Table 1

| Time interval 1995-1997 | | | | Time interval 2013-2015 | | | | Temporal trend | |
|---|---|---|---|---|---|---|---|---|---|
| T[1] °C | fCO2@13 µatm | N | standard deviation µatm | T[1] °C | fCO2@13 µatm | N | standard deviation µatm | dfCO 2@13 µatm | standard error[2] µatm |
| 13.45 | 331.58 | 1212 | 28.09 | 13.55 | 363.14 | 6869 | 18.07 | 31.56 | 4.09 |
| 14.45 | 305.28 | 495 | 26.02 | 14.43 | 337.16 | 3270 | 16.65 | 31.87 | 5.91 |
| 15.37 | 281.54 | 447 | 9.62 | 15.57 | 321.10 | 3112 | 11.09 | 39.56 | 2.43 |
| 16.44 | 274.43 | 182 | 8.53 | 16.42 | 313.79 | 1818 | 11.09 | 39.36 | 3.35 |
| 17.58 | 275.54 | 190 | 7.04 | 17.56 | 306.83 | 1528 | 14.65 | 31.29 | 3.10 |
| 18.47 | 277.34 | 300 | 9.04 | 18.45 | 296.57 | 2621 | 10.95 | 19.23 | 2.76 |
| 19.62 | 265.43 | 342 | 15.58 | 19.41 | 291.84 | 1406 | 13.45 | 26.40 | 4.49 |
| 20.50 | 258.08 | 529 | 145 | 20.50 | 293.16 | 1135 | 18.21 | 35.08 | 4.01 |
| 21.56 | 271.15 | 239 | 12.98 | 21.54 | 297.96 | 1200 | 20.41 | 26.82 | 5.02 |
| 22.49 | 250.75 | 742 | 13.66 | 22.49 | 290.27 | 2385 | 18.57 | 39.52 | 3.08 |
| 23.57 | 252.22 | 320 | 13.00 | 23.47 | 296.92 | 747 | 21.77 | 44.70 | 5.28 |
| 24.41 | 245.85 | 506 | 7.08 | 24.40 | 280.44 | 959 | 14.82 | 34.59 | 2.81 |
| 25.50 | 250.06 | 215 | 10.77 | 25.53 | 284.05 | 456 | 14.81 | 33.99 | 4.95 |
| 26.42 | 256.29 | 279 | 6.24 | 26.29 | 286.71 | 249 | 11.23 | 30.42 | 3.94 |

1)The mean temperatures within each 1° step differ for the 2 periods as the distribution of individual measurements are not identical.
2) The daily scale is used to compute the standard error (n=N/24)

218
219 Table 1:
220 Distribution of temperature, fCO2@13, and increase dfCO2@13 data binned by 1°C
221 temperature interval for the 2 periods 1995-1997 and 2013-2015 .
222
223 **3.4** Changes of seawater carbonate chemistry in surface waters
224 We estimated the DIC and $pH_T$ changes related to the increase of $fCO_2@13$ measured at the
225 sea surface 18 years apart, assuming a mean salinity equal to 38.2, a mean alkalinity equal to
226 2562.3 µmol $kg^{-1}$ following equation (1), and a mean in situ temperature, T, equal to 18.25°C.
227 The dissociation constants of Mehrbach refitted by Dickson and Millero [*Dickson and*
228 *Millero*, 1987; *Mehrbach et al.*, 1973] were used. pH is calculated on the seawater scale.
229 In the range of the $fCO_2$ observations, DIC and $fCO_2@T$ or $pH_T$ and $fCO_2@T$ are linearly
230 related with slopes respectively equal to 0.5982 (+/-0.0046) µmol$kg^{-1}$/µatm ($r^2$=0.9993) and -

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231 0.0009 (+/-0.0002) $pH_T$ unit/µatm ($r^2$=0.9997). We used these sensitivity factors to compute
232 the increase of DIC, dDIC, equal to 24.78+/-1.26 µmol $kg^{-1}$ (1.38+/-0.07 µmol $kg^{-1}yr^{-1}$) and
233 the decrease of $pH_T$ ,$dpH_T$ equal to -0.0373+/-0.0019 $pH_T$ unit (-0.0021+/-0.0001 $pH_T$ uniyr$^{-1}$)
234 (Table 2).

Table 2

| | d $fCO_2^*$ @ 13°C µatm | d $fCO_2^*$ @ T µatm | d $DIC^*$ µmol$kg^{-1}$ | d $pH_T^*$ pH unit | dfCO2@T annual µatm $yr^{-1}$ | d DIC annual µmol$kg^{-1}yr^{-1}$ | d $pH_T$ annual pH unit $yr^{-1}$ |
|---|---|---|---|---|---|---|---|
| sea surface | 33.17 +/-1.68 | 41.42 +/-2.10 | 24.78 +/-1.26 | -0.0373 +/-0.0019 | 2.30 +/-0.12 | 1.38 +/-0.07 | -0.0021 +/-0.0001 |
| atmosphere Lampedusa data | | 34.9 +/-0.9 | **20.88+/-0.53 | | 1.94 +/-0.05 | | |
| $dfCO_2@T_{air}/dfCO_2@T_{sea}$ | | 0.84 +/-0.05 | | | | | |

T, mean annual temperature equal to 18.25°C
* Change from 1993-1995 to 2013-2015
** $dDIC_{ant}$

235
236 Table 2
237 Seasonally detrended long term and annual trends of seawater carbonate chemistry and
238 atmosphere composition.
239
240 **3.5** Changes in atmospheric and seawater $fCO_2$
241 The increase of atmospheric $fCO_2$ from 1995-1997 to 2013-2015 was computed from the
242 monthly atmospheric $xCO_2$ concentrations measured at the Lampedusa Island station (Italy)
243 (35°31'N, 12°37'E) (http://ds.data.jma.go.jp/gmd/wdcgg/). Considering a mean annual in situ
244 temperature equal to 18.25°C and an atmospheric pressure equal to 1 atm, we derived a mean
245 atmospheric $fCO_2$ equal to 355.2+/-0.6 µatm and 390.1+/-0.7 µatm for 1995-1997 and 2013-
246 2015, that is an increase equal to 34.9+/-0.9 µatm (Table 2). At this temperature, the change
247 of $fCO_2$ at the sea surface is equal to 41.4+/-2.1µatm. Thus the contribution of the increase in
248 atmospheric $CO_2$ is responsible for 84+/-5 % of the increase of $fCO_2$ measured in the surface
249 waters. Assuming the same salinity and alkalinity as previously, the corresponding amount of
250 anthropogenic carbon taken up from the atmosphere in order to maintain a chemical
251 equilibrium at the sea surface would be equal to 20.88+/- 0.53 µmol $kg^{-1}$ (Table 2).
252
253 **4 Discussion**

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**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 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°, 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 355.2µatm and 390.1 µatm respectively . The close values of $fCO_{2\ sea}$ and $fCO_{2\ air}$ in 1995-1997 indicate an a near-balanced air to sea $CO_2$ flux on an annual time scale as previously shown by [*Hood and Merlivat*, 2001]. For the 2013-2015 period, a positive annual average air-sea disequilibrium is observed leading to a medium source for the atmospheric $CO_2$.This is consistent as the result of the supplementary contribution of Atlantic waters anthropogenic carbon (+6.5 µatm) (Table 2) in this region of the Mediterranean sea.

**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 $yr^{-1}$. It is thus interesting to notice that such a change in alkalinity does not impact significantly 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 due to the uptake of atmospheric $CO_2$, referred here as anthropogenic DIC ($dDIC_{ant}$), is equal to 24.78+/-1.26 µmol $kg^{-1}$ (Table 2). ($dDIC_{ant}$) predicted solely from chemical equilibrium of the sea surface with the atmosphere is equal to 20.88+/-0.53 µmol $kg^{-1}$. The ratio of these two terms is equal to 0.84+/-0.05. This calls upon an additional contribution to the local $CO_2$ air-sea exchange. 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. [*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 estimate that the contribution of the change of $DIC_{ant}$ over the last 18 years represents ~30% of the total change since the beginning of the industrial period (t>~1800).

**4.4** The signal of acidification

The annual decrease of $pH_T$ calculated between 1995-1997 and 2013-2015 is equal to -0.0021+/-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 $CO_2$-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 implies a relatively high uptake capacity for anthropogenic carbon, $C_{ant}$. However,, this barely modifies the pH trend for a given change of $fCO_2$.

## 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 variability of these properties at the sea surface. We have estimated a large change of sea surface carbonate chemistry and a decrease of pH due to uptake of anthropogenic $CO_2$. In addition to providing first in situ estimates of the change expected from chemical equilibrium with atmospheric $CO_2$, our results support modeling work and analysis of vertical profiles measurements that suggest that the Atlantic Ocean contributes as a source of 15% of the anthropogenic carbon for the basin.

*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 $CO_2$Sys toolbox of [*Pierrot et al.*, 2006] has been used for the calculations of DIC and

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.

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Biogeosciences Discuss., https://doi.org/10.5194/bg-2017-284
Manuscript under review for journal Biogeosciences
Discussion started: 6 July 2017




448 Figure caption and tables

449

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

454

455 Figure 2. Interannual variability of CARIOCA data: a) T, b) $fCO_2$, c) $fCO_2$@13 The dotted
456 lines indicate the period strongly affected by stratification and internal waves (July, 26 $^{th}$ to
457 October 1$^{st}$, 2014 and July, 8 $^{th}$ to October 1$^{st}$, 2015). On 2(b), the open circles correspond to
458 $_{fCO2}$ data derived from DIC and alkalinity measurements of samples taken at 5 and 10 meters.
459 (d), (e), (f), seasonal variability. Note that the color code on (d), (e), (f) is different from (a),
460 (b), (c).

461

462 Figure 3. (a) $fCO_2$@13 as a function of temperature for hourly data in 2013, 2014 and 2015
463 (b) as in (a) but for all hourly data in 1995-1997 (black) and in 2013-2015 (red) (c) As in (b),
464 but for average values per 1°C interval (standard deviation as dotted line). The difference
465 between the two periods is also displayed (dashed black curve; scale on the right axis). (d)
466 Mean monthly sea surface temperature for 1993-1995 (black curve; CARIOCA sensors),
467 2013-2015 (green; CARIOCA sensors), 2013-2015 (red, meteorological buoy).
468 Corresponding mean annual values are indicated by dotted lines.

469

470 Table 1:
471 Distribution of temperature, $fCO_2$@13, and increase $dfCO_2$@13 data binned by 1°C
472 temperature interval for the 2 periods 1995-1997 and 2013-2015 .

473

474 Table 2
475 Seasonally detrended long term and annual trends of seawater carbonate chemistry and
476 atmosphere composition.

477