

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

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5 Liliane. Merlivat <sup>a</sup>, Jacqueline. Boutin <sup>a</sup>, David. Antoine <sup>b,c</sup>, Laurence. Beaumont <sup>d</sup>, Melek.  
6 Golbol <sup>c</sup>, Vincenzo. Vellucci. <sup>c</sup>

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8 <sup>a</sup> Sorbonne Université-CNRS-IRD-MNHN, LOCEAN, F-75005 Paris, France

9 <sup>b</sup> Remote Sensing and Satellite Research Group, School of Earth and Planetary Sciences,  
10 Curtin University, Perth, Australia

11 <sup>c</sup> Sorbonne Université-CNRS, Laboratoire d'Océanographie de Villefranche, LOV, F-06230  
12 Villefranche-sur-Mer, France

13 <sup>d</sup> Division Technique INSU-CNRS, F- 92195 Meudon Cedex, France

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

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17

18 **Abstract**

19 Two 3-year time series of hourly measurements of the fugacity of CO<sub>2</sub> (fCO<sub>2</sub>) in the upper 10  
20 m of the surface layer of the northwestern Mediterranean Sea have been recorded by  
21 CARIOCA sensors almost two decades apart, in 1995-1997 and 2013-2015. By combining  
22 them with alkalinity derived from measured temperature and salinity, we calculate changes of  
23 pH and dissolved inorganic carbon (DIC). DIC increased in surface seawater by ~ 25 μmol  
24 kg<sup>-1</sup> and fCO<sub>2</sub> by 40 μatm, whereas seawater pH decreased by ~ 0.04 (0.0022 yr<sup>-1</sup>). The DIC  
25 increase is about 15% larger than expected from equilibrium with atmospheric CO<sub>2</sub>. This  
26 could result from natural variability, e.g. the increase between the two periods in the  
27 frequency and intensity of winter convection events. Likewise, it could be the signature of the  
28 contribution of the Atlantic Ocean as a source of anthropogenic carbon to the Mediterranean  
29 Sea through the strait of Gibraltar. We then estimate that the part of DIC accumulated over  
30 the last 18 years represents ~30% of the total inventory of anthropogenic carbon in the  
31 Mediterranean Sea.

## 33 1 Introduction

34 The concentration of atmospheric carbon dioxide (CO<sub>2</sub>) has been increasing rapidly over  
35 the 20<sup>th</sup> century and, as a result, the concentration of dissolved inorganic carbon (DIC) in  
36 the near surface ocean increases, which drives a decrease in pH in order to maintain a  
37 chemical equilibrium. 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<sub>2</sub> penetration in the ocean since the industrial revolution  
40 have improved over the past few decades [*Chen and Millero, 1979; Gruber et al., 1996;*  
41 *Sabine et al., 2008; F Touratier and Goyet, 2004; 2009; Woosley et al., 2016*]. As the  
42 concentration of anthropogenic carbon, C<sub>ant</sub>, cannot be distinguished from the natural  
43 background of DIC through total DIC measurements, these methods are based on the  
44 analysis of different chemical properties of the water column. Direct estimates of the  
45 anthropogenic CO<sub>2</sub> absorption in the sea surface layers are difficult owing to the large  
46 natural variability driven by physical and biological phenomena. Bates et al [2014] have  
47 extracted the trend from the large variability, based on analysis of a long time series  
48 (monthly or seasonal sampling). For the global surface ocean, Lauvset et al. [2015] have  
49 used the Surface Ocean CO<sub>2</sub> Atlas (SOCAT) database [*Bakker et al., 2014*] combined with  
50 an interpolation method. Estimates of anthropogenic storage in the Mediterranean Sea  
51 differ by about a factor of two [*Huertas et al., 2009; F Touratier and Goyet, 2009*]. In  
52 addition to the anthropogenic signal, oceanic DIC can also be the signature of a strong  
53 interannual variability. In the North Atlantic, for instance, McKinley et al. [2011] have  
54 shown that the long term trend emerges only after more than 25 years because of natural  
55 variability.

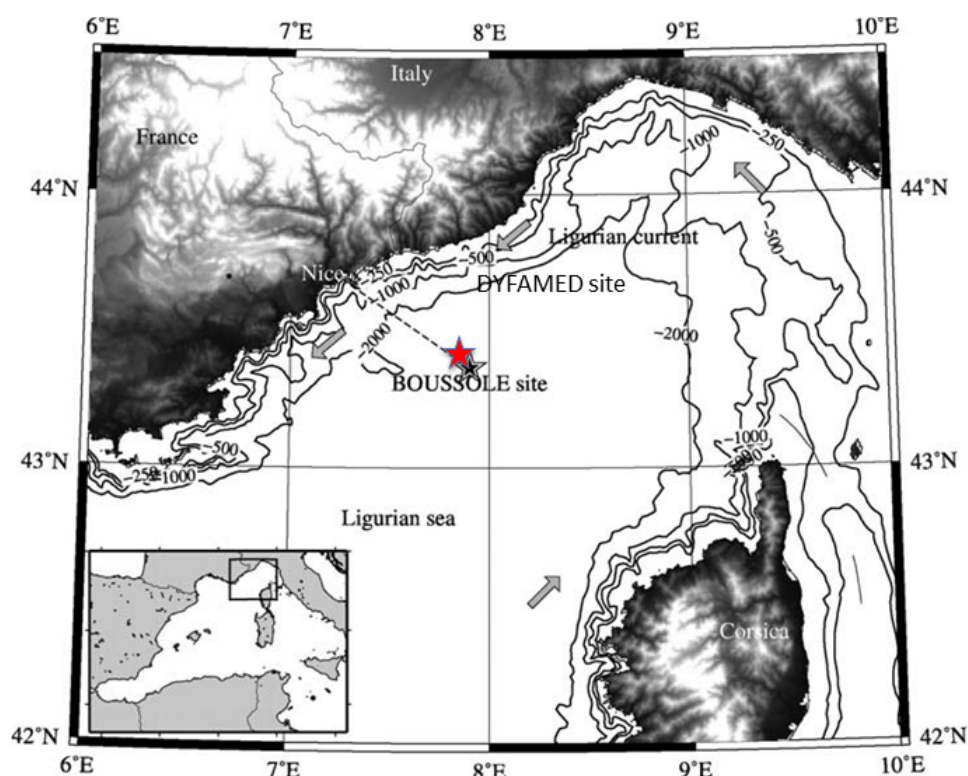
56 A high frequency sampling of the seawater carbon chemistry at the air-water interface over  
57 extended periods of time is useful to assess trends and variability of DIC. In this paper we  
58 analyze two three-year time series of hourly fugacity of CO<sub>2</sub>, fCO<sub>2</sub>, measured with  
59 autonomous CARIOCA sensors [*Copin-Montégut et al., 2004; Merlivat and Brault, 1995*] in  
60 1995-1997 and 2013-2015, at two nearby locations in the northwestern Mediterranean Sea  
61 (Fig. 1). Using measured fCO<sub>2</sub>, temperature (T) and salinity (S), we derive the other variables  
62 of the carbonate system (pH and DIC). The experimental setting is first described, and the  
63 recent data obtained over the 2013-2015 period are presented. Combined with the 1995-1997

64 measurements previously published [Hood and Merlivat, 2001], we estimate the decrease of  
65 pH and the increase of DIC. The results are discussed with respect to the contributions of the  
66 exchange with atmospheric CO<sub>2</sub>, to the possible impact of vertical mixing and to recent  
67 estimates of the transport of anthropogenic carbon from the Atlantic Ocean over a 18-year  
68 period.

69

## 70 2 Material and methods

### 71 2.1-The BOUSSOLE and DYFAMED sites



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73 Fig.1. The area of the northwestern Mediterranean Sea showing the southern coast of France,  
74 the Island of Corsica, the main current branches (gray arrows), and the location of the  
75 DYFAMED site (43°25'N, 7°52'E, red star) (<http://doi.org/10.17882/43749>) and the  
76 BOUSSOLE buoy (43°22'N, 7°54'E, black star) in the Ligurian Sea.

77

78 Data collection was carried out at the BOUSSOLE site (43°22'N, 7°54'E) in 2013-2015  
79 [Antoine et al., 2008; Antoine. and others, 2006] and at the DYFAMED site (43°25'N,  
80 7°52'E) in 1995-1997 [J.C. Marty et al., 2002]. These sites are 3 nautical miles apart, both  
81 located in the Ligurian Sea, one of the basins of the northwestern Mediterranean Sea (Fig.1).  
82 The water depth is of ~2400 m. The prevailing ocean currents are usually weak (<20 cm s<sup>-1</sup>),  
83 because these sites are in the central area of the cyclonic circulation that characterizes the

84 Ligurian Sea. The two sites surrounded by the permanent geostrophic Ligurian frontal jet  
85 flow are protected from coastal inputs [Antoine *et al.*, 2008; Heimbürger *et al.*, 2013; Millot,  
86 1999]. Monthly cruises are carried out at the same location .

87

## 88 2.2- Analytical methods

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

103 At Boussole, newly designed fCO<sub>2</sub> sensors have been calibrated using in situ seawater  
104 samples taken at 5 and 10 m depth during the monthly servicing cruises to the mooring. The  
105 total alkalinity, Alk, and DIC of the samples were determined by potentiometric titration  
106 using a closed cell according to the method developed by [Edmond, 1970]. Certified  
107 Reference Materials (CRMs) supplied by Dr. A.G. Dickson (Scripps Institution of  
108 Oceanography, San Diego, USA) were used for calibration [Dickson *et al.*, 2007]. The  
109 accuracy is estimated at 3 µmol kg<sup>-1</sup> for both DIC and Alk. fCO<sub>2</sub> is calculated using the  
110 dissociation constants of Mehrbach refitted by Dickson and Millero [Dickson and Millero,  
111 1987; Mehrbach *et al.*, 1973] as recommended by Alvarez *et al.*[2014] for the Mediterranean  
112 Sea. Uncertainty in derived from an individual sample is expected to be on the order of 5  
113 µatm [Millero, 2007]. About 8 samples have been used to calibrate each CARIOCA sensor so  
114 that the uncertainty of the absolute calibration of each fCO<sub>2</sub> CARIOCA sensor, is estimated at  
115 1.8 µatm. In addition, we observe that the standard deviation of the difference between the  
116 CARIOCA fCO<sub>2</sub> and fCO<sub>2</sub> computed with the monthly discrete samples (Fig. 2b) is equal to  
117 4.4 µatm, consistent with the expected precision on CARIOCA fCO<sub>2</sub> of 5 µatm. Alk and S of

118 the 56 samples taken at BOUSSOLE are linearly correlated according the following  
 119 relationship :

120 
$$\text{Alk } (\mu\text{mol kg}^{-1}) = 87.647 \text{ S} - 785.5 \quad (1)$$

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

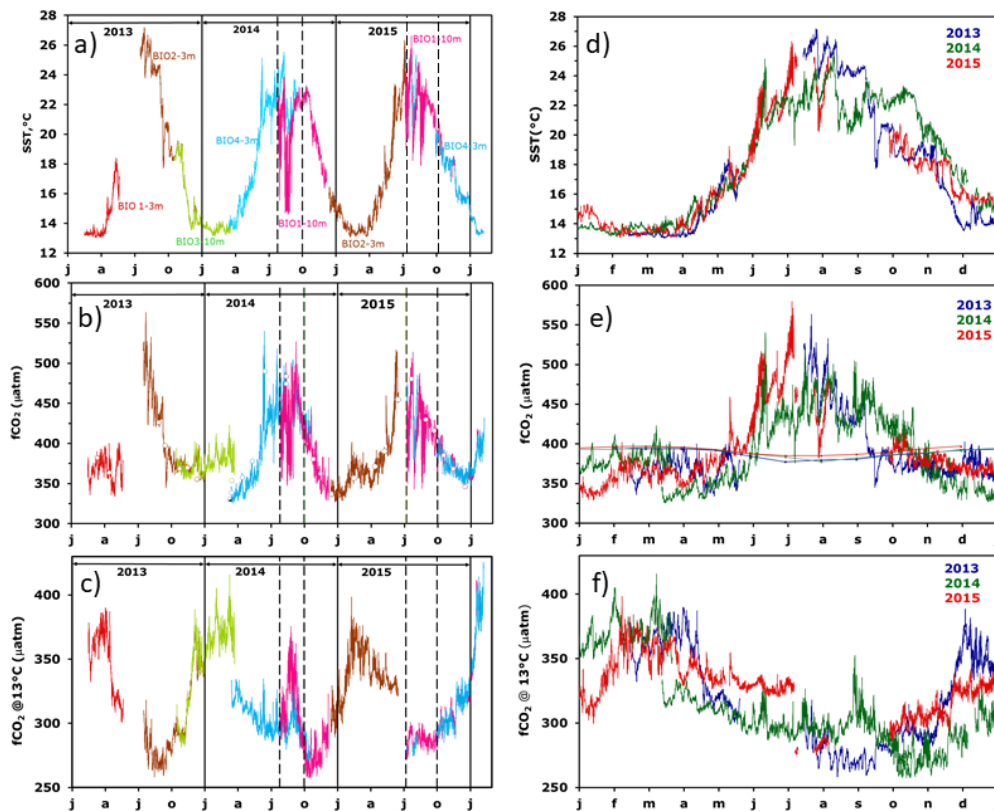
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124 **3 Results**

125 **3.1 The BOUSSOLE mooring (2013-2015) time series**

126 Temperature and  $f\text{CO}_2$  were measured from February 2013 to February 2016. All seasons  
 127 were well represented, with missing data only in May-July 2013. For some periods,  
 128 simultaneous measurements were made at 3 and 10 m depth (Fig. 2, a, b, c).

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131 Fig.2. Interannual variability of CARIOCA data on the BOUSSOLE mooring: left column, as  
 132 a function of time, right column as a function of months for a given year (blue, 2013, green,  
 133 2014, red, 2015). (a, d) T, (b, e),  $f\text{CO}_2$ , (c, f)  $f\text{CO}_2@13^\circ\text{C}$ . On a, b, c, the dotted lines indicate  
 134 the period affected by stratification and internal waves (July, 26<sup>th</sup> to October 1<sup>st</sup>, 2014 and  
 135 July, 8<sup>th</sup> to October 1<sup>st</sup>, 2015). On 2(b), the open circles correspond to  $f\text{CO}_2$  data derived from

136 DIC and alkalinity measurements of samples taken at 5 and 10 m. On 2(e), the thin lines  
137 indicate  $f\text{CO}_{2\text{atm}}$ . Note that the color code on (d), (e), (f) is different from (a), (b), (c).

138  
139 The range of temperature (Fig. 2a) extends from 13°C in winter up to 27°C in summer,  
140 followed by progressive cooling in fall. The coldest temperature, 13°C, results from the  
141 winter vertical mixing with the deeper Levantine Intermediate Water, LIW, marked by  
142 extremes in temperature and salinity [Copin-Montegut and Begovic, 2002]. Temperature  
143 provides the main control of the seasonality of  $f\text{CO}_2$ , from 350  $\mu\text{atm}$  to more than 550  $\mu\text{atm}$  in  
144 summer 2013 (Fig. 2b). The fugacity of  $\text{CO}_2$  in seawater is a function of temperature, DIC,  
145 alkalinity, salinity and dissolved nutrients. In the oligotrophic surface waters of the  
146 Mediterranean Sea, the effect of nutrients may be neglected. Temperature and DIC have the  
147 strongest influences. By normalizing  $f\text{CO}_2$  to a constant temperature, the temperature effect  
148 can be removed and changes in  $f\text{CO}_2$  resulting from changes in DIC can be more easily  
149 identified. Figure 2c shows the variability of  $f\text{CO}_2$  normalized to the constant temperature of  
150 13°C, ( $f\text{CO}_2@13$ ), using the equation of Takahashi et al. [1993]. The underlying processes  
151 that govern the seasonal variability of  $f\text{CO}_2@13$  are successively winter mixing, biological  
152 activity (organic matter formation and remineralization) and deepening of mixed layer in fall  
153 [Begovic and Copin-Montegut, 2002; Hood and Merlivat, 2001]. Biological processes  
154 account for the decline in  $f\text{CO}_2@13$  observed from March-April to late summer; the ensuing  
155 increase of surface  $f\text{CO}_2@13$  is associated with the deepening of the mixed layer in the fall or  
156 convection in winter as the vertical distribution of  $f\text{CO}_2@13$  at DYFAMED shows a  
157 maximum in the 50-150 m layer where a large remineralization of organic matter occurs, the  
158 productive layer being mostly between 0 and 40 m [Copin-Montegut and Begovic, 2002]. The  
159 contribution of air-sea exchange is not significant [Begovic and Copin-Montegut, 2002].  
160 Over the period 2013-2015, the air-sea  $\text{CO}_2$  flux from the atmosphere to the ocean surface is  
161 equal to  $-0.45 \text{ mol m}^{-2} \text{ yr}^{-1}$ .

162 During summer 2014, large differences between measurements at 3 and 10 m were  
163 observed (Fig. 2, a, b, c between dashed lines). A detailed analysis of the temporal  
164 variability during that period underscores the role of inertial waves at the frequency of  
165 17.4 hours that create the observed differences between the 2 depths of observations,  
166 the deeper waters being colder and enriched in  $f\text{CO}_2@13$ . T and  $f\text{CO}_2@13$  variability is  
167 dominated by inertial waves. In particular, from 15 to 26 of August 2014, the difference  
168 in T between the two depths is as large as 7.6°C, and 5.1°C on average.  $f\text{CO}_2$  decreases on  
169 average by 32.7  $\mu\text{atm}$  corresponding to an increase of  $f\text{CO}_2@13$  equal to 42.8  $\mu\text{atm}$ .

170 The 2013-2015 seasonal and inter-annual variability of T, fCO<sub>2</sub> and fCO<sub>2</sub>@13 is  
171 illustrated on Fig. 2, d, e, f. The larger interannual changes in temperature (Fig.2, d) are  
172 observed during summer, both at 3 m and 10 m depth, while over February and March, a  
173 constant value of 13°C is observed as the result of vertical mixing with the LIW. A very  
174 large inter-annual variability of fCO<sub>2</sub>@13 is observed for T<14°C (Fig. 2,f). This is  
175 associated with the winter mixing at the mooring site, which is highly variable from year  
176 to year. Winter mixed-layer depth, MLD, varies between 50 and 160 m, at the top of the  
177 LIW over the 2013-2015 period [Coppola et al., 2016]. The variable depth of the winter  
178 vertical mixing causes the difference in fCO<sub>2</sub>@13 as fCO<sub>2</sub> increases with depth [Copin-  
179 Montegut and Begovic, 2002]. The deepening of MLD is driven by episodic and intense  
180 mixing processes characterized by a succession of events lasting several days, related to  
181 atmospheric forcing [Antoine et al., 2008] which lead to increase in fCO<sub>2</sub>@13. Figure 2,e  
182 illustrates the solubility control of the variability of fCO<sub>2</sub>, as fCO<sub>2</sub> increases when T  
183 increases. Another cause of inter-annual variability of fCO<sub>2</sub> for T~14°C is the timing of  
184 the spring increase of biological activity which differs by a month between years; for  
185 instance, it happened at the beginning of April in 2013, T~15-16°C and by mid March in  
186 2014, T~14°C. Another cause is the deepening of the mixed layer due to the fall cooling  
187 which varies by a month between years.

188

### 189 3.2 Decadal changes of hydrography

#### 190 3.2.1 Sea surface temperature changes

191 Monthly mean values of temperature have been computed for the two three-year periods,  
192 1995-1997 and 2013-2015. In 1995-1997, fCO<sub>2</sub> and T at 2 m were measured with CARIOCA  
193 sensors installed on a buoy at DYFAMED [Hood and Merlivat, 2001]. The mean annual  
194 temperature of hourly CARIOCA data is equal to 18.21°C. For 2013-2015, temperature  
195 measurements made on the BOUSSOLE mooring at 3 and 10 meters have been used. For the  
196 April to September time interval, there are only data at 3m depth. In addition, temperature  
197 data measured half hourly at 0.7 m at a nearby meteorological buoy (43°23'N, 7°50'E)  
198 (<http://www.meteo.shom.fr/real-time/html/DYFAMED.html>) have been used (Fig.3d). Mean  
199 annual temperatures are equal to 18.29°C and 17.97°C respectively, based on the  
200 meteorological buoy and the BOUSSOLE mooring data. The two sets of data differ  
201 essentially during July and August, with the temperatures at 3 m being colder than at 0.7 m,  
202 indicating a thermal gradient between the two depths during summer. Therefore, for 2013-

203 2015, we select the mean annual value computed with the meteorological buoy, 18.29°C, as  
204 better representing the sea surface. This value is close to 18.21°C computed for 1995-1997.  
205 Then, no significant change of SST is found between the 2 decades, with a mean value equal  
206 to 18.25°C.

### 207 **3.2.2** Sea surface salinity changes

208 The mean value of salinity and the standard error of the mean computed from 56 samples  
209 taken at BOUSSOLE in 2013-2015 are respectively 38.19 and 0.02. In 1998-1999, ship  
210 measurements of surface salinity were made during monthly cruises at the DYFAMED site  
211 [*Copin-Montégut et al.*, 2004]. The mean salinity and the standard error of the mean of this  
212 set of 19 data are respectively 38.21 and 0.03. Thus, there is no significant salinity change  
213 between the two decades .

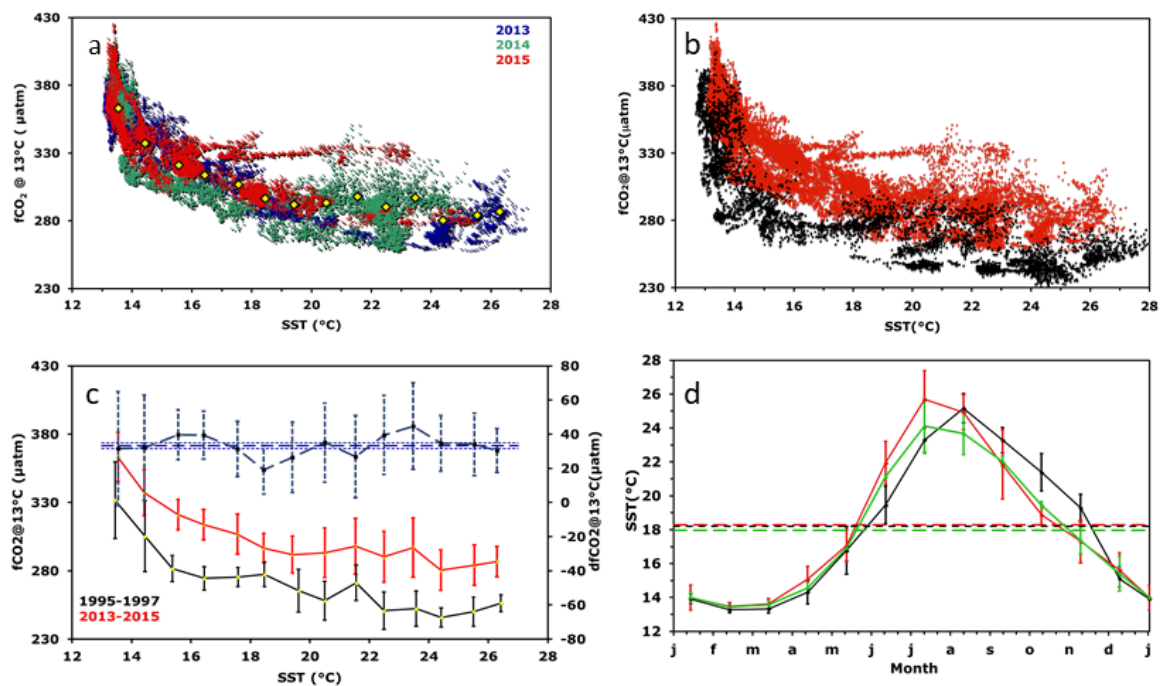
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## 215 **3.3** Decadal changes of fCO<sub>2</sub>@13

### 216 **3.3.1** Time series of fCO<sub>2</sub>@13 in 1995-1997 and 2013-2015

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





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230 Fig.3. (a)  $fCO_2@13$  as a function of temperature for hourly data in 2013, 2014 and 2015. The  
231 yellow dots indicate mean  $fCO_2@13$ . (b) as in (a) but for all hourly data in 1995-1997 (black)  
232 and in 2013-2015 (red). (c) as in (b), but for average values per  $1^\circ C$  interval (standard  
233 deviation as dotted line). The difference between the two periods is also displayed (dashed  
234 blue curve, scale on the right axis ; the mean difference over all SST is represented by the  
235 horizontal blue line). (d) Mean monthly sea surface temperature for 1993-1995 (black curve;  
236 CARIOCA sensors), 2013-2015 (green; CARIOCA sensors), 2013-2015 (red, meteorological  
237 buoy). Corresponding mean annual values are indicated by dotted lines.

238

### 239 3.3.2 Trend analysis and statistics

240 To quantify the change of  $fCO_2@13$  between the two data sets, we proceed as follows: data  
241 are binned by  $1^\circ C$  temperature intervals, thereby removing any potential seasonal weighting,  
242 especially towards the  $13-14^\circ C$  winter months temperature. The measurements made in this  
243 temperature interval represent about 25% of the total number of data for both periods. For  
244 each of the fourteen  $1^\circ C$  step, the mean and standard deviation of hourly  $fCO_2@13$   
245 measurements are reported in Table 1 and on Fig. 3c. The mean temperature within each  $1^\circ$   
246 step differ for the two periods as the distribution of individual measurements are not identical.

247

248 For both data sets, a monotonic relationship between  $f\text{CO}_2@13$  and T is observed with  
249 correlation coefficients respectively equal to -0.861 and -0.857. The difference in  $f\text{CO}_2@13$   
250 between the two periods,  $df\text{CO}_2@13$ , is derived in each temperature step, as the difference  
251 between column 2 and 6 of Table 1. The variability of this difference is estimated as the  
252 quadratic mean of the standard deviation in each time series. Both values are reported in  
253 Table 1, column 9 and 10, and on Fig. 3c. The distribution of each  $df\text{CO}_2@13$  values  
254 around the mean over all SST of  $df\text{CO}_2@13$  seems random and indicates no trend  
255 dependency with SST (Fig. 3c). This suggests that the processes which control the  
256 seasonal variation of  $f\text{CO}_2@13$  at the sea surface have not changed over the last two  
257 decades.

258 We have estimated the uncertainties in the estimates of the difference  $df\text{CO}_2@13$  with 2  
259 methods. Firstly, the arithmetic mean of  $df\text{CO}_2@13$  is equal to  $33.17\mu\text{atm}$ , with a standard  
260 deviation, SD, and standard error, SE, respectively equal to  $6.29\mu\text{atm}$  and  $1.68\mu\text{atm}$ . A 95%  
261 confidence interval is thereby achieved within 1.96 SE, i.e  $3.29\mu\text{atm}$ . A second approach  
262 consists of computing a weighted average of the mean of  $df\text{CO}_2@13$ . In this case, mean  
263 weighted value of  $df\text{CO}_2@13$  over the whole range of temperature is estimated, the weights  
264 being equal to the variance of  $df\text{CO}_2@13$  in each temperature step. It is equal to  $32.70\mu\text{atm}$ .  
265 The weighted SD, and the associated SE, of the 14 data points are respectively equal to  $4.85$   
266  $\mu\text{atm}$  and  $1.30\mu\text{atm}$ . A 95% confidence interval is achieved within  $2.54\mu\text{atm}$ . The difference  
267 between the two mean  $df\text{CO}_2@13$  estimates is  $0.47\mu\text{atm}$ , well below SE. In the following,  
268 we have chosen the former method.

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Table 1:

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

Time interval 1995-1997				Time interval 2013-2015				Temporal change	
T <sup>1</sup> °C	fCO <sub>2</sub> @13 µatm	N	standard deviation µatm	T <sup>1</sup> °C	fCO <sub>2</sub> @13 µatm	N	standard deviation µatm	dfCO 2@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

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### 288 3.4 Changes of seawater carbonate chemistry in surface waters

289 We estimated the DIC and pH changes related to the increase of fCO<sub>2</sub>@13 measured at the  
290 sea surface 18 years apart, assuming a mean salinity equal to 38.2, a mean alkalinity equal to  
291 2562.3 µmol kg<sup>-1</sup> following equation (1), and a mean in situ temperature, T, equal to  
292 18.25°C. The dissociation constants of Mehrbach refitted by Dickson and Millero [*Dickson*  
293 *and Millero*, 1987; *Mehrbach et al.*, 1973] were used. pH is calculated on the seawater scale.

294 The uncertainty of  $dfCO_2@13$ ,  $3.3\mu atm$ , has been propagated to compute the combined  
 295 uncertainty in  $dDIC$  and  $dpH_{SWS}$ . The uncertainties in the equilibrium constants are neglected  
 296 in this propagation of uncertainties. Likewise, an implicit assumption is that there is no  
 297 systematic error on  $DIC$  and  $pH_{SWS}$  derived from  $fCO_2@13$  between the two time periods; in  
 298 particular, mean temperature and salinity remain the same (section 3.2). This is further  
 299 discussed in section 4.1. We compute an increase of  $DIC$ ,  $dDIC$ , equal to  $25.2\pm 2.7\ \mu mol\ kg^{-1}$   
 300  $^1$  ( $1.40\pm 0.15\ \mu mol\ kg^{-1}yr^{-1}$ ) and the decrease of  $pH_{SWS}$ ,  $dpH_{SWS}$  equal to  $-0.0397\pm 0.0042$   
 301  $pH_{SWS}$  ( $-0.0022\pm 0.0002\ pH_{SWS}\ yr^{-1}$ ) (Table 2).

302  
 303 Table 2  
 304  
 305

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

306 T, mean annual temperature equal to  $18.25^\circ C$

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

308 \*\*,  $dDIC_{ant}$

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

310

### 311 3.5 Changes in atmospheric and seawater $fCO_2$

312 The increase of atmospheric  $fCO_2$  from 1995-1997 to 2013-2015 was computed from  
 313 monthly atmospheric  $xCO_2$  concentrations measured at the Lampedusa Island station (Italy)  
 314 ( $35^\circ 31' N$ ,  $12^\circ 37' E$ ) (<http://ds.data.jma.go.jp/gmd/wdcgg/>) (see equation 3 in [Hood and  
 315 Merlivat, 2001]). Considering a mean annual in situ temperature equal to  $18.25^\circ C$  and an  
 316 atmospheric pressure of 1 atm, we derived a mean atmospheric  $fCO_2$  equal to  $355.3\pm 0.8$   
 317  $\mu atm$  for 1995-1997 and  $389.6\pm 0.9\ \mu atm$  for 2013-2015, that is an increase of  $34.3\pm 2.3$   
 318  $\mu atm$  (95% confidence interval) (Table 2). At this temperature, the change of  $fCO_2$  at the sea  
 319 surface is  $41.4\pm 4.1\ \mu atm$ . Thus the contribution of the increase in atmospheric  $CO_2$  is

320 responsible for 84+/-5 % of the increase of fCO<sub>2</sub> measured in the surface waters. With the  
321 same salinity and alkalinity as previously, the corresponding change in surface DIC, assuming  
322 air-sea equilibrium, would be 20.8+/- 1.3 μmol kg<sup>-1</sup> (Table 2).

323

## 324 **4 Discussion**

### 325 **4.1 Time change of surface alkalinity**

326 High frequency measurements of fCO<sub>2</sub> and temperature over 2 periods of 3 years, 2 decades  
327 apart, have allowed the computation of an increase of DIC equal to 25.1+/-2.3 μmol kg<sup>-1</sup>  
328 assuming no change of alkalinity. In the range of salinity of the BOUSSOLE samples, 37.9 to  
329 38.5, the alkalinity values computed with Eq (1) are larger than those predicted by the  
330 relationship established for the DYFAMED site, with a mean difference equal to 10+/-2 μmol  
331 kg<sup>-1</sup> [Copin-Montegut and Begovic, 2002]. In both cases alkalinity measurements were made  
332 with a potentiometric method using certified reference material supplied by A.G. Dickson for  
333 calibration. It is difficult to identify the cause for a possible change of alkalinity between the 2  
334 periods, 18 years apart, while no salinity change has been observed. At a coastal site 50 km  
335 away from DYFAMED, Kapsenberg et al. [2017] have measured an increase of alkalinity  
336 unrelated to salinity over the period from 2007 to 2015. They attribute it to changes in  
337 freshwater inputs from land. However, based on data from Coppola et al. [2016], alkalinity in  
338 the upper 50m at DYFAMED did not change significantly from 2007 through 2014 (3.204  
339 μmol kg<sup>-1</sup>, P=0.0794, r<sup>2</sup>=0.08). Thus, we cannot conclude on whether the difference  
340 observed at DYFAMED/BOUSSOLE between the two periods is real or an artifact of  
341 measurement techniques. As a sensitivity test, we compute the expected changes of DIC and  
342 pH from 1995-1997 to 2013-2015 for a mean alkalinity increase of 10 μmol kg<sup>-1</sup>: we get  
343 annual changes, dDIC=+0.46 μmol kg<sup>-1</sup> yr<sup>-1</sup> and dpH=-0.0001 pH unit yr<sup>-1</sup>, which are well  
344 below errors estimated in section 3.4. Hence, such a change in alkalinity does not  
345 significantly affect the increase of DIC and the decrease of pH shown in Table 2.

346

### 347 **4.2 Drivers of the temporal change of DIC in surface waters**

348 The increase in sea surface DIC from 1995-1997 to 2013-2015 is 25.2+/-2.7 μmol kg<sup>-1</sup> (Table  
349 2) whereas the expected contribution due to ocean uptake of anthropogenic CO<sub>2</sub> is 20.8+/-1.3  
350 μmol kg<sup>-1</sup>. In order to interpret the difference between these two values, we examine potential  
351 changes that may result from interannual variability in local physical and biological processes  
352 or anthropogenic carbon invasion from lateral advection of Atlantic waters.

#### 353 **4.2.1 Natural variability**

354 Time series of the mixed layer depth, MLD, show a strong variability in winter at interannual  
355 scale. During the two periods, 1995-1997 and 2013-2015, the winter MLD never exceeded  
356 220 m, whereas values over 300 m were observed in 1999 and especially in February and  
357 March 2006 with values close to 2000 m [*Coppola et al.*, 2016; *Pasqueron de Fommervault et*  
358 *al.*, 2015]. These episodes of strong and deep vertical mixing must have entrained DIC-rich  
359 LIW in the surface waters. This entrainment could be causing an increase in DIC between the  
360 1995-1997 and 2013-2015 periods. Monthly surface samples collected at the Dyfamed time  
361 series station between 1998 and 2013 indicate an increasing DIC trend of  $1.35 \mu\text{mol kg}^{-1} \text{yr}^{-1}$ .  
362 This value is known with great uncertainty ( $r^2 = 0.05$ ) because of the large seasonal variability  
363 displayed in the monthly samples [*Gemayel et al.*, 2015]. Nevertheless, this value is closer to  
364 the trend we calculated between the two periods, 1993-1995 and 2013-2015 ( $1.40 \mu\text{mol kg}^{-1}$   
365  $\text{yr}^{-1}$ ) than to the trend inferred from the atmospheric increase ( $1.15 \mu\text{mol kg}^{-1} \text{yr}^{-1}$ ). On  
366 DYFAMED time series, we find no evidence that the strong increase in MLD observed  
367 during winters 1999 and especially 2006 resulted in a further increase in DIC.

368 The monthly cruises of the Dyfamed time-series study have also been analyzed in order to  
369 investigate the hydrological changes and some biological consequences over the period 1995-  
370 2007 [*J. C. Marty and Chiavérini*, 2010]. These authors show that extreme convective mixing  
371 events such as recorded in 1999 and 2006 are responsible for large increases in nutrient  
372 content in surface layers and conclude that the biological productivity is increasing especially  
373 during the 2003-2006 period, which could lead to a larger consumption of carbon, i.e. a  
374 decrease of DIC.

#### 375 **4.2.2 Anthropogenic carbon exchange through the Strait of Gibraltar.**

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

384 Schneider et al. [2010], using the transit time distribution method applied to a dataset of a  
385 Mediterranean cruise in 2001, estimated a net anthropogenic carbon flux across the Strait of  
386 Gibraltar into the Mediterranean Sea of  $3.5 \text{ Tg C yr}^{-1}$ . Over the whole period from 1850 to  
387 2001, this contribution of  $C_{\text{ant}}$  represents almost 10% of the total  $C_{\text{ant}}$  inventory of the

388 Mediterranean Sea. Accordingly, about 90% must have been taken directly by equilibrium  
389 with atmospheric CO<sub>2</sub>. Based on a high-resolution regional model, Palmieri et al. [2015]  
390 computed the anthropogenic carbon storage in the Mediterranean basin. They concluded that  
391 75% of the total storage of C<sub>ant</sub> in the whole basin comes from the atmosphere and 25% from  
392 net transport from the Atlantic through the Strait of Gibraltar. The findings of these two  
393 studies support our estimated change of DIC of (17±10) % in addition to the direct  
394 contribution of air-sea exchange suggesting that it could result from the anthropogenic carbon  
395 input from the Atlantic Ocean towards the Mediterranean basin.

396 Huertas et al. [2009] and Schneider et al. [2010] report DIC<sub>ant</sub> surface concentrations  
397 respectively equal to 65-70 μmol kg<sup>-1</sup> at the Strait of Gibraltar in the years 2005-2007 and  
398 close to 65 μmol kg<sup>-1</sup> in the western basin in 2001. We extrapolate these figures to the year  
399 2014, assuming a mean increase rate of DIC equal to 1.4 μmol kg<sup>-1</sup>yr<sup>-1</sup> as previously  
400 computed (Table 2). Taking into account the increase of DIC<sub>ant</sub> equal to 25.2 μmol kg<sup>-1</sup>  
401 between 1995-1997 and 2013-2015, we estimate that the contribution of the change of DIC<sub>ant</sub>  
402 over the last 18 years represents ~30% of the total change since the beginning of the industrial  
403 period (t>~1800).

404

#### 405 **4.3 Long-term trends in surface DIC and pH**

406 The annual changes of DIC and pH<sub>SWS</sub> calculated between 1995-1997 and 2013-2015 are  
407 respectively equal to 1.40 ±0.15 μmol kg<sup>-1</sup> and -0.0022±/-0.0002. At the DYFAMED site, at  
408 10 m, Marcellin Yao et al. [2016] studied the time variability of pH over 1995-2011, based on  
409 measurements of T, S, Alk and DIC sampled approximately once a month. They computed a  
410 mean annual decrease of -0.003 ± 0.001 pH units on the seawater scale that is not  
411 significantly different from our estimate. For the global surface ocean, Lauvset et al. [2015]  
412 have reported a mean rate of decrease of pH, -0.0018±/-0.0004 for 1991-2011. This value is  
413 also within the limits of uncertainty of the pH change computed in our study.

414 Bates et al. [2014] examined changes in surface seawater CO<sub>2</sub>-carbonate chemistry at the  
415 locations of seven ocean CO<sub>2</sub> time series that have been gathering sustained observations  
416 from 15 to 30 years with monthly or seasonal sampling. Six stations are located in the  
417 Atlantic and Pacific oceans in a latitudinal band between 10° N and 68°N. The range of  
418 increasing and decreasing annual trends of DIC and pH extends from 0.93 ±0.24 to 1.89 ±/  
419 0.45 μmol kg<sup>-1</sup>yr<sup>-1</sup> and -0.0014±/-0.0005 to -0.0026±/-0.0006 respectively. The Revelle factor  
420 of surface waters vary from 9-10 in the low latitude to 12-15 in the subpolar time series sites,  
421 with higher Revelle factor values reflecting reduced capacity to absorb atmospheric CO<sub>2</sub>. The

422 data show that the increase of DIC is not only controlled by the buffer capacity of the water  
423 but also compounding effects of changes in physical factors as strengthening of winter mixing  
424 or larger air-sea uptake [Olafson *et al.*, 2010].

425 The increase of DIC computed at DYFAMED is in the upper range of values reported at the  
426 other time series. A low Revelle factor, close to 10, characterizes the Mediterranean Sea  
427 because of its warm and high-alkalinity waters. Moreover, as the result of a relatively short  
428 deep water renewal time estimated to be 20-40 years in the western basin [Schneider *et al.*,  
429 2010], the waters of the Mediterranean Sea have a relatively high capacity to absorb  
430 anthropogenic CO<sub>2</sub> from the atmosphere and transport it to depth.

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

437

## 438 **5 Conclusion**

439 High-frequency ocean fCO<sub>2</sub> measurements made by CARIOCA sensors have been used to  
440 calculate trends in fCO<sub>2</sub>, DIC and pH over a period of two decades notwithstanding a short-  
441 time and natural seasonal variability of these properties at the sea surface. We have estimated  
442 a large change of sea surface carbonate chemistry, an increase of DIC and a decrease of pH.  
443 The computed increase of DIC is larger than the change expected from chemical equilibrium  
444 with atmospheric CO<sub>2</sub>. This could be the result of a strong interannual variability of the winter  
445 mixing as observed between the two periods 1993-1995 and 2013-2015. Likewise, our results  
446 support modeling work and analysis of vertical profiles measurements that suggest that the  
447 Atlantic Ocean contributes a substantial amount of anthropogenic carbon to the  
448 Mediterranean basin, (17+/-10) %, which lies between the estimates of 10% by Schneider *et*  
449 *al.* [2010] and 25% by Palmieri *et al.* [2015].

450

451 *Data availability:* Time series data from Dyfamed (1995-1997) are available in the SOCAT v3  
452 database. Boussole data (2013-2015) will be available in SOCAT v6.

453

## 454 **Acknowledgments**

455 Seawater samples were analyzed for DIC and Alk by the SNAPO-CO<sub>2</sub> at LOCEAN in Paris.



456 The CO2Sys toolbox of [Pierrot *et al.*, 2006] has been used for the calculations of DIC and  
457 pH. The adaptation of CARIOCA sensors to high pressure has been supported by the BIO-  
458 optics and CARbon EXperiment (BIOCAREX) project, funded by the Agence Nationale de la  
459 Recherche (ANR,Paris). We are grateful for helpful comments from Gilles Reverdin and the  
460 reviewers on the manuscript. Many thanks to Laurent Coppola who kindly provided  
461 additional MLD data at Dyfamed.

462

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586  
587

587

Table 1:

588

589 Distribution of temperature, fCO<sub>2</sub>@13, and increase dfCO<sub>2</sub>@13 data binned by 1°C  
 590 temperature interval for the 2 periods 1995-1997 and 2013-2015 .

591

592

Time interval 1995-1997				Time interval 2013-2015				Temporal change	
T <sup>1</sup> °C	fCO <sub>2</sub> @13 µatm	N	standard deviation µatm	T <sup>1</sup> °C	fCO <sub>2</sub> @13 µatm	N	standard deviation µatm	dfCO 2@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

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Table 2

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

	d fCO <sub>2</sub> <sup>*</sup> @ 13 µatm	d fCO <sub>2</sub> <sup>*</sup> @ T µatm	d DIC <sup>*</sup> µmolkg <sup>-1</sup>	d pH <sub>SWS</sub> <sup>***</sup> pH unit	dfCO <sub>2</sub> @T annual µatm yr <sup>-1</sup>	d DIC annual µmolkg <sup>-1</sup> yr <sup>-1</sup>	d pH <sub>SWS</sub> <sup>***</sup> annual pH unit yr <sup>-1</sup>
sea surface	33.2 +/-3.3	41.4 +/-4.1	25.2 +/-2.7	-0.0397 +/-0.0042	2.30 +/-0.23	1.40 +/-0.15	-0.0022 +/-0.0002
atmosphere Lampedusa data		34.3 +/-2.3	**20.8 +/-1.3		1.91 +/-0.13	1.15 +/-0.07	
dfCO <sub>2</sub> @T <sub>air</sub> /dfCO <sub>2</sub> @T <sub>sea</sub>		0.83 +/-0.10	0.83 +/-0.09				

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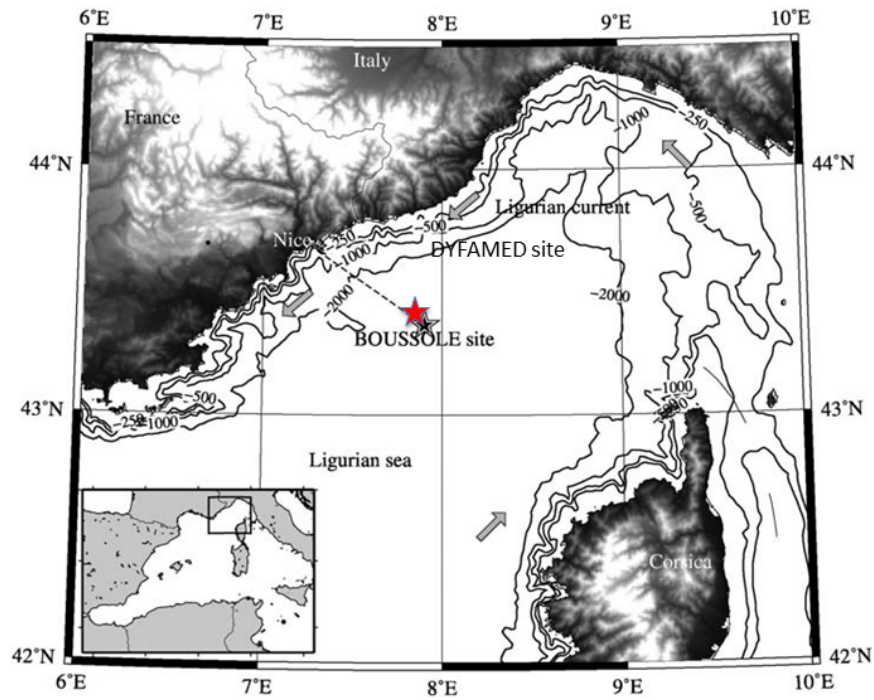
T, mean annual temperature equal to 18.25°C

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

\*\*, dDIC<sub>ant</sub>

\*\*\*, dpH<sub>SWS</sub> computed at T

626 Figure 1. Fig.1. The area of the northwestern Mediterranean Sea showing the southern coast  
627 of France, the Island of Corsica, the main current branches (gray arrows), and the location of  
628 the DYFAMED site (43°25'N, 7°52'E, red star) (<http://doi.org/10.17882/43749>) and the  
629 BOUSSOLE buoy (43°22'N, 7°54'E, black star) in the Ligurian Sea.  
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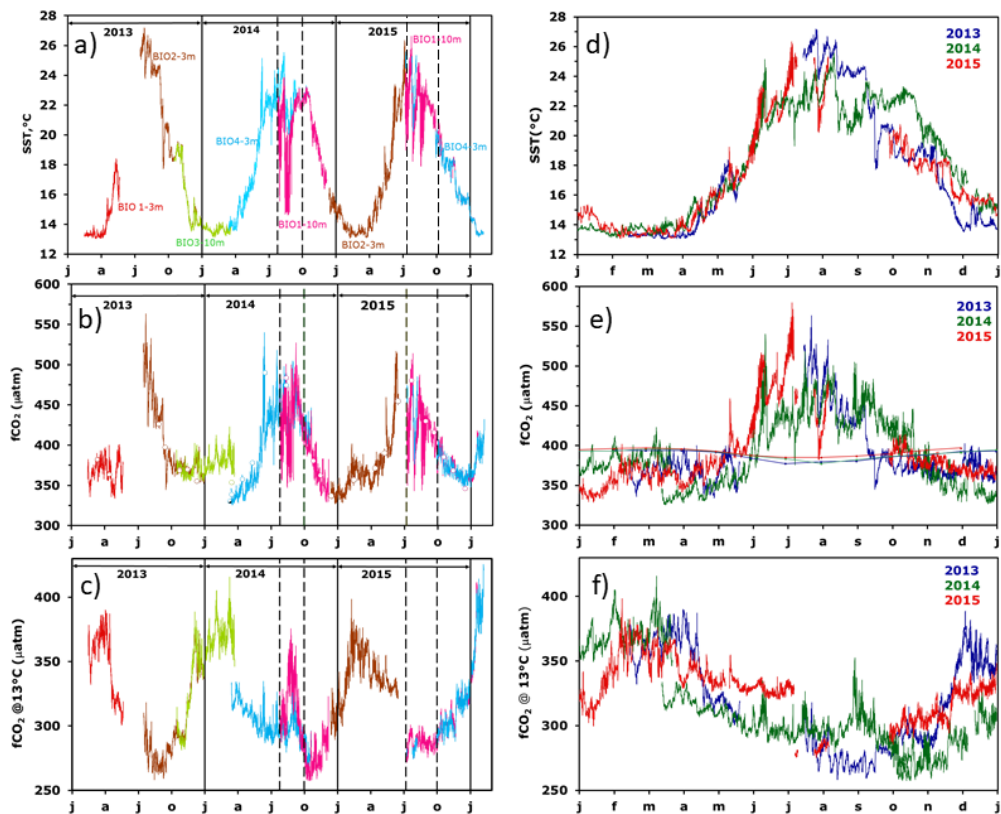


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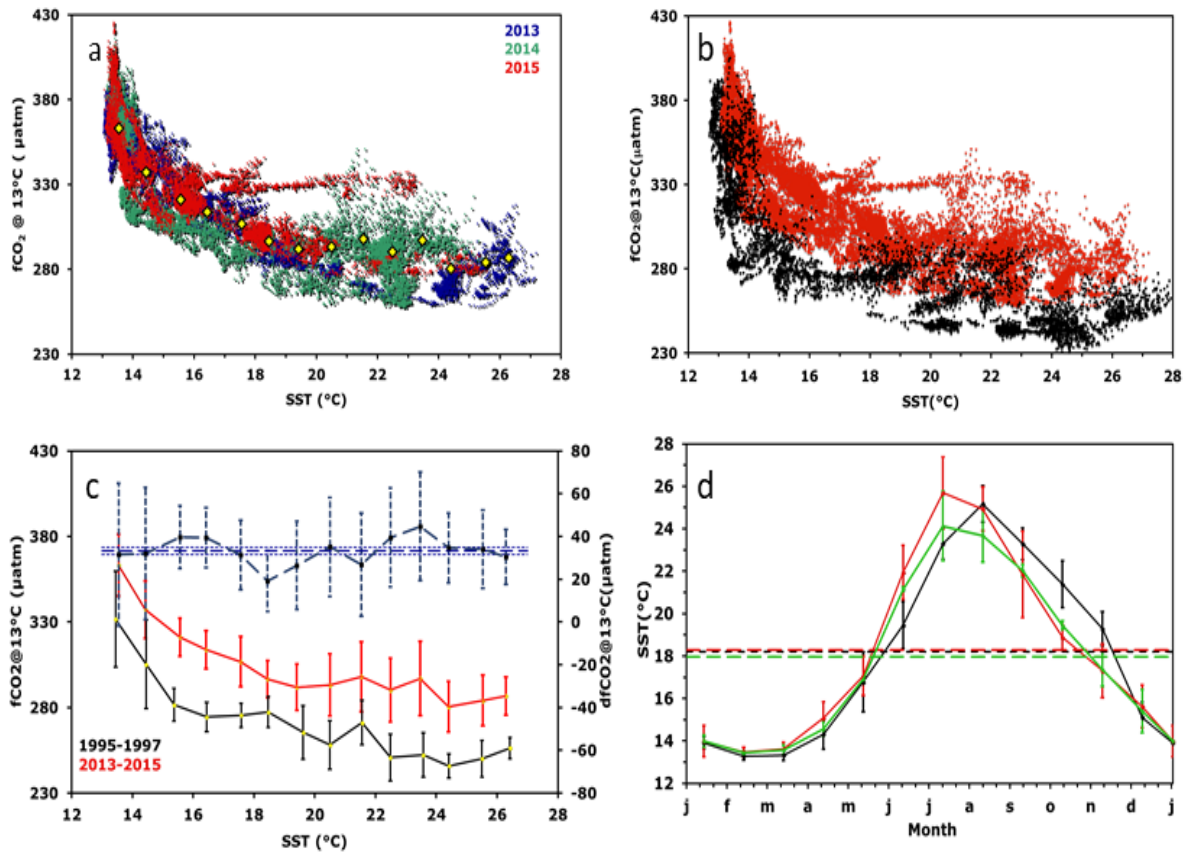
Fig.2. Interannual variability of CARIOCA data on the BOUSSOLE mooring: left column, as a function of time, right column as a function of months for a given year (blue, 2013, green, 2014, red, 2015). (a, d) T, (b, e),  $f\text{CO}_2$ , (c, f)  $f\text{CO}_2@13^\circ\text{C}$ . On a, b, c, the dotted lines indicate the period affected by stratification and internal waves (July, 26<sup>th</sup> to October 1<sup>st</sup>, 2014 and July, 8<sup>th</sup> to October 1<sup>st</sup>, 2015). On 2(b), the open circles correspond to  $f\text{CO}_2$  data derived from DIC and alkalinity measurements of samples taken at 5 and 10 m. On 2(e), the thin lines indicate  $f\text{CO}_{2\text{atm}}$ . Note that the color code on (d), (e), (f) is different from (a), (b), (c).



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Fig.3. (a)  $f\text{CO}_2@13$  as a function of temperature for hourly data in 2013, 2014 and 2015. The yellow dots indicate mean  $f\text{CO}_2@13$ . (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  $1^\circ\text{C}$  interval (standard deviation as dotted line). The difference between the two periods is also displayed (dashed blue curve, scale on the right axis; the mean difference over all SST is represented by the horizontal blue line). (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.



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