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

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Abstract

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

the last 18 years represents ~30% of the total change of anthropogenic carbon since the beginning of the industrial period.

1 Introduction

The concentration of atmospheric carbon dioxide (CO_2) has been increasing rapidly over the 20th century and, as a result, the concentration of dissolved inorganic carbon (DIC) in the near surface ocean increases, which drives a decrease in pH in order to maintain a chemical equilibrium [*Millero*, 2007]. These changes have complex direct and indirect impacts on marine organisms and ecosystems [*Gattuso and Hansson*, 2011]. Empirical methods to estimate the anthropogenic CO_2 penetration in the ocean since the industrial revolution have improved over the past few decades [*Chen and Millero*, 1979; *Gruber et al.*, 1996]; [*Sabine et al.*, 2008]; [*Touratier and Goyet*, 2004; 2009; *Woosley et al.*, 2016]. As the concentration of anthropogenic carbon, C_{ant}, cannot be distinguished from the natural background of DIC through total DIC measurements, these methods are based on the analysis of different chemical properties of the water column. Direct estimates of the anthropogenic CO_2 absorption in the sea surface layers are difficult owing to the large natural variability driven by physical and biological phenomena. [*Bates et al.*, 2014] have extracted the trend from the large variability, based on analysis of a long time series (monthly or seasonal sampling). For the global surface ocean, **[***Lauvset et al.*, 2015] have used the Surface Ocean CO_2 Atlas (SOCAT) database [*Bakker et al.*, 2014] combined with an interpolation method. Constraints on the Mediterranean Sea's storage of anthropogenic CO_2 are limited, as the data based approaches disagree by more than a factor of two [*Huertas et al.*, 2009; *Touratier and Goyet*, 2009]. In addition to the anthropogenic signal, oceanic DIC can also be the signature of a strong interannual variability. In the North Atlantic, for instance it has been shown that because of decadal variability it requires 25 years for the long-term trend to emerge [*McKinley et al.*, 2011][*McKinley et al.*, 2011][*McKinley et al.*, 2011][*McKinley et al.*, 2011]**.**

A high frequency sampling of the seawater carbon chemistry at the air-water interface over extended periods of time is a way to detect a possible trend in DIC. In this paper we analyze two three-year time series of hourly fugacity of CO_2, fCO_2, measured with autonomous CARIOCA sensors [*Copin-Montégut et al.*, 2004; *Merlivat and Brault*, 1995] in 1995-1997 and 2013-2015, at two very close locations in the northwestern Mediterranean Sea (Fig. 1). Using measured fCO_2, temperature (T) and salinity (S), we derive the other variables of the

carbonate system (pH and DIC). The experimental setting is first described, and the recent data obtained over the 2013-2015 period are presented. Combined with the 1995-1997 measurements previously published [*Hood and Merlivat*, 2001], we estimate the decrease of pH and the increase of DIC. The results are discussed with respect to the contributions of the exchange with atmospheric CO_2, to the possible impact of vertical mixing and to recent estimates of the transport of anthropogenic carbon from the Atlantic Ocean over a 18 years period.

2 Material and methods

2.1-The BOUSSOLE and DYFAMED sites

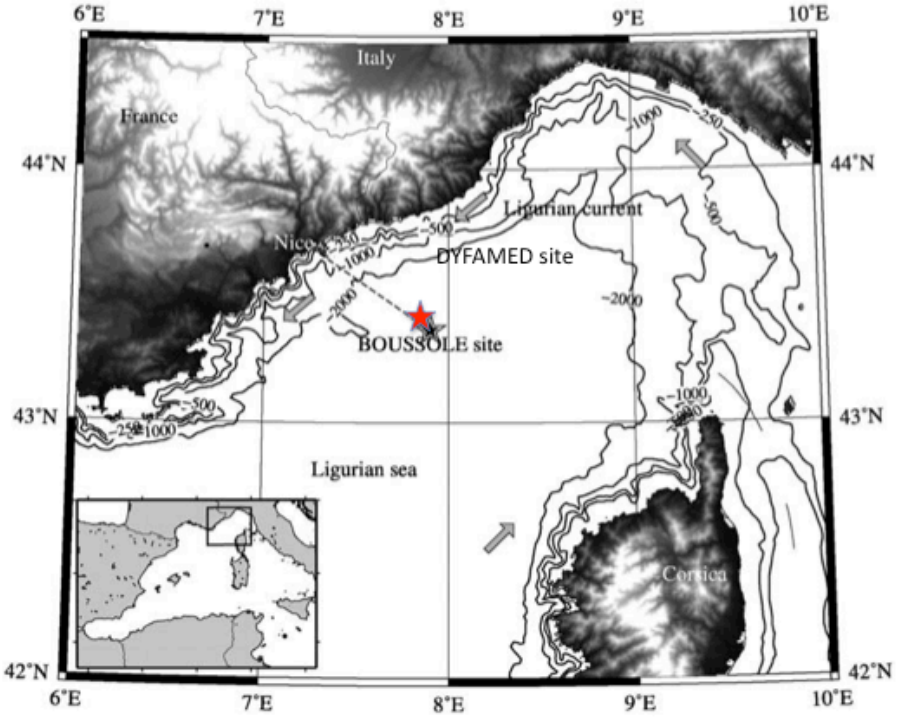

Fig. 1. The area of the northwestern Mediterranean Sea showing the southern coast of France, the island of Corsica, the main current branches (gray arrows), and the location of the DYFAMED site (red star) and the BOUSSOLE buoy (black star) in the Ligurian Sea.

Data collection was carried out at the BOUSSOLE site (43°22'N, 7°54'E) in 2013-2015 [*Antoine et al.*, 2008; *Antoine. and others*, 2006] and at the DYFAMED site (43°25'N, 7°52'E) in 1995-1997 [*Marty et al.*, 2002]. These sites are 3 nautical miles apart, both located in the Ligurian Sea, one of the basins of the northwestern Mediterranean Sea (Fig.1). The water depth is of ~2400 m. The prevailing ocean currents are usually weak (<20 cm s^{-1}), because these sites are in the central area of the cyclonic circulation that characterizes the Ligurian Sea. The two sites surrounded by the permanent geostrophic Ligurian frontal jet

82 flow are protected from coastal inputs [*Antoine et al.*, 2008; *Heimbürger et al.*, 2013; *Millot*,
83 1999]. Monthly cruises are carried out at the same location .
84
85 **2.2**- Analytical methods
86 At DYFAMED, fCO_2 measurements at 2 m depth were provided by an anchored floating
87 buoy fitted with a CARIOCA sensor. At BOUSSOLE, measurements were carried out from a
88 mooring normally dedicated to radiometry and optical measurements, and onto which two
89 CARIOCA sensors were installed. Both monitored fCO_2 hourly at 3 and 10 meters depth
90 (although only one of the two depths was equipped with a functional sensor at some periods);
91 S and T were monitored at the same two depths using a Seabird SBE 37-SM MicroCat
92 instrument. The CARIOCA sensors were adapted to work under pressure in the water column.
93 They were swapped about every 6 months, with serviced and calibrated instruments replacing
94 those having been previously deployed. The accuracy of CARIOCA fCO_2 measurements
95 using the spectrophotometric method with thymol blue is estimated at 2 µatm during both
96 periods. [*Hood and Merlivat*, 2001] have reported agreement between fCO_2 measured by
97 CARIOCA buoys, similar to the one deployed at DYFAMED, with ship based measurements,
98 during a number of field programs, with an accuracy of 2 µatm and a precision of 5 µatm .
99 At Boussole, newly designed fCO_2 sensors have been calibrated using in situ seawater
100 samples taken at 5 and 10 meters depth during the monthly servicing cruises to the mooring.
101 The samples were analyzed using potentiometric titration from the method developed by
102 [*Edmond*, 1970] with a closed cell, and provides measurements of DIC, and total alkalinity,
103 Alk. For calibration, Certified Reference Materials (CRMs) provided by Prof. A. Dickson
104 (Scripps Institution of Oceanography, San Diego, USA) were used. The accuracy is estimated
105 at 3 µmol kg^{-1} for both DIC and Alk. fCO_2 is calculated using the dissociation constants of
106 Mehrbach refitted by Dickson and Millero [*Dickson and Millero*, 1987; *Mehrbach et al.*,
107 1973]. Error on fCO_2 derived from an individual sample is expected to be on the order of 5
108 µatm [*Millero*, 2007]. About 8 samples have been used to calibrate each CARIOCA sensor so
109 that the error on the absolute calibration of each fCO_2 CARIOCA sensor, is estimated at 1.8
110 µatm. In addition, we observe that the standard deviation of the difference between the
111 CARIOCA fCO_2 and fCO_2 computed with the monthly discrete samples (Fig. 2b) is equal to
112 4.4 µatm, consistent with the expected precision on CARIOCA fCO_2 of 5 µatm. Alk and S of
113 the 56 samples taken at BOUSSOLE are linearly correlated according the following
114 relationship :
115 $$Alk\ (\mu mol\ kg^{-1}) = 87.647\ S - 785.5 \qquad (1)$$

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

3 Results

3.1 The BOUSSOLE mooring (2013-2015) time series

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

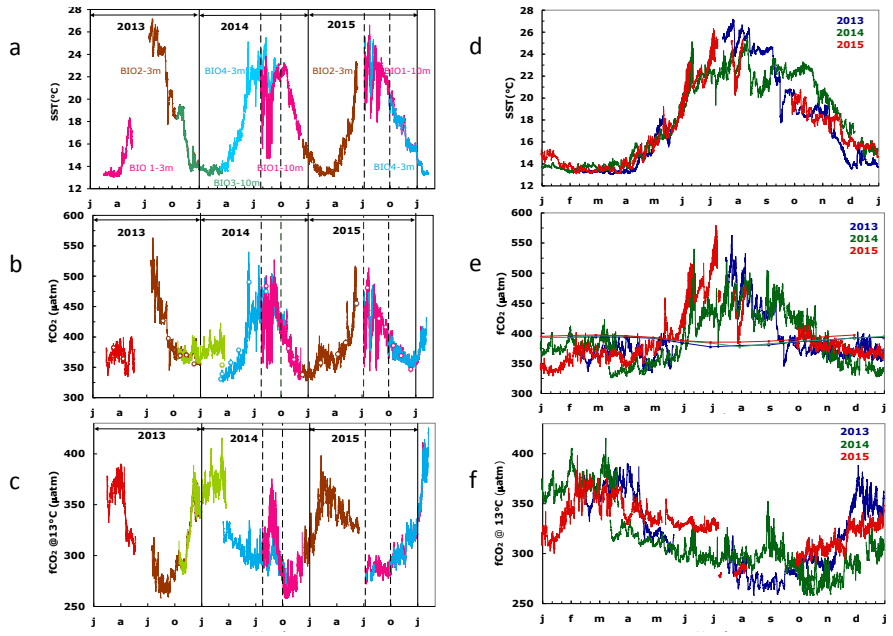

Fig.2. Interannual variability of CARIOCA data: a) T, b) fCO_2, c) fCO_2@13 The dotted lines indicate the period affected by stratification and internal waves (July, 26 th to October 1st, 2014 and July, 8 th to October 1st, 2015). On 2(b), the open circles correspond to fCO2 data derived from DIC and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

The range of temperature (Fig. 2a) extends from 13°C in winter up to 27°C in summer, followed by progressive cooling in fall. The coldest temperature, 13°C, results from the winter vertical mixing with the deeper Levantine Intermediate Water, LIW, marked by extrema in temperature and salinity [*Copin-Montegut and Begovic*, 2002]. Temperature provides the main control of the seasonality of fCO_2, from 350 µatm to more than 550 µatm in summer 2013 (Fig. 2b). The fugacity of CO_2 in seawater is a function of temperature, DIC, alkalinity, salinity and dissolved nutrients. In the oligotrophic surface waters of the Mediterranean sea, this last effect should be negligible. Temperature and DIC have the strongest influences. By normalizing fCO_2 to a constant temperature, the thermodynamic

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 mmol 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 fCO2 increases when T increases. Another cause of inter-annual variability of fCO_2 for T~14°C is the timing of the spring increase of biological activity which differs by a month between years; for instance, it happened at the beginning of April in 2013, T~15-16°C and by mid March in 2014, T~14°C. Another cause is the deepening of the mixed layer due to the fall cooling which varies by a month between years.

3.2 Decadal changes of hydrography

3.2.1 Sea surface temperature changes

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

3.2.2 Sea surface salinity changes

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

3.3 Decadal changes of fCO_2@13

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

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

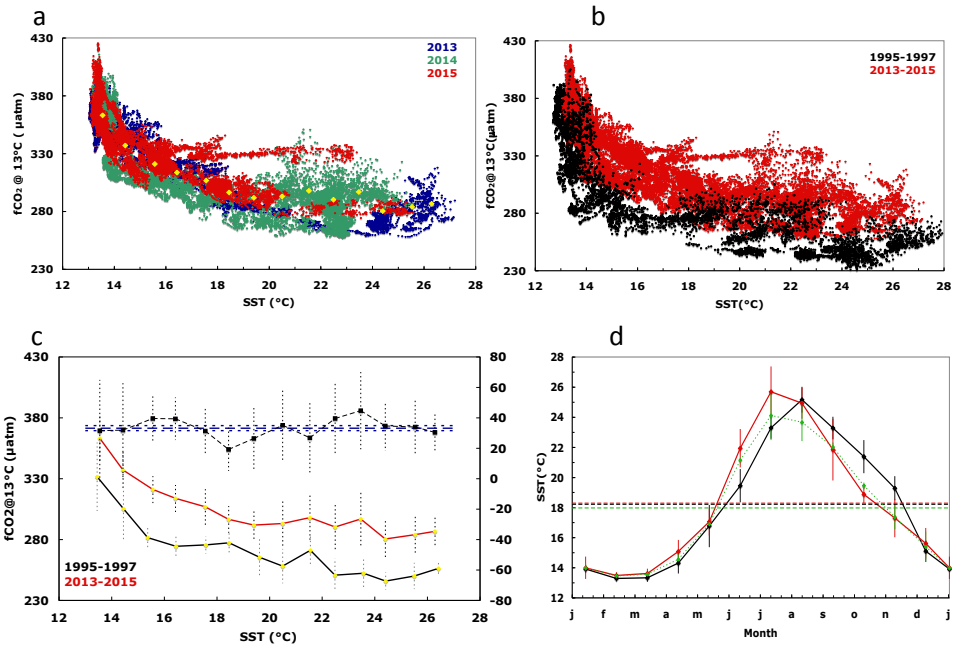

Fig.3. (a) fCO_2@13°C as a function of temperature for hourly data in 2013, 2014 and 2015.The yellow dots indicate mean fCO_2@13°C (b) as in (a) but for all hourly data in 1995-1997 (black) and in 2013-2015 (red) (c) As in (b), but for average values per 1°C interval (standard deviation as dotted line).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

219 temperature interval represent about 25% of the total number of data for both periods. For
220 each of the fourteen 1°C step, the mean and standard deviation of hourly $fCO_2@13$
221 measurements are reported in Table 1 and on Fig. 3c.
222

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

223
224 Table 1:
225 Distribution of temperature, fCO2@13, and increase dfCO2@13 data binned by 1°C
226 temperature interval for the 2 periods 1995-1997 and 2013-2015 .
227 The mean temperature within each 1° step differ for the two periods as the distribution of
228 individual measurements are not identical.
229 For both data sets, a monotonic relationship between $fCO_2@13$ and T is observed with
230 correlation coefficients respectively equal to -0.861 and -0.857. The difference in fCO2@13
231 between the two periods, dfCO2@13, is derived in each temperature step, as the difference

between column 2 and 6 of Table 1. The variability of this difference is estimated as the quadratic mean of the standard deviation in each time series. Both values are reported in Table 1, column 9 and 10, and on Fig. 3c.

It is interesting to note that the distribution of values around the mean seems random and indicates no trend dependency with SST (Fig. 3c). This suggests that the processes which control the seasonal variation of fCO_2@13 at the sea surface have not changed over the last two decades. The mean weighted value of dfCO2@13 over the whole range of temperature is estimated as the mean of dfCO2@13 in each temperature step weighted by the variance. It is equal to 32.7µatm. We estimate the accuracy on this value as follows. For each time interval, the mean fCO2@13 per temperature step has been derived from at least three independent CARIOCA sensors. Given that the accuracy on fCO_2 from each CARIOCA sensor is estimated at 2 µatm and that the calibrations of the three sensors are independent, the accuracy on fCO_2 averaged in each time interval is $2/\sqrt{3}=1.15$ 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 uniyr^{-1}) (Table 2).

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

257 Table 2

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

260 T,mean annual temperature equal to 18.25°C

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

262 **, $dDIC_{ant}$

263

264 **3.5** Changes in atmospheric and seawater fCO_2

265 The increase of atmospheric fCO_2 from 1995-1997 to 2013-2015 was computed from the
266 monthly atmospheric xCO_2 concentrations measured at the Lampedusa Island station (Italy)
267 (35°31'N, 12°37'E) (http://ds.data.jma.go.jp/gmd/wdcgg/) (see equation 3 in [*Hood and*
268 *Merlivat*, 2001]). Considering a mean annual in situ temperature equal to 18.25°C and an
269 atmospheric pressure equal to 1 atm, we derived a mean atmospheric fCO_2 equal to 355.3+/-
270 0.8 µatm and 389.6+/-0.9 µatm for 1995-1997 and 2013-2015, that is an increase equal to
271 34.3+/-1.2 µatm (Table 2). At this temperature, the change of fCO_2 at the sea surface is equal
272 to 40.8+/-2.0 µatm. Thus the contribution of the increase in atmospheric CO_2 is responsible
273 for 84+/-5 % of the increase of fCO_2 measured in the surface waters. Assuming the same
274 salinity and alkalinity as previously, the corresponding amount of anthropogenic carbon taken
275 up from the atmosphere in order to maintain a chemical equilibrium at the sea surface would
276 be equal to 20.8+/- 0.8 µmol kg^{-1} (Table 2).

277

278 **4 Discussion**

279 **4.1** fCO_2 at the air-sea interface

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

290 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, dDIC=+0.46 µmol $kg^{-1}yr^{-1}$ and dpH=-0.0001 pH unit yr^{-1}. Such a change in alkalinity does not significantly affect the decrease of pH shown in Table 2.

4.3 Anthropogenic carbon storage in surface waters

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

MLD time series show a strong variability in winter at interannual scale. During the two periods, 1995-1997 and 2013-2015, the winter MLD never exceeded 220 m, whereas values over 300 m were observed in 1999 and especially in February and March 2006 with values close to 2000 m [*Coppola et al.*, 2016; *Pasqueron de Fommervault et al.*, 2015]. These episodes of strong and deep vertical mixing must have entrained DIC rich LIW in the surface waters. This could be a cause for the observed increase of DIC measured between the two periods 1995 -1997 and 2013-2015.

As a result of a monitoring program in the Strait of Gibraltar, [*Huertas et al.*, 2009] calculated a net flux of C_{ant} from the Atlantic towards the Mediterranean basin. [*Schneider et al.*, 2010], using the transit time distribution method applied to a dataset from a cruise in the Mediterranean Sea in 2001, estimated that the input of C_{ant} through the Strait of Gibraltar from 1850 to 2001 accounts for almost 10% of the total C_{ant} inventory of the Mediterranean Sea, which means that ~90% must have been taken up directly from the atmosphere. Based on a high-resolution regional model, [*Palmiéri et al.*, 2015] computed the anthropogenic carbon storage in the Mediterranean basin. They concluded that 75% of the total storage of C_{ant} in the whole basin comes from the atmosphere and 25% from net transport from the Atlantic across the Strait of Gibraltar. The findings of these two studies support the conclusion that computed change of DIC in excess of 16+/-5% over the direct contribution of air-sea exchange could result from the anthropogenic carbon input from the Atlantic Ocean towards the Mediterranean basin. [*Huertas et al.*, 2009] and [*Schneider et al.*, 2010] report DIC_{ant} surface concentrations respectively equal to 65-70 µmol kg^{-1} at the strait of Gibraltar in the years 2005-2007 and close to 65 µmol kg^{-1} in the western basin in 2001. We extrapolate these figures to the year 2014, assuming a mean increase rate of DIC equal to 1.38 µmol $kg^{-1}yr^{-1}$ as previously computed (Table 2). Taking into account the increase of DIC_{ant} equal to 24.8 µmol kg^{-1} between 1995-1997 and 2013-2015, we would estimate that the contribution of the change of DIC_{ant} over the last 18 years represents ~30% of the total change since the beginning of the industrial period (t>~1800).

4.4 The signal of acidification

The annual decrease of pH_T calculated between 1995-1997 and 2013-2015 is equal to -0.0022+/-0.0001. At the DYFAMED site, at 10 m depth, [*Marcellin Yao et al.*, 2016] studied the time variability of pH over 1995-2011, based on measurements of T, S, Alk and DIC sampled approximately once a month. They computed a mean annual decrease of -0.003 ± 0.001 pH units on the seawater scale that is not significantly different from our estimate.

[*Bates et al.*, 2014] examined changes in surface seawater CO_2-carbonate chemistry at the locations of seven ocean CO_2 time series that have been gathering sustained observations from 15 to 30 years with monthly or seasonal sampling. The range of decreasing trends of pH extends from -0.0026+/-0.0006 unit yr^{-1} at the Irminger Sea time series site to -0.0014+/-0.0005 unit yr^{-1} at the Iceland Sea time series. For the global surface ocean, [*Lauvset et al.*, 2015] have reported a mean rate of decrease of -0.0018+/-0.0004 for 1991-2011.The decrease of pH computed here at DYFAMED is in the upper range of values compared to other time series. The Mediterranean Sea is actually able to absorb more anthropogenic CO_2 per unit area, first because of its higher total alkalinity that leads to a greater chemical capacity to take up anthropogenic CO_2 and, second, because deep waters are ventilated on relatively short timescales (30-40 years in the western basin), which allows deeper penetration of anthropogenic tracers [*Schneider et al.*, 2010], [*Palmiéri et al.*, 2015]. The lowering effect of high alkalinity on the Revelle factor, close to ten, implies a relatively high uptake capacity for anthropogenic carbon, $C_{ant.}$.

5 Conclusion

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

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

Acknowledgments

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

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Figure caption and tables

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

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

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

Table 1:

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

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

Table 2

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

T,mean annual temperature equal to 18.25°C

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

**, $dDIC_{ant}$