Hourly to decadal variability of sea surface carbon parameters in the north western Mediterranean Sea

J. Boutin, L. Merlivat, D. Antoine
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 (black star) and the BOUSSOLE buoy (red star) in the Ligurian Sea.
Goal of the study

• \( \text{pCO}_2 \) at 2 depths during 3 years (2013-2015):
  – Strong vertical variability between 3m & 10m depth during summer => Importance of measuring \( \text{pCO}_2 \) close to the surface ocean in stratified conditions
  – Comparison with measurements taken 18 years ago at DYFAMED site by CARIOCA sensors => for the first time estimate decadal variability from 2 mutiyear time series of hourly \( \text{pCO}_2 \) measurements
Outline

• Data and method
• High frequency variability during summer 2014
CARIOCA/BIOCAREX sensor

Membrane semipermeable to gas - Spectrophotometer (3 λ)
See description of measurement principle in (Copin-Montegut et al., Mar. Chem. 2004)

⇒ Hourly measurements of CO₂ partial pressure, pCO₂ + CTD: salinity and temperature

⇒ pCO₂ at constant temperature (13°C) using Takahashi’s relationship (4.23% °C⁻¹)

⇒ Total alkalinity from S (using a relationship derived from monthly surface samples):
  \[ TA = 87.664 \, S - 786.5 \quad \sigma = 4.1 \, \text{μmol kg}^{-1} \]

⇒ Dissolved Inorganic Carbon (DIC) and pH using CO₂ dissociation constants of Mehrbach et al. (1973) as refitted by Dickson and Millero (1987) and solubility from Weiss (1974).
Boussole mooring equipped with 2 CARIOCA/BIOCAREX pCO2 sensors

- BOUSSOLE ‘Bouée pour acquisition d'une série optique à long terme’ (2005)

- ANR BIOCAREX ('BIOoptics and CARbon Experiment'): add 2 miniaturized CARIOCA pCO2 sensors at 3m and 10m depth (2012) to complement optical radiometer measurements
Main driver of pCO$_2$ variability = seasonal variability of temperature

$\sigma (pCO_2 - pCO_2 (DIC, TA)) \sim 4.4 \mu$atm
(NB uncertainty $pCO_2(DIC,TA) \sim 5\mu$atm)
Mixing in Winter and Biological productivity in Spring - Summer
Strong variability in Summer 2014
Strong stratification between 3m and 9m depth during Summer 2014
Spectral analysis
Summer 2014

3m: inertial waves dominates hourly variability of pCO$_2$ although diurnal cycle on T

10m: both T and pCO$_2$ variability dominated by inertial waves

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Spectre de la Température

Spectre du pCO2
Wavelet analysis

3m
Spectre de puissance en ondelette de la température

10m
Spectre de puissance en ondelette de la température

Spectre de puissance en ondelette du pCO2

Spectre de puissance en ondelette du pCO2
Variability between 1995-1997 and 2013-2015 periods

CARIOCA sensor at 2m depth on DYFAMED mooring (Hood and Merlivat 2001)
Figure 4. (a) $f$CO$_2$ data from all three years; 1995 = dark triangles, 1996 = medium gray squares, and 1997 = light gray diamonds. (b) Temperature-normalized $f$CO$_2$ data from all three years; symbols are the same as for (a). (c) Sea-surface temperature data from all three years.

(in the following we remove the 10m depth measurements during summer)
pCO$_2$ at 13° C as a function of temperature

1995-1997

2013-2015
pCO$_2$ at 13° C as a function of temperature

1995-1997

2013-2015

Decadal variability computed with the whole data set or with data >18°C (to avoid large variability in winter)
Assuming that the surface ocean follows the CO$_2$ increase in the atmosphere (+35µatm at Lampedusa station) the surface ocean DIC should have increased by ~1.2 µmol kg$^{-1}$ yr$^{-1}$. This explains only 72% of the DIC increase we observe supporting the hypothesis of another source of anthropogenic carbon entering in the Mediterranean sea like Atlantic waters through the Gibraltar straight (Palmieri et al. 2015, Schneider et al 2010, Huertas et al., 2009)

<table>
<thead>
<tr>
<th>All temperature</th>
<th>T&gt;18°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>sea surface mixed layer</td>
<td>1.63</td>
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</table>

### Table 1

<table>
<thead>
<tr>
<th>Year</th>
<th>fCO$_2$ at 13°C µatm</th>
<th>σ µatm</th>
<th>N number of data</th>
<th>confidence interval, µatm (&gt;99.7%) 3σ/√N</th>
<th>d fCO$_2$ at 13°C µatm</th>
<th>DIC µmolkg$^{-1}$</th>
<th>pH at13°C</th>
<th>d DIC µmolkg$^{-1}$</th>
<th>dpH unit</th>
<th>d DIC annual µmolkg$^{-1}$yr$^{-1}$</th>
<th>d pH annual pH unit yr$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1995-1997</td>
<td>282.2</td>
<td>38.8</td>
<td>6450</td>
<td>1.45</td>
<td>2229.7</td>
<td>N=3</td>
<td>σ=0.96</td>
<td>8.1945</td>
<td>N=3</td>
<td>σ=0.0015</td>
<td></td>
</tr>
<tr>
<td>2013-2015</td>
<td>321.7</td>
<td>33.2</td>
<td>27852</td>
<td>0.60</td>
<td>39.5+/1.57</td>
<td>2259.1</td>
<td>N=3</td>
<td>σ=0.33</td>
<td>29.4+/1.8</td>
<td>-0.468+/-.0027</td>
<td>1.63+/-.010</td>
</tr>
<tr>
<td>1995-1997</td>
<td>256.9</td>
<td>15.1</td>
<td>3617</td>
<td>0.75</td>
<td>2208.0</td>
<td>N=3</td>
<td>σ=0.56</td>
<td>8.2276</td>
<td>N=3</td>
<td>σ=0.0008</td>
<td>1.53+/-.06</td>
</tr>
<tr>
<td>2013-2015</td>
<td>289.6</td>
<td>13.9</td>
<td>10184</td>
<td>0.41</td>
<td>32.7+/0.86</td>
<td>2235.6</td>
<td>N=3</td>
<td>σ=0.26</td>
<td>27.6+/1.1</td>
<td>-0.0423+/-.0015</td>
<td>-0.0024+/-.0001</td>
</tr>
</tbody>
</table>

(1), Larger range of variability when including winter data
Summary

-During Summer, western mediterranean sea is very stratified => importance of:
   - measuring pCO$_2$ as close as possible to the surface, otherwise strong impact of inertial waves
   - monitor high frequency variations (high influence of wind)

- With respect to measurements performed 18 years ago, DIC in surface ocean increases by 25% more than expected from atmospheric CO$_2$ increase: for the first time, surface ocean measurements support the hypothesis of another source of anthropogenic carbon than the atmosphere in the Mediterranean Sea (Palmieri et al. 2015, Schneider et al 2010, Huertas et al. 2009 suggest that anthropogenic carbon from the Atlantic Ocean enters in the Mediterranean Sea through the Gibraltar straight)

⇒ Importance of long term monitoring of high frequency variability of pCO$_2$