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

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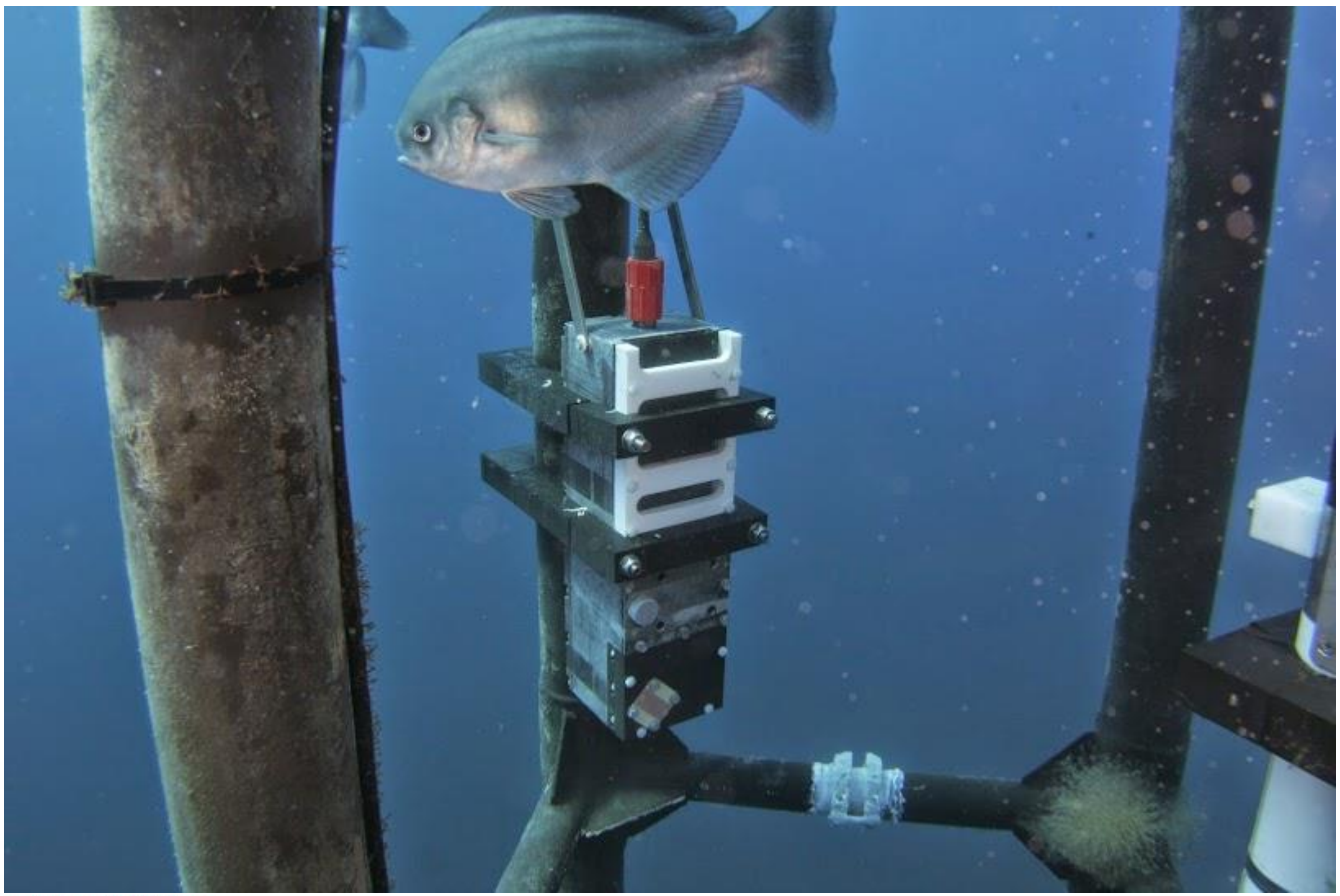


# Location of the experiment: Boussole

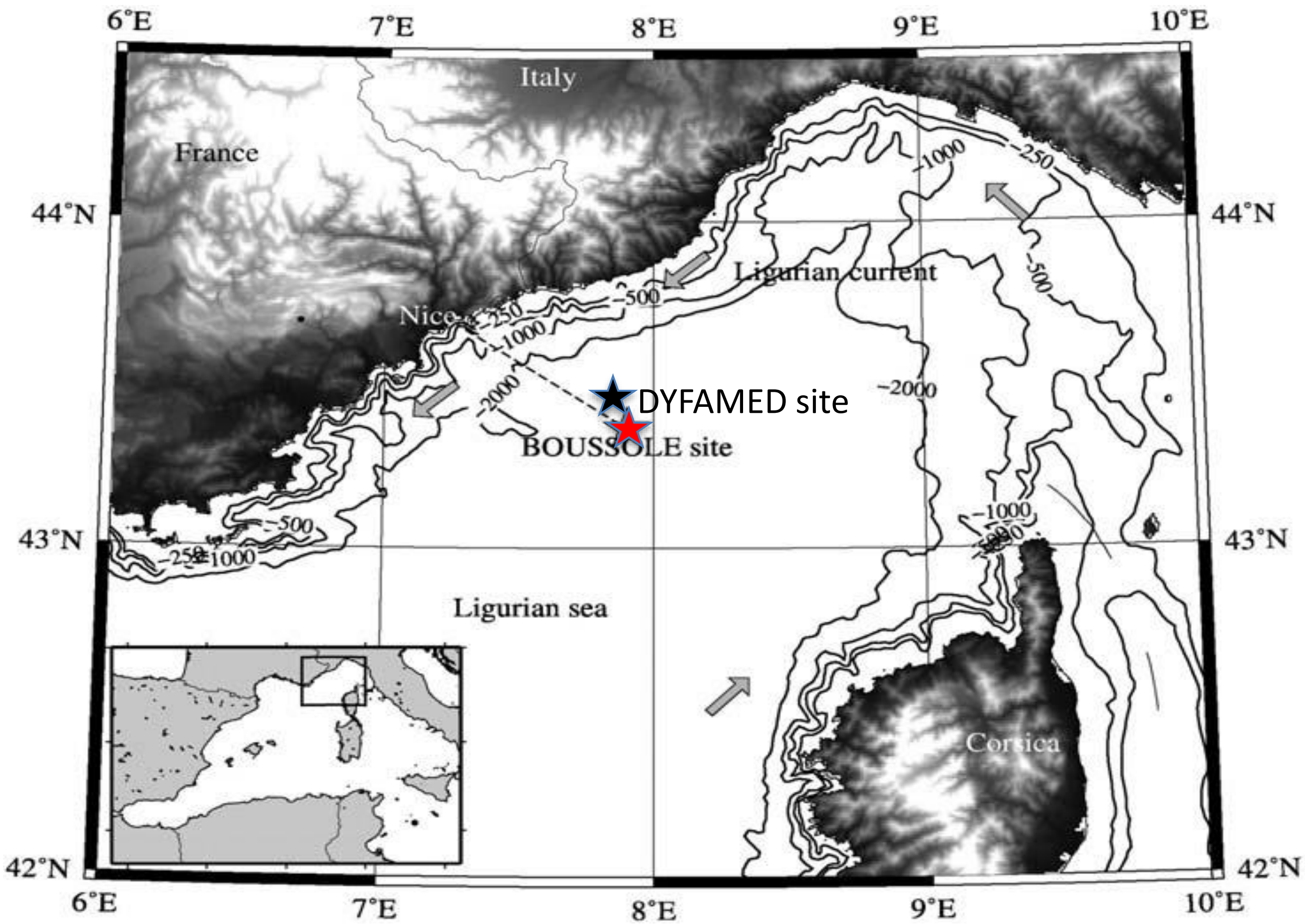



Fig. 1. The area of the northwestern Mediterranean Sea showing the southern coast of France, the island of Corsica, the main current branches (gray arrows), and the location of the DYFAMED site (black star) and the BOUSSOLE buoy (red star) in the Ligurian Sea.

# Goal of the study

- $pCO_2$ at 2 depths during 3 years (2013-2015):
  - Strong vertical variability between 3m & 10m depth during summer => Importance of measuring $pCO_2$ 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 $pCO_2$ measurements

# Outline

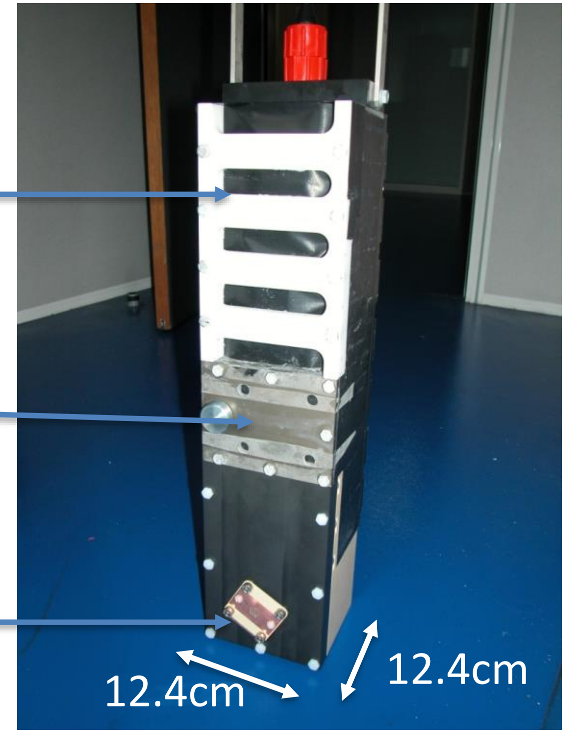
- Data and method
- High frequency variability during summer 2014
- Decadal variability (1995-1997 versus 2013-2015)

# CARIOCA/BIOCAREX sensor

Dye enveloppe

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

Water intake




41cm

⇒ Hourly measurements of $CO_2$ partial pressure, $pCO_2$ + CTD : salinity and temperature

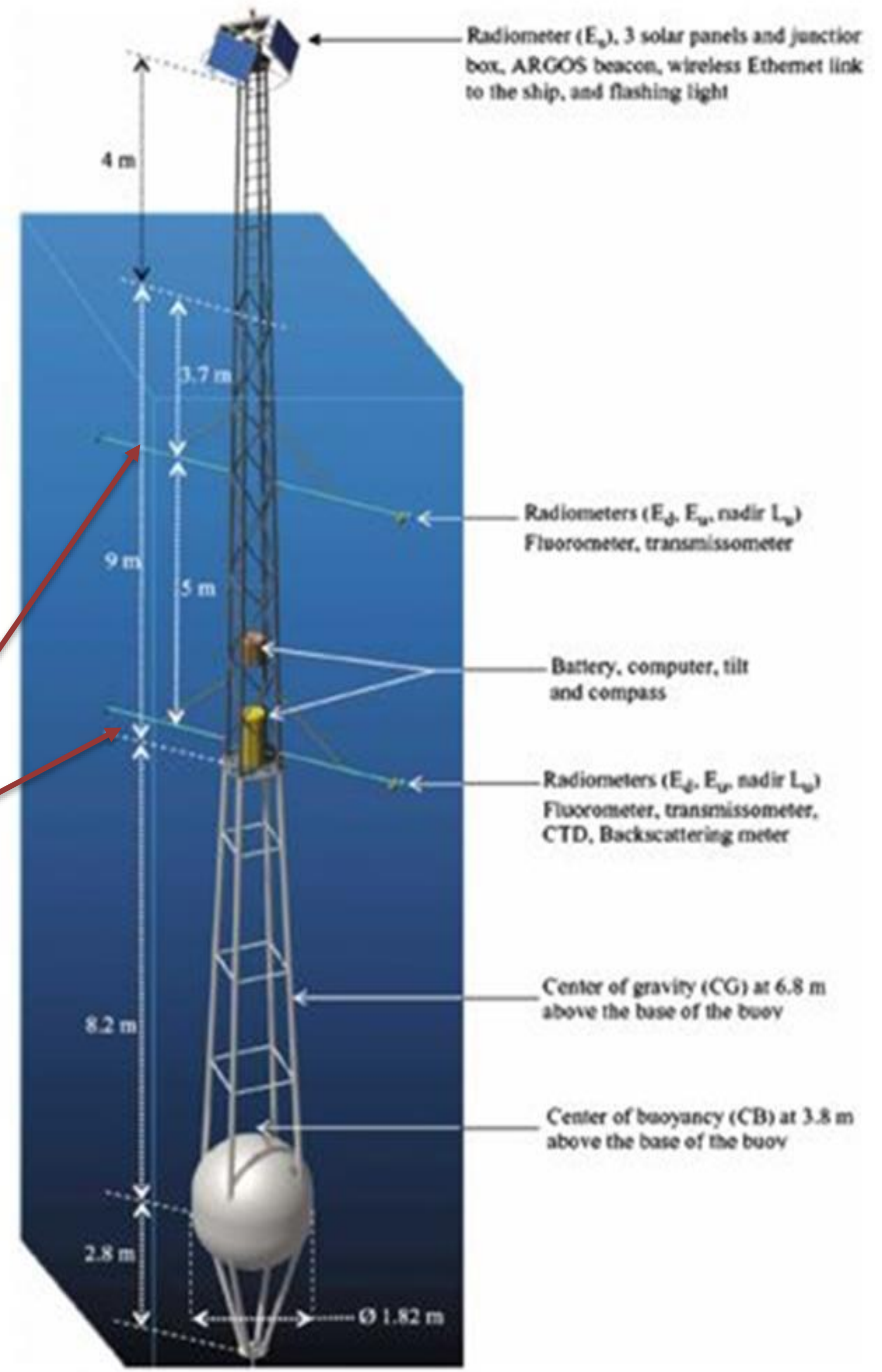
⇒ $pCO_2$ at constant temperature (13°C) using Takahashi's relationship (4.23% $°C^{-1}$)

⇒ Total alkalinity from S (using a relationship derived from monthly surface samples):
TA= 87.664 S – 786.5 $\sigma$=4.1 $\mu$mol $kg^{-1}$

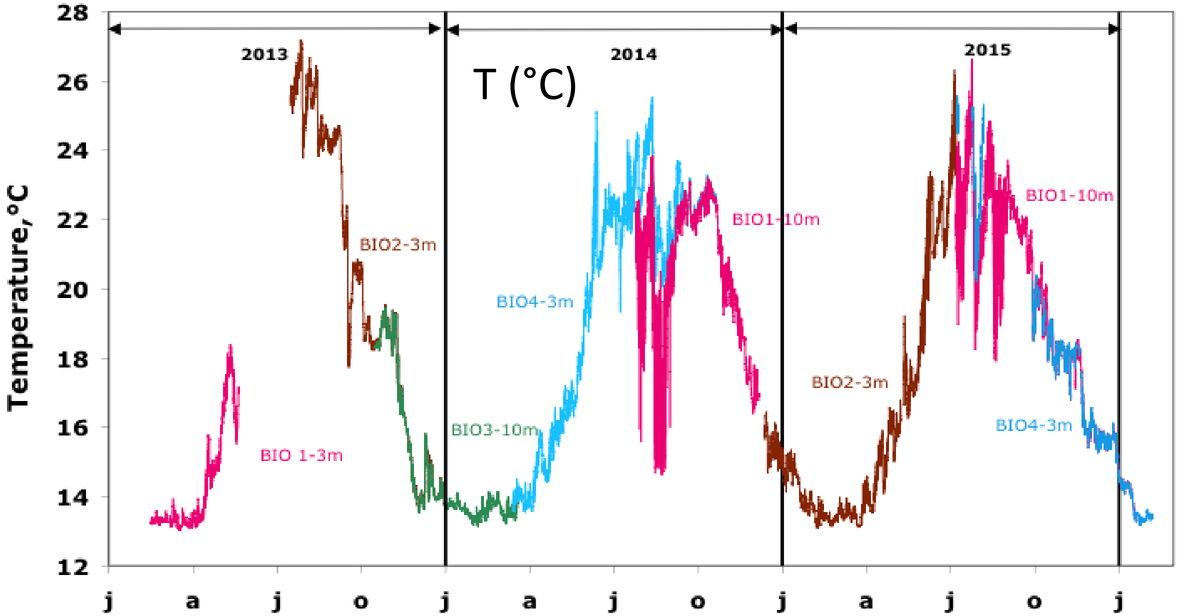
⇒ Dissolved Inorganic Carbon (DIC) and pH using $CO_2$ dissociation constants of Mehrbach et al. (1973) as refitted by Dickson and Millero (1987) and solubility from Weiss (1974).

# Boussole mooring equipped with 2 CARIOCA/BIOCAREX pCO2 sensors

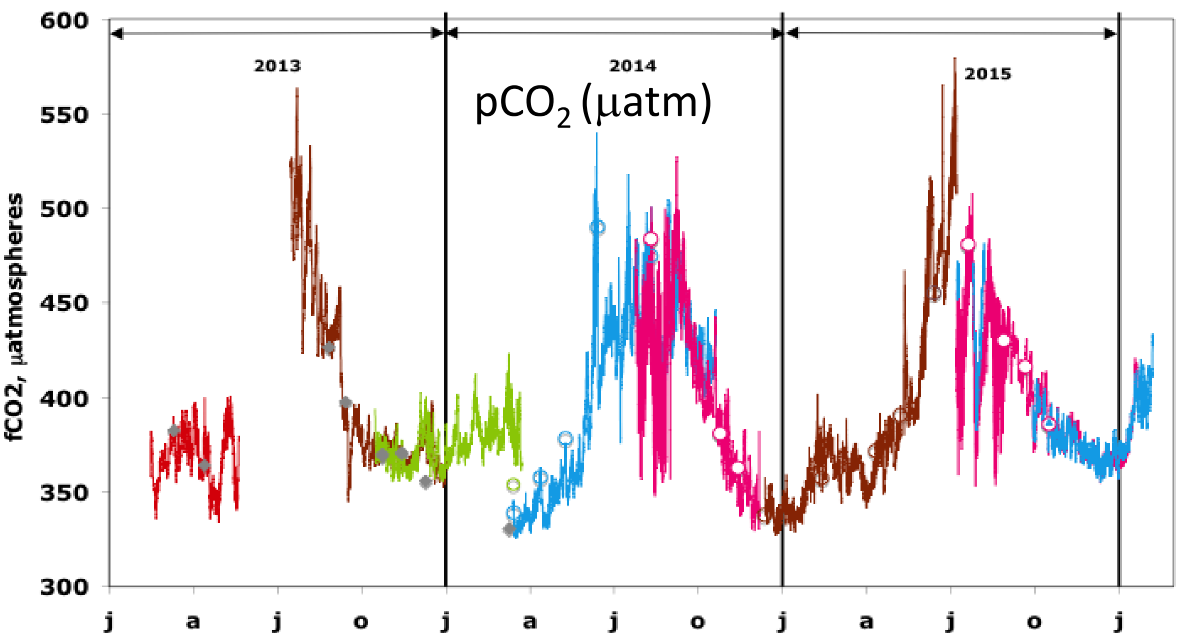
- BOUSSOLE *'Bouée pour acquisition d'une série optique à long terme'* (2005)
- ANR BI0CAREX (*'BIOoptics and CARbon Experiment'*): add 2 miniaturized CARIOCA $pCO_2$ sensors at 3m and 10m depth (2012) to complement optical radiometer measurements



# 2013-2015 time series



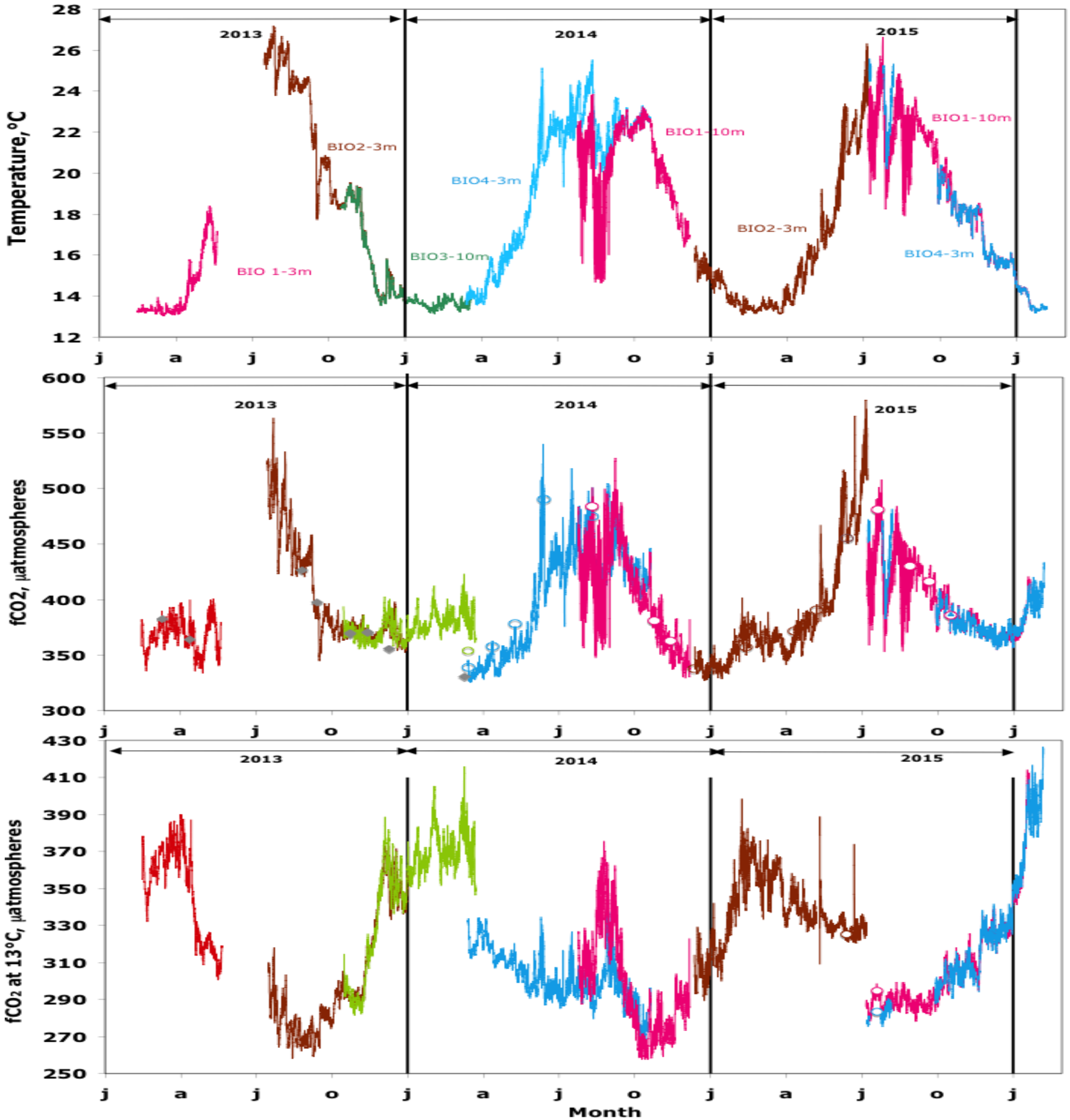

Main driver of $pCO_2$ variability = seasonal variability of temperature




o= $pCO_2$ (DIC, TA)

σ ($pCO_2$ – $pCO_2$ (DIC, TA))~ 4.4 µatm

(NB uncertainty $pCO_2$(DIC,TA) ~5µatm)

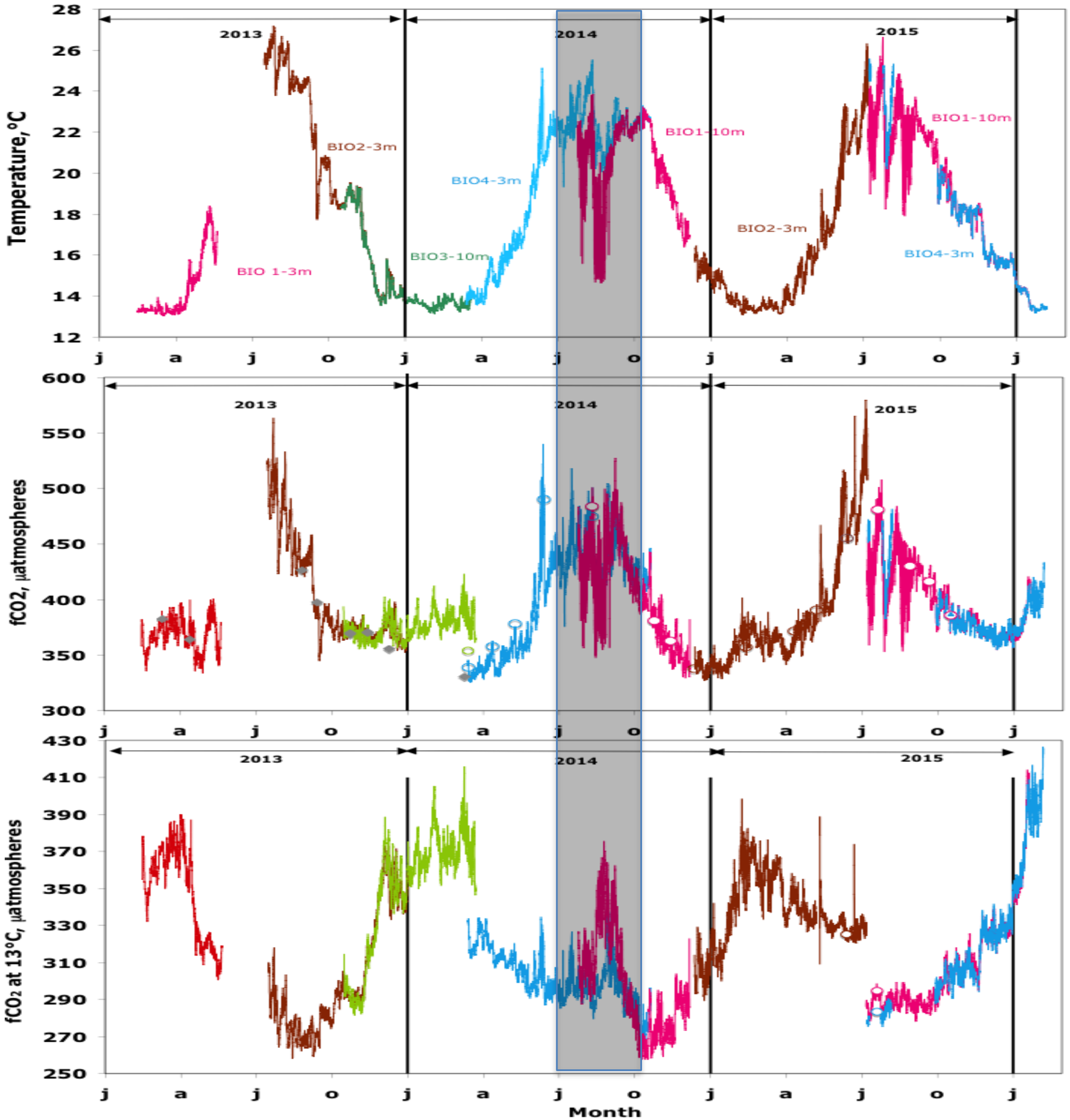



T (°C)

$pCO_2$ (μatm)

$pCO_2$ @ 13°C (μatm)

Mixing in Winter and Biological productivity in Spring -Summer



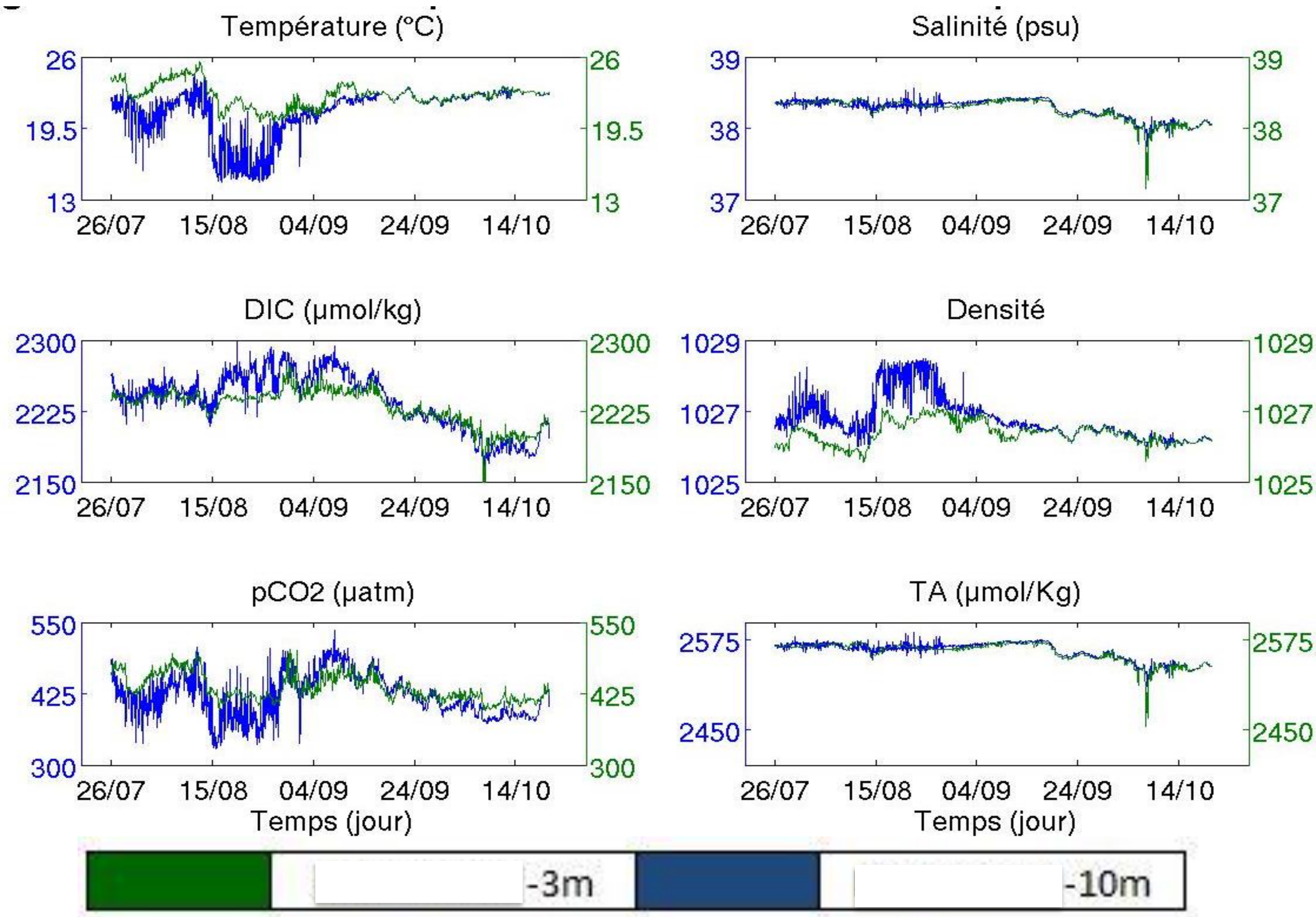

T (°C)

$pCO_2$ (µatm)

$pCO_2$ @ 13°C (µatm)

Strong variability in Summer 2014

# Strong stratification between 3m and 9m depth during Summer 2014

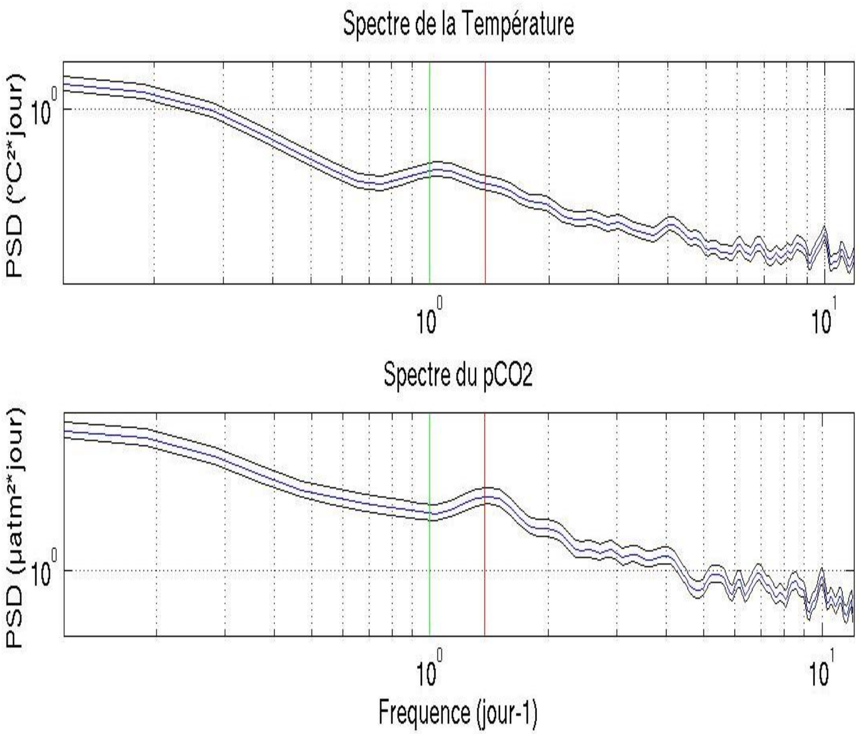


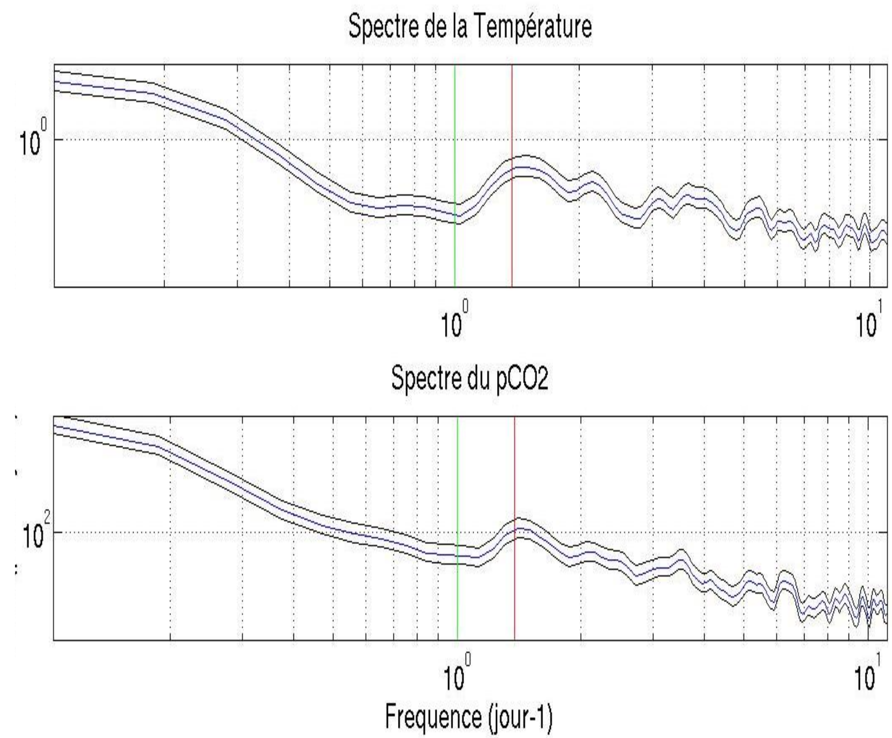
# Spectral analysis
# Summer 2014

Diurnal cycle 24h
Inertial waves 17.4h

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

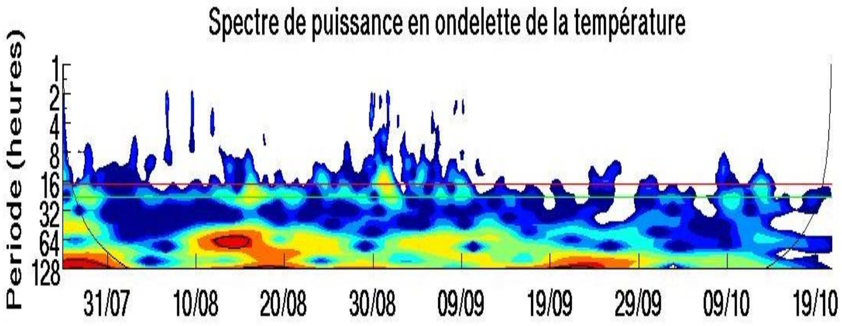


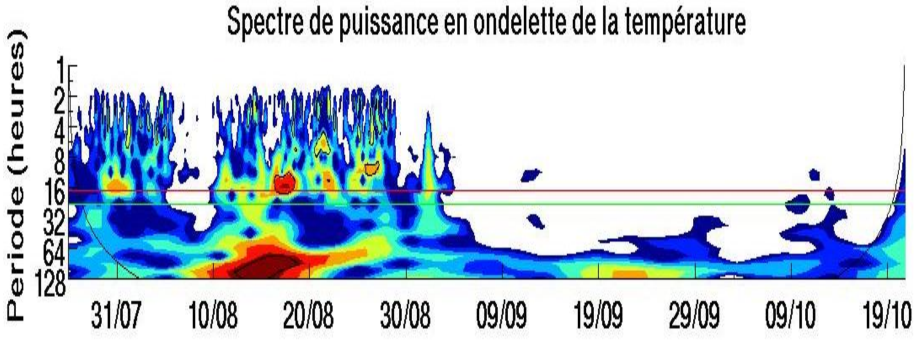



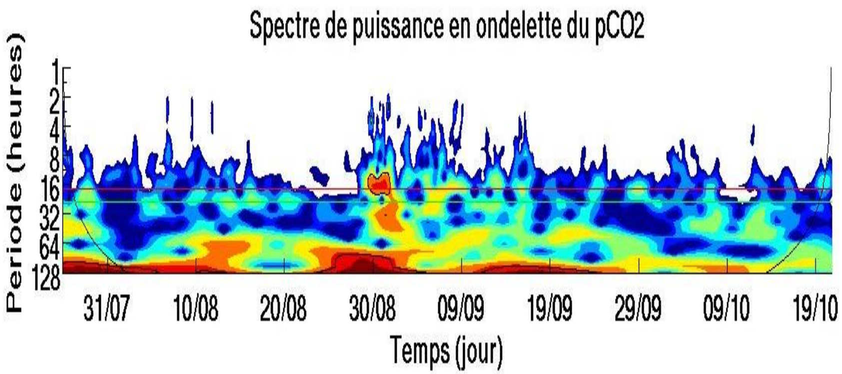
# Wavelet analysis

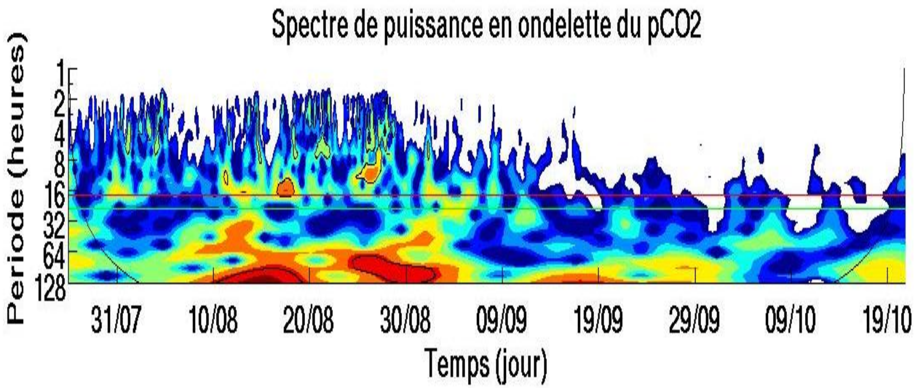
3m

10m



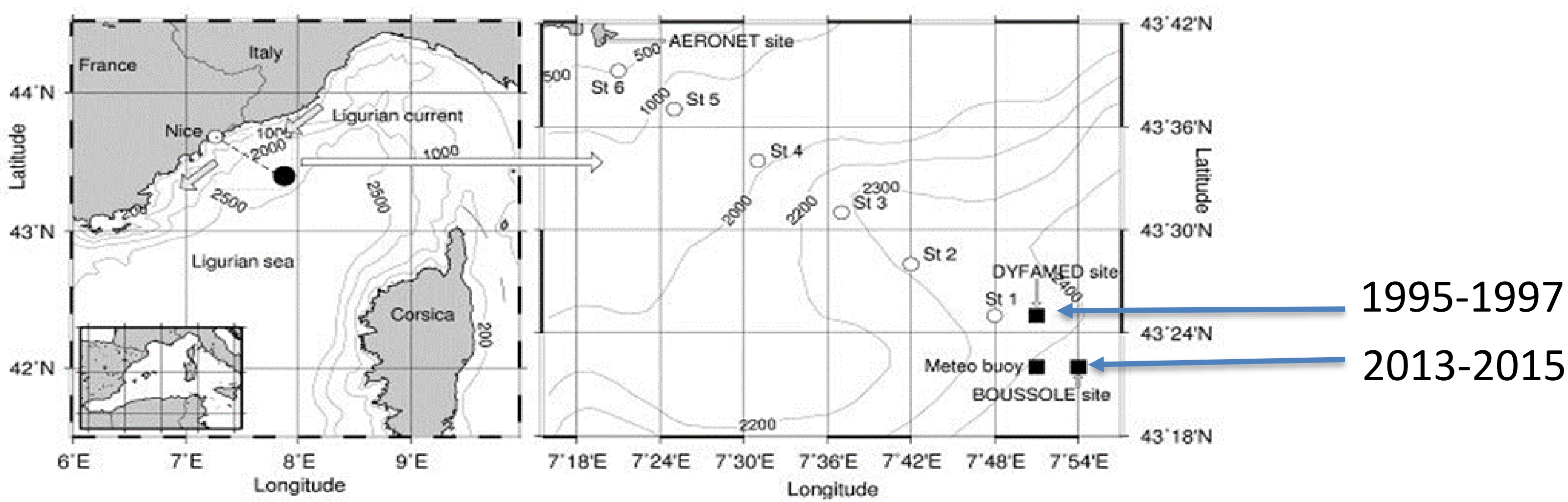



# Variability between 1995-1997 and 2013-2015 periods

CARIOCA sensor at 2m depth on DYFAMED mooring (Hood and Merlivat 2001)



## 1995-1997 (Hood and Merlivat 2001)

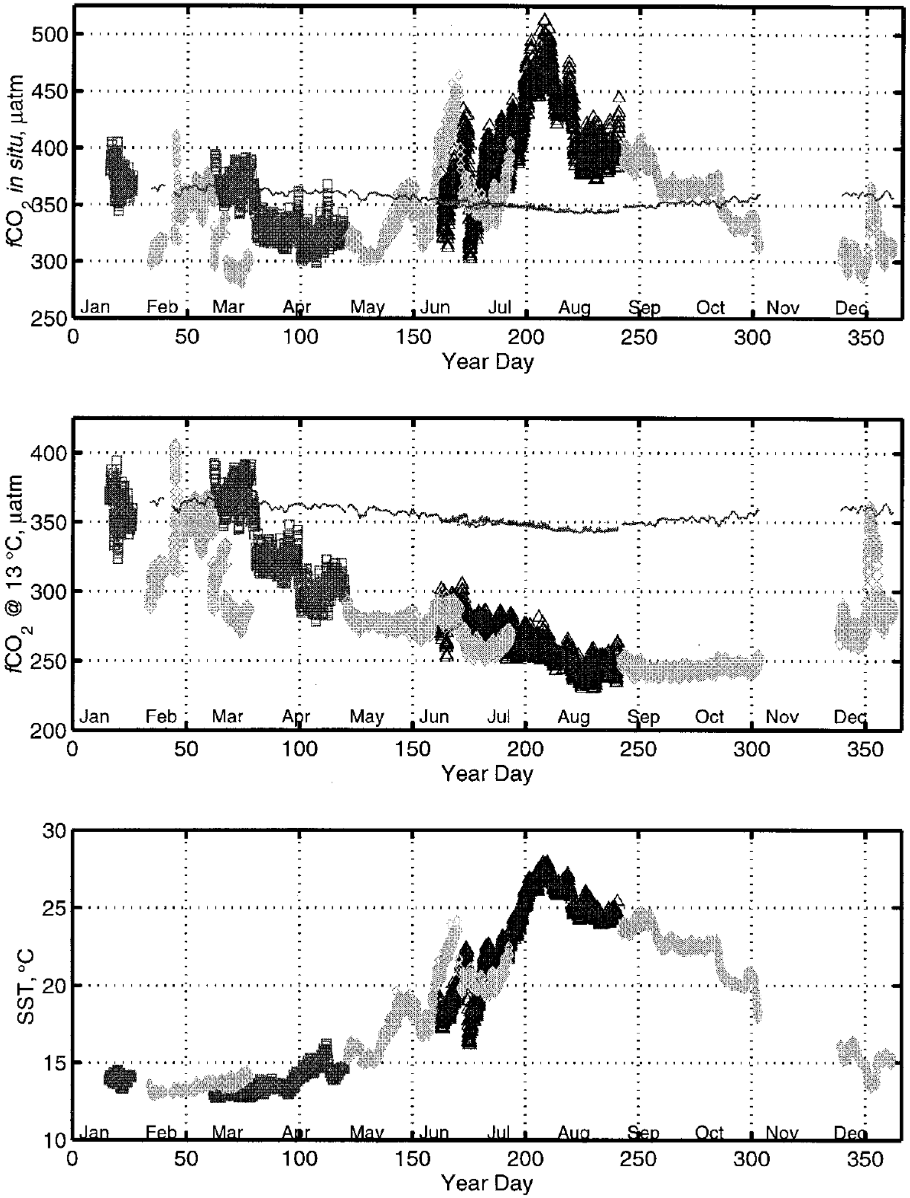
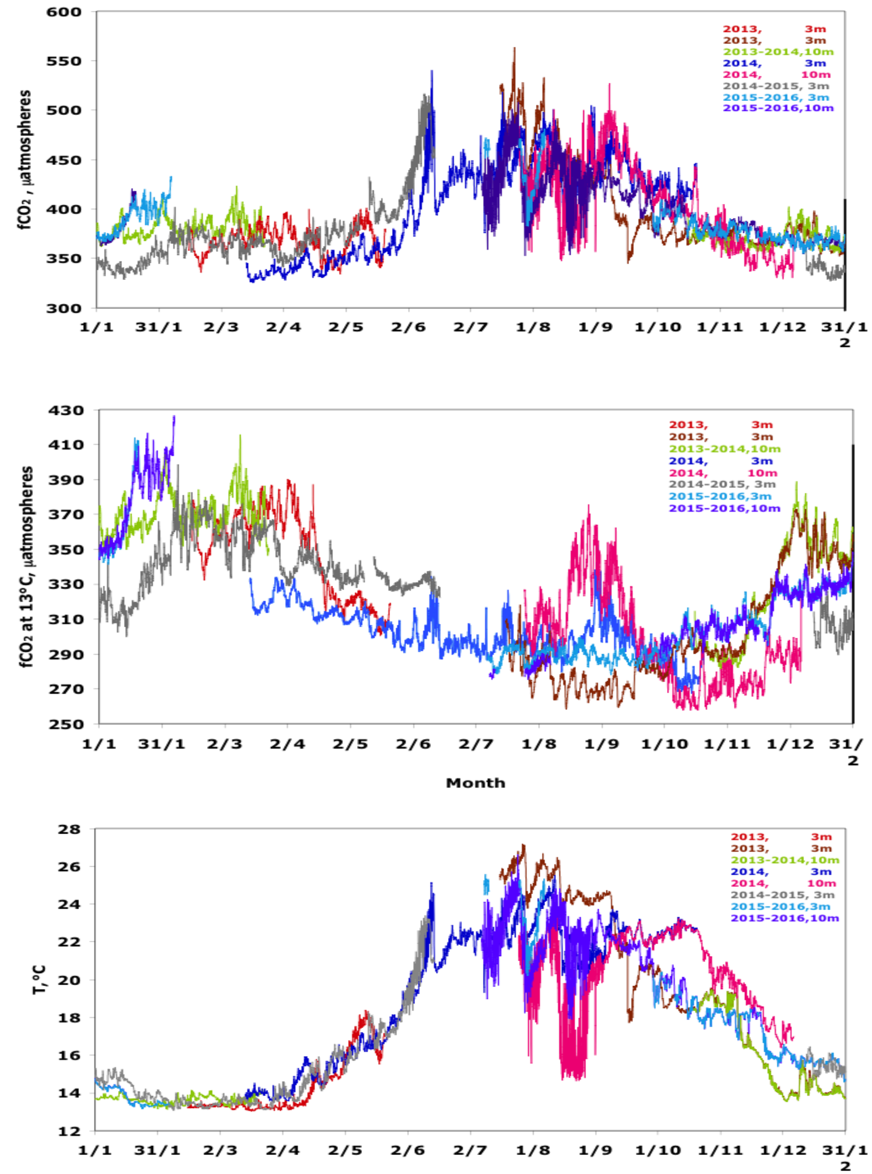



Figure 4. (a) $fCO_2$ data from all three years; 1995 = dark triangles, 1996 = medium gray squares, and 1997 = light gray diamonds. (b) Temperature-normalized $fCO_2$ data from all three years; symbols are the same as for (a). (c) Sea-surface temperature data from all three years.

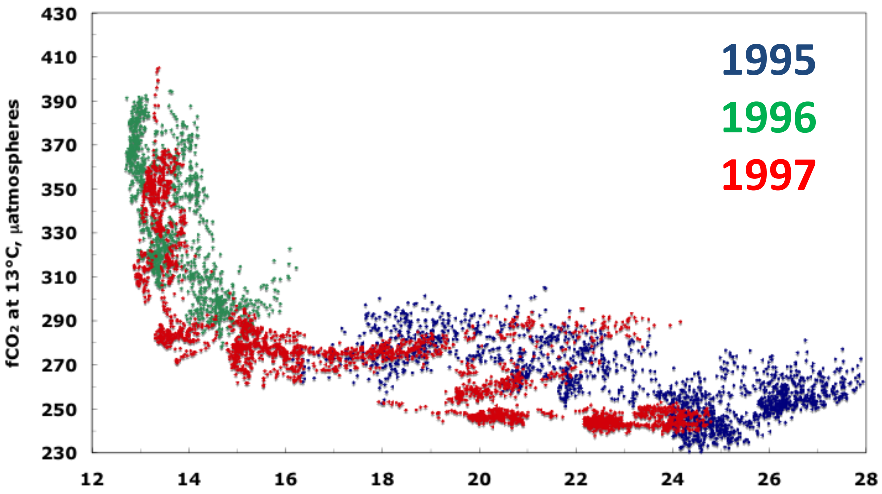
## 2013-2015 (This study)



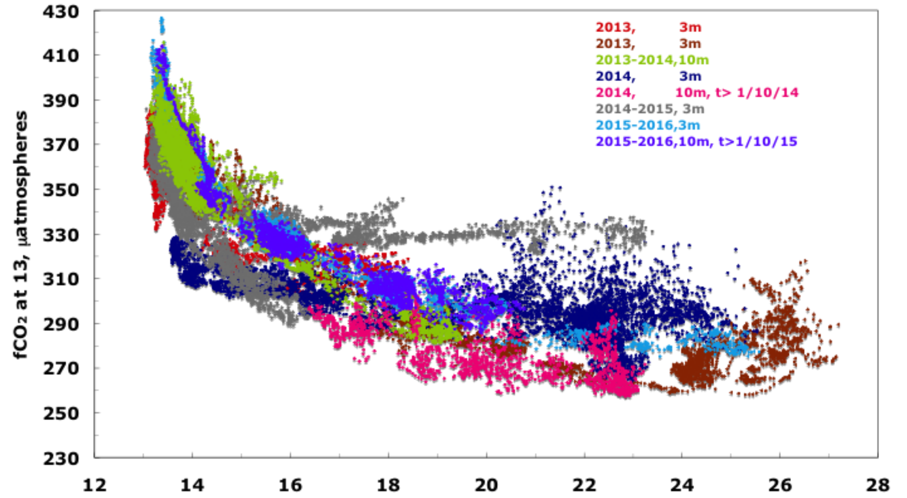

(in the following we remove the 10m depth measurements during summer)

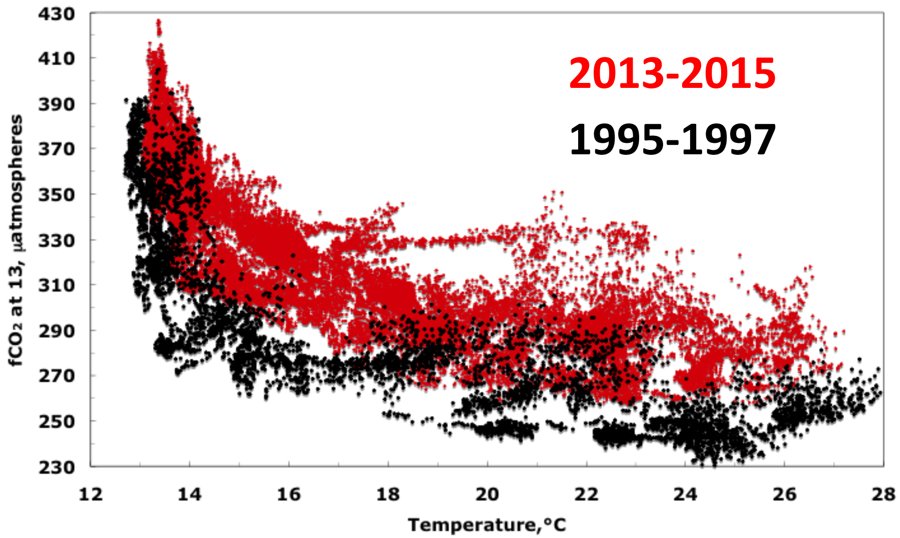
# $pCO_2$ at 13° C as a function of temperature

1995-1997



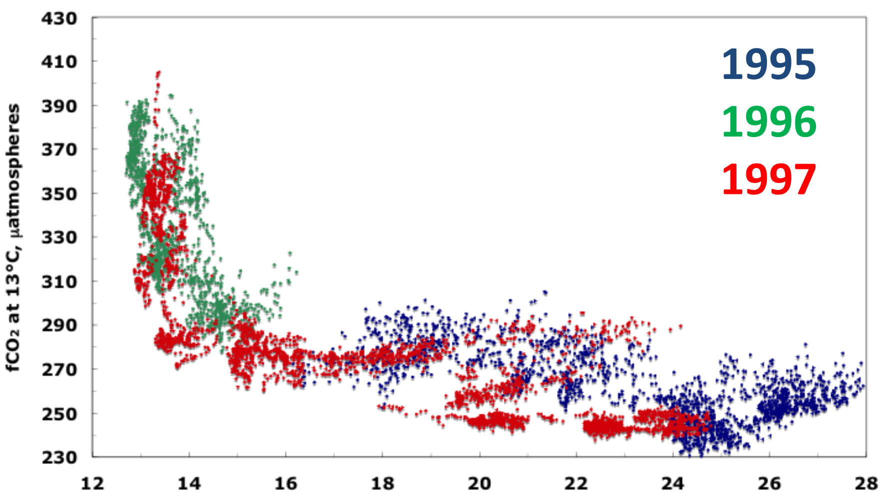

2013-2015



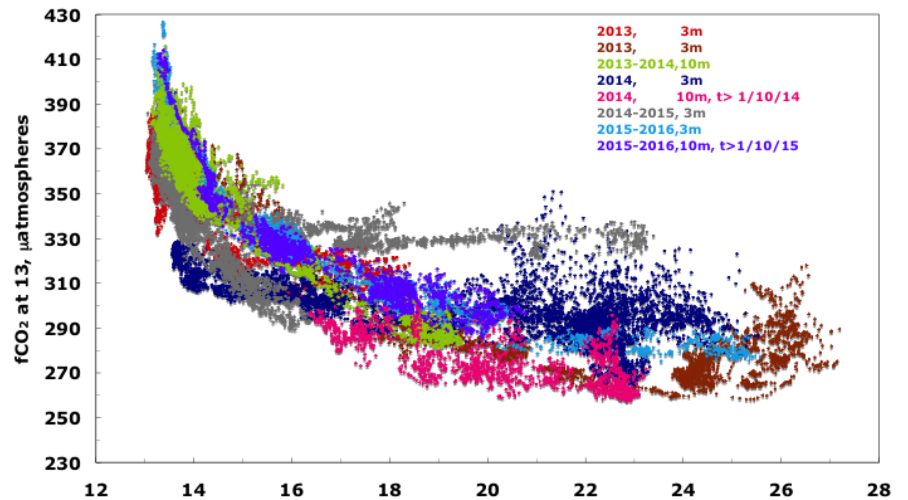



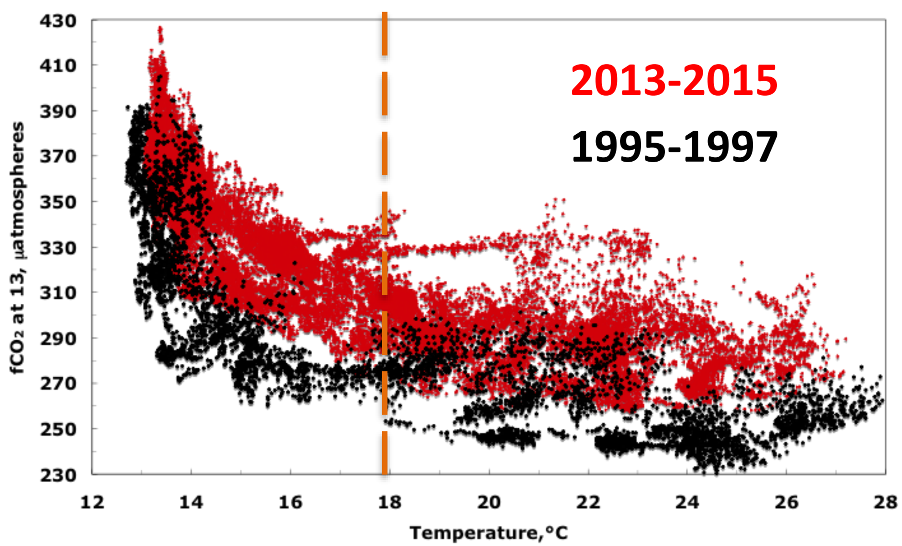
# $pCO_2$ at 13° C as a function of temperature

1995-1997




2013-2015




Decadal variability computed with the whole data set or with data >18°C (to avoid large variability in winter)

Table 1

| sea surface mixed layer | fCO2 at 13°C µatm | σ µatm (1) | N number of data | confidence interval, µatm (>99.7%) 3σ/√N | d fCO2 at 13°C µatm | DIC $\mu mol kg^{-1}$ | pH at13°C | d DIC $\mu mol kg^{-1}$ | dpH unit | d DIC annual $\mu mol kg^{-1} yr^{-1}$ | d pH annual pH unit $yr^{-1}$ |
|---|---|---|---|---|---|---|---|---|---|---|---|
| **All temperature** | | | | | | | | | | | |
| 1995-1997 | 282.2 | 38.8 | 6450 | 1.45 | | 2229.7 N=3 σ=0.96 | 8.1945 N=3 σ=0.0015 | | | | |
| 2013-2015 | 321.7 | 33.2 | 27852 | 0.60 | 39.5+/1.57 | 2259,1 N=3 σ=0.33 | 8.1477 N=3 σ=0.0005 | **29.4+/-1.8** | **-0.0468+/- 0.0027** | **1.63+/-0.10** 1.63 | **-0.0026+/- 0.0002** |
| **T>18°C** | | | | | | | | | | | |
| 1995-1997 | 256.9 | 15.1 | 3617 | 0.75 | | 2208,0 N=3 σ=0.56 | 8.2276 N=3 σ=0.0008 | | | | |
| 2013-2015 | 289.6 | 13.9 | 10184 | 0.41 | 32.7+/0.86 | 2235,6 N=3 σ=0.26 | 8.1853 N=3 σ=0.0004 | **27.6+/-1.1** | **-0.0423+/- 0.0015** | **1.53+/-0.06** 1.53 | **-0.0024+/- 0.0001** |

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

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 $\mu mol\ kg^{-1}\ yr^{-1}$. This explains only 72% of the DIC increase we observe supporting the hypothesis of another source of anthropogenic carbon entering in the Mediteranean sea like Atlantic waters through the Gibraltar straight (Palmieri et al. 2015, Schneider et al 2010, Huertas et al., 2009)

# 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 Mediteranean Sea through the Gibraltar straight )

## $\Rightarrow$ Importance of long term monitoring of high frequency variability of $pCO_2$