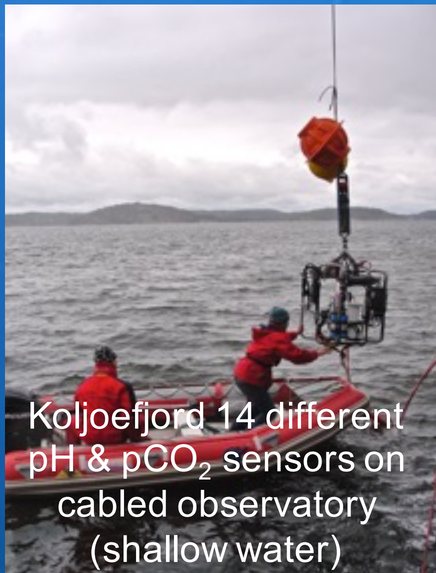
pCO_2 sensors and measurements on moorings

Sensors inter-comparison results (FIXO3)

NW Mediterranean Sea experiment (Biocarex)

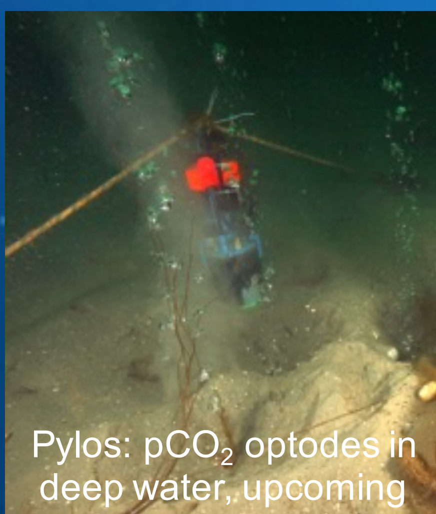
FIXO3/EMSO group (CNRS, NOC, HMCR, UGOT) + ICOS-FR group

WP12. Enhancement of pCO_2 & pH measurement technology on Fixed Observatories

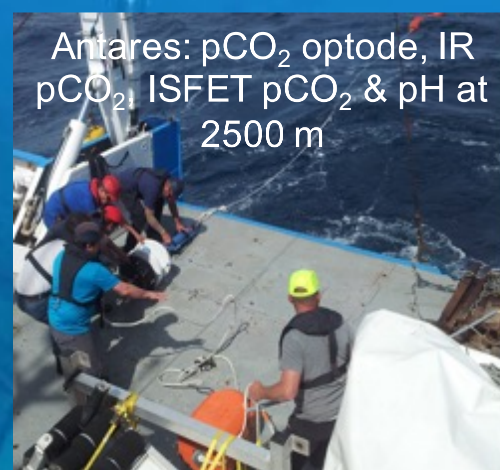


Koljoefjord 14 different pH & pCO_2 sensors on cabled observatory (shallow water)

E2-M3A pH & pCO_2 optodes in surface waters



Pylos: pCO_2 optodes in deep water, upcoming



Antares: pCO_2 optode, IR pCO_2, ISFET pCO_2 & pH at 2500 m

Chapter about pCO_2 optodes

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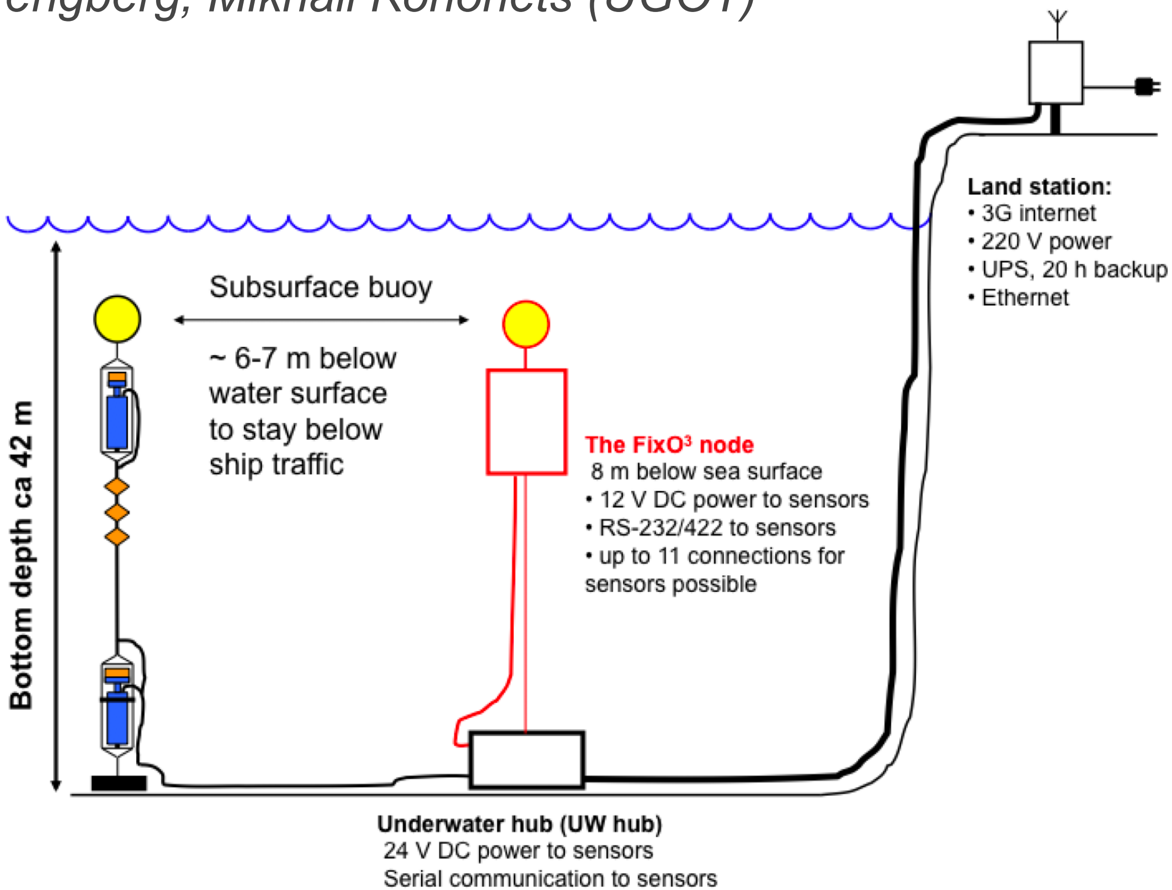
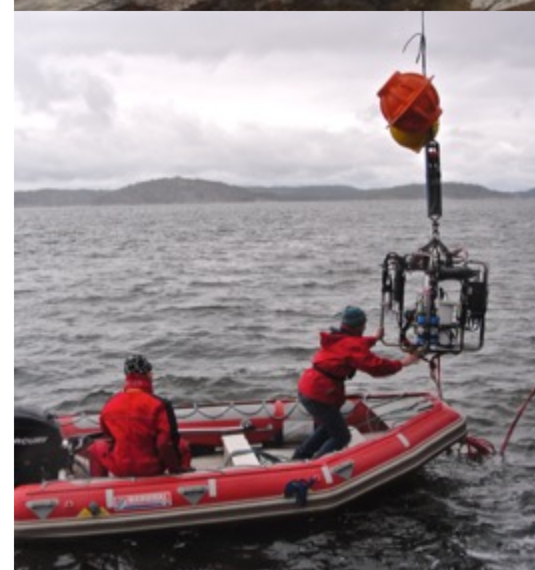
FixO3
FIXED-POINT OPEN OCEAN OBSERVATORIES

Koljoe Fjord cabled observatory for FIXO3 pH/pCO2 intercomparison

Dariia Atamanchuk, Per Hall, Anders Tengberg, Mikhail Kononets (UGOT)





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FixO3 FIXED-POINT OPEN OCEAN OBSERVATORIES

A total of 15 instruments/sensors became available for the inter-comparison

- 4 different technologies (fluorometry, IR, ISFET-based and laser) from 5 different manufacturers for pCO2
- 4 different technologies (fluorometry, colorimetry, electrochemical and ISFET-based) from 5 different manufacturers for pH measurements

Instruments connected to power supply and communication :

CONTROS HydroC® CO2, Seaguard®, PSI® *p*CO2 Pro CV + pump, PSI® *p*CO2 Pro+ pump, Franatech® CO2, SensorLab pH

Instruments not connected (standalone):

pH electrode from Univ. of Kyushu – no serial communication was pre-arranged; can easily work on internal batteries

pH/*p*CO2 ISFET –12 VDC-24VDC power adapter was missing, can easily operate on internal batteries

EXO2® YSI – arranging the on-line communication was rather complicated - hardware additions in the multiplexer were required - and it was decided to skip this; can easily operate on internal batteries

RCM9® - not a part of the inter-comparison, provided auxiliary data; can easily operate on internal batteries.

Deployment Apr 09 to June 03 = 55 days

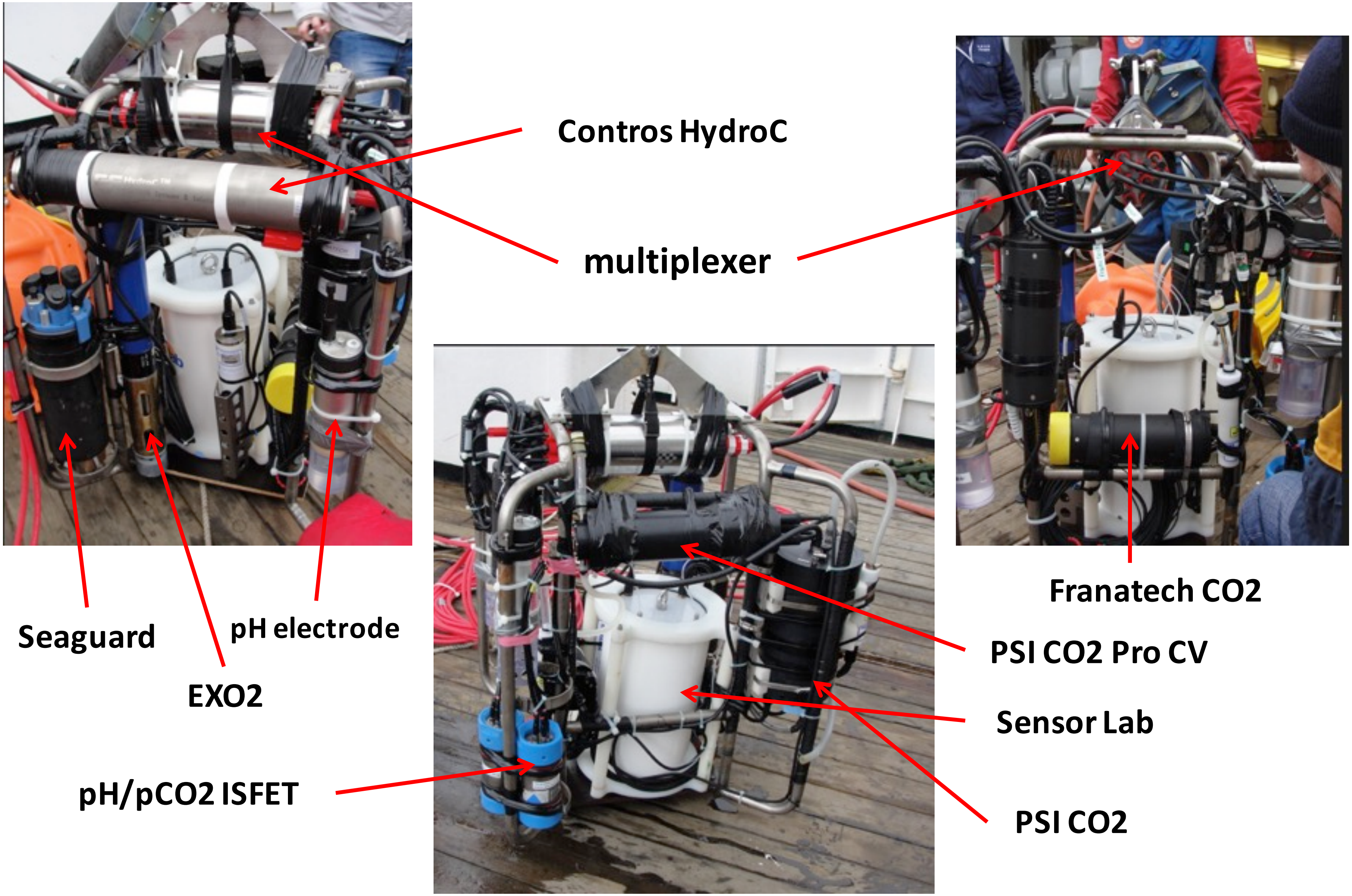
For CONTROS: a warm-up time of **30 minutes** is needed depending on the environmental conditions (water temperature) and settings of the sensor

Measuring range: from 0 to 3.000 ppm (Standard calibration: from 200 to 1.000 ppm)

Resolution: < 1 ppm

Accuracy: ± 1% of upper range value (as the total sum of all errors).

Instrument	Parameter(s)	Interval	Antifouling	Sensing technology pH/pCO_2
Contros HydroC™ CO_2	pCO_2	1 min	Copper shield	NDIR
Aanderaa Seaguard®	2*pCO_2,pH,O_2,P,C,T	1 min	No	Fluorescence
PSI CO_2-Pro™ CV	pCO_2	30 min	Pumped	NDIR
PSI CO_2-Pro™	pCO_2	60 min	Pumped	NDIR
Franatech CO_2	pCO_2	1 sec	No	Tunable Laser Diode
2*pH electrode	pH	60 min	No	Electrochemical
2 *pH/2* pCO_2 ISFET	pH/pCO_2	30 sec	No	ISFET
EXO2, YSI	pH/ORP C/T, BGA-PC, Turb, fDOM, O_2	15 min	Wiper (every 6h)	Electrochemical
SensorLab	pH	15 min	No	Spectrophotometry
Aanderaa RCM9	O_2,C/T, P, currents	15 min	No	-


Contros HydroC
multiplexer
Franatech CO2
Seaguard
pH electrode
EXO2
PSI CO2 Pro CV
Sensor Lab
pH/pCO2 ISFET
PSI CO2

In situ measurements for inter-comparison

- pH : spectrophotometric detection
- TA and DIC: potentiometric titration and acidification with LICOR (respectively) + standards

The *p*CO2 was calculated using the set of constants from Lueker et al. (2000). Nutrients were not measured so were not included into calculations

Most of data were recovered. Some gaps due to power failure

Important for the ICOS/EMSO communities to include ‘on-board’ standards or in situ DIC/TA sampling

The good …

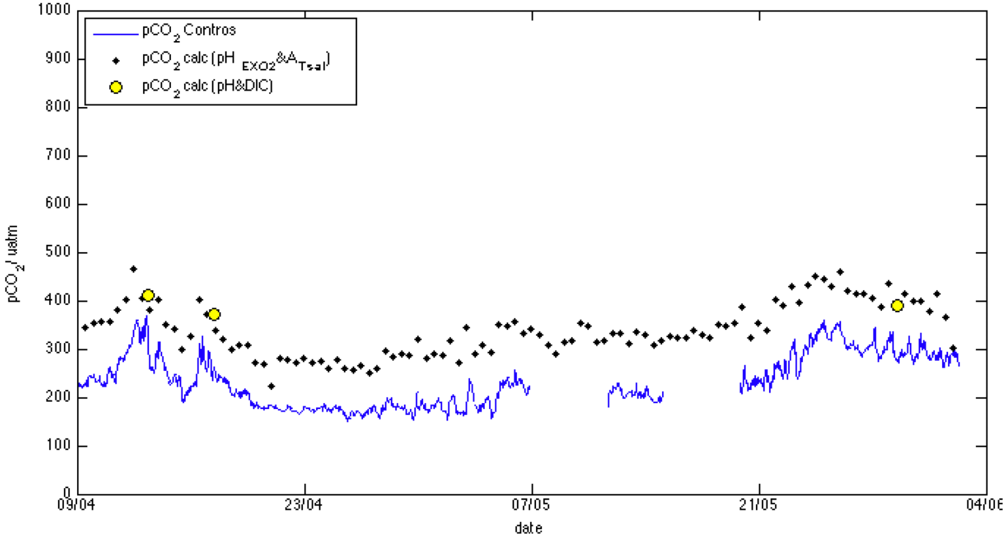


Fig.6a. Overview of pCO_2 data recorded with CONTROS HydroC™.

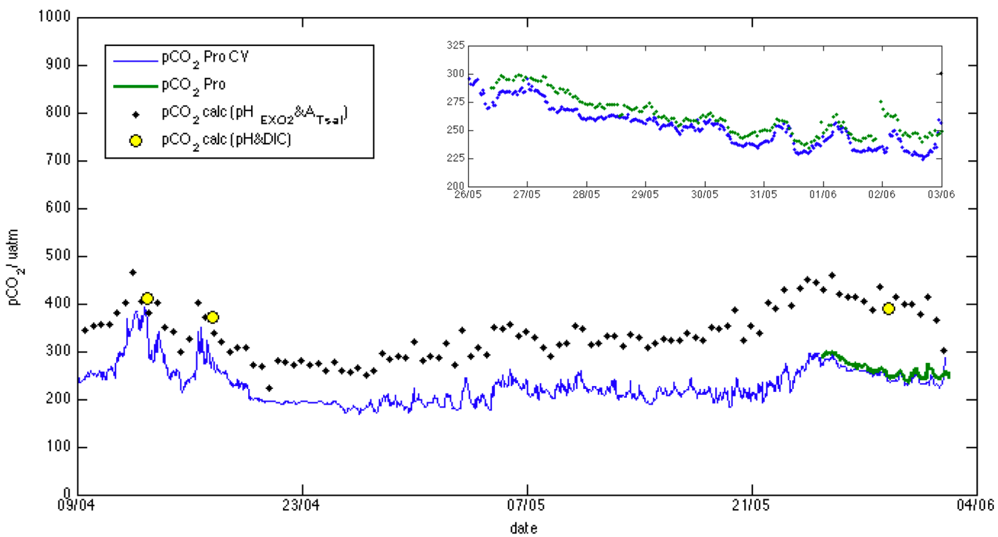


Fig.8a. Overview of pCO_2 data recorded with PSI CO_2-Pro™ *and* PSI CO_2-Pro™ CV. *The insert is a blow-up of data from the last part of the measurement campaign.*

CONTROS HydroC™ data were averaged over 15 min

Gaps in the data were due to power cut-offs and were not related to the sensor performance

The sensor demonstrated good tolerance towards fouling and only the last 10 days of data indicated fouling on the membrane surface

An constant offsets for the 3 sensors between the measured and calculated values are visible

Intercalibration efficiency ? Storage ?

The bad …

Power failure and biofouling impacts on pCO2 data: the fouling, increasing with time, increased the pCO2 variability

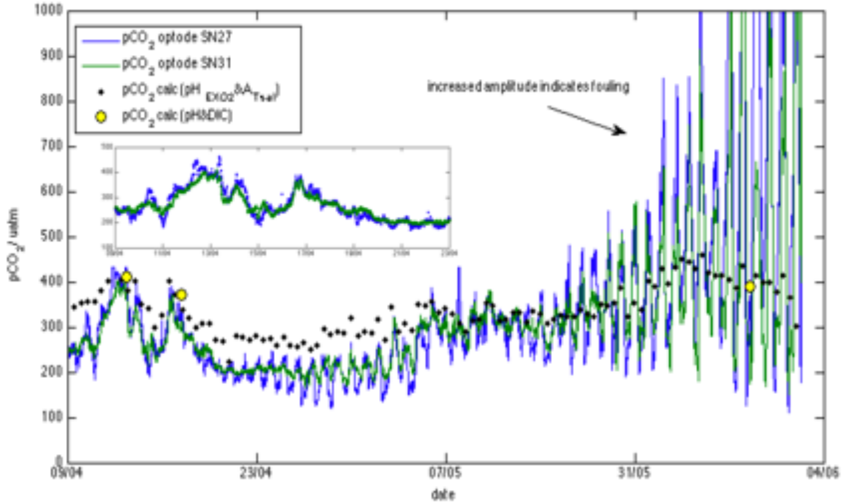


Fig.7a. Overview of pCO_2 *data recorded with* Aanderaa pCO_2 optodes. *The insert is a blow-up of data from the first part of the measurement campaign.*

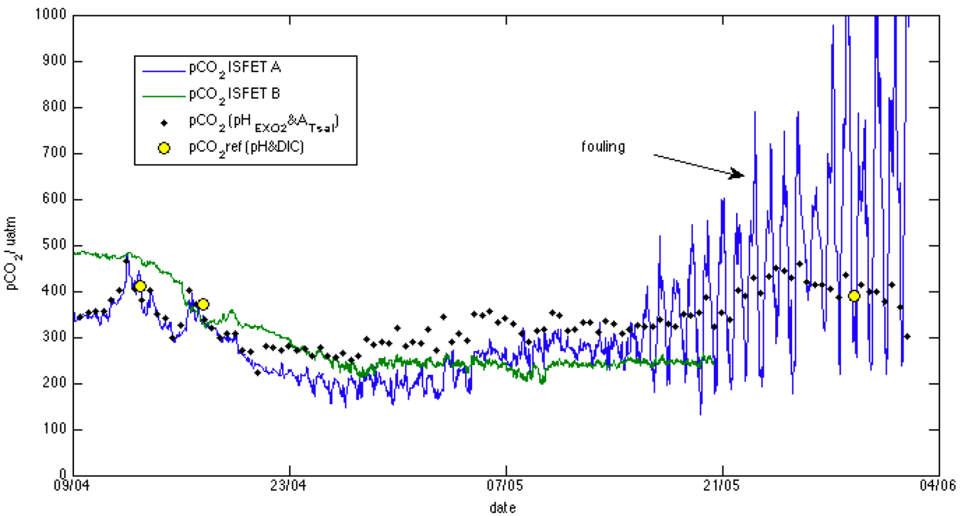


Fig.10a. Overview of pCO_2 *data recorded with* pCO_2 ISFET A and B.

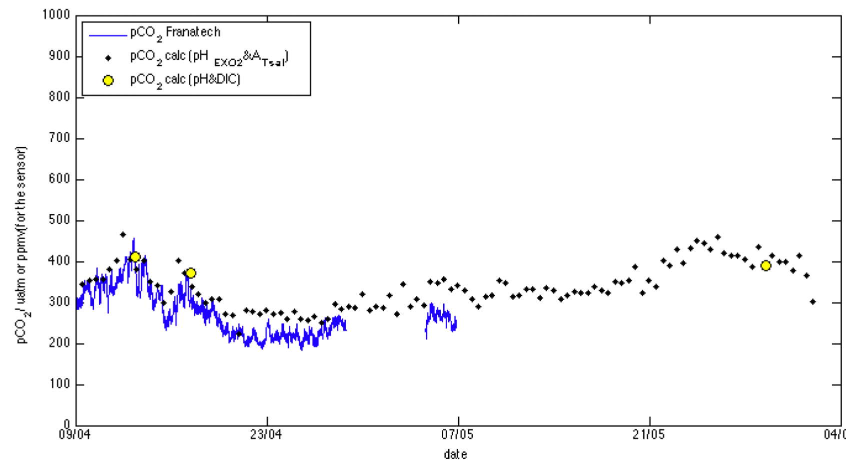
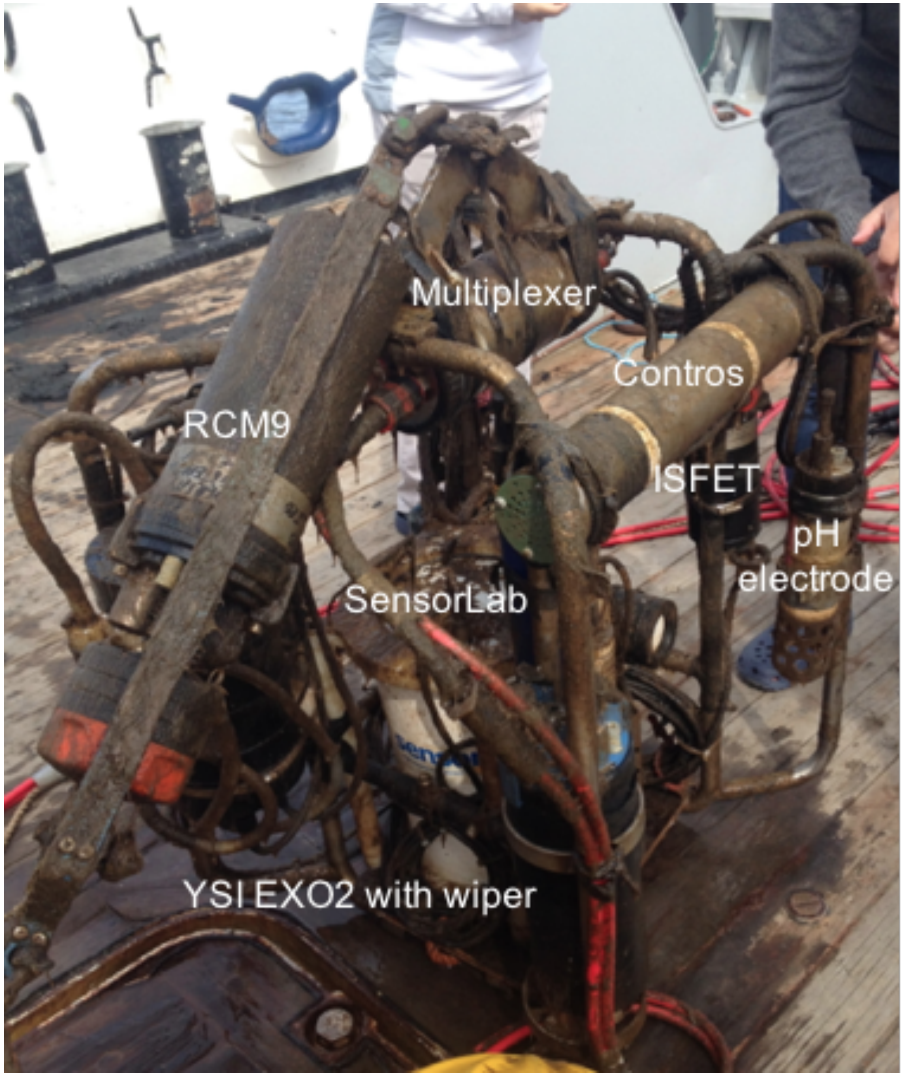


Fig.9a. Overview of pCO_2 *data recorded with* Franatech® CO2.

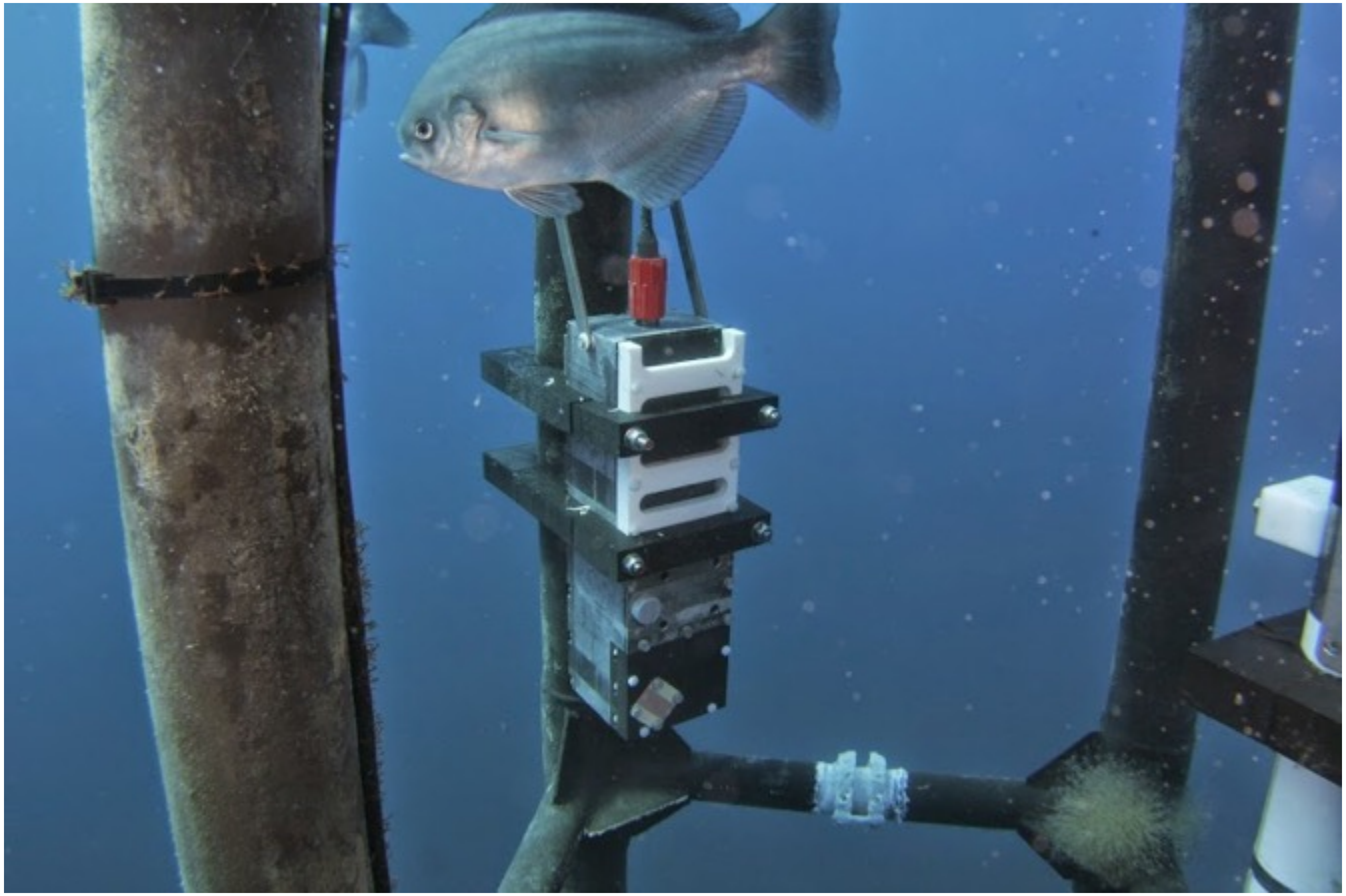


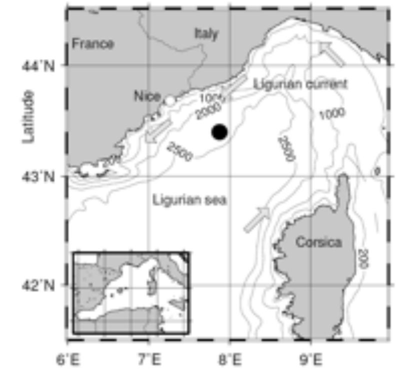
Recovery of frame on June 3, 2014. Frame covered in slimy fouling, algae and sea grass. Changes in the local environment expected at the end when fouling was important.

Examples of successful antifouling strategies: Contros with copper, PSI pumped with TBT, YSI EXO2 with wiper

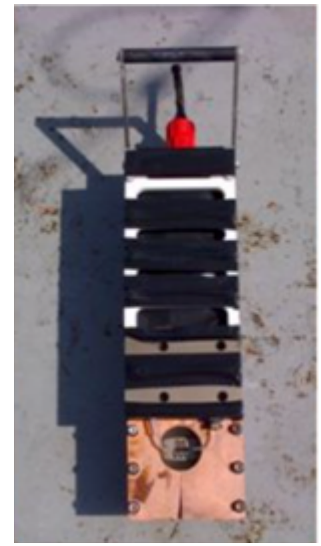
Hourly to decadal variability of sea surface carbon parameters in the NW Mediterranean Sea

J. Boutin, L. Merlivat, D. Antoine, L. Beaumont, M. Golbol, V. Vellucci (CNRS, Sorbonne Univ., DT-INSU)





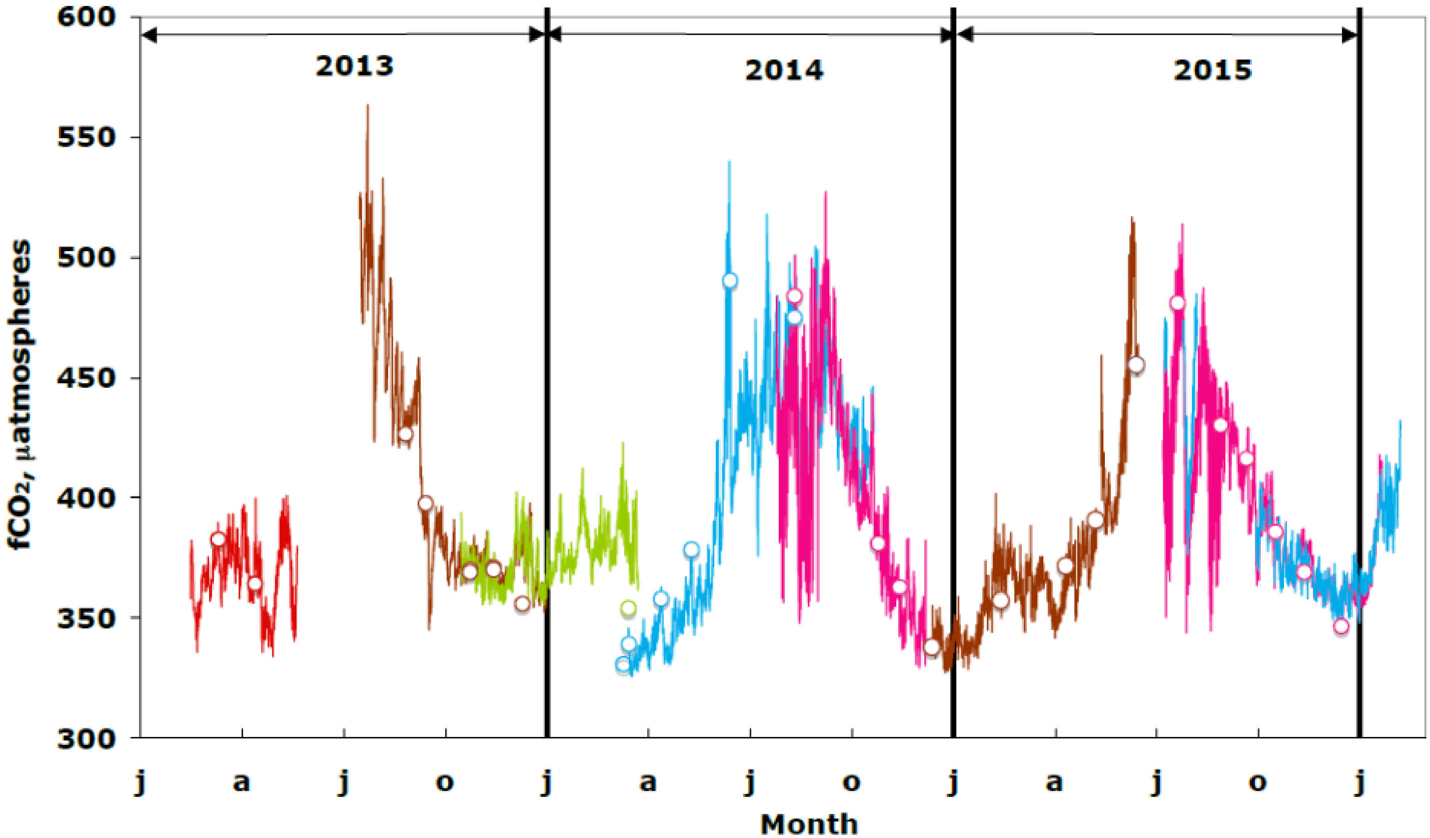
- CARIOCA sensor (NKE): colorimetry system (Lefèvre et al., 1993)
- Compact (max pressure 4 bars)
- Available with real-time connection
- Deployed at 2 and 9 m with maintenance every 6 months
- Deployed with CTDO2 sensors
- Sensor modified in 2013 with pump to limit the noise due to the day light and the wind effect (pCO2 decreases when wind speed increases)



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
- Need HF measurements due to strong wind variability
- Comparison with measurements taken 18 years ago at DYFAMED site by CARIOCA sensors → for the first time estimate decadal variability from 2 multiyear time series of hourly pCO_2 measurements

Calibration check of CARIOCA-BIOCAREX pCO_2 with DIC/TA samples analyzed at SNAPO (LOCEAN)



pCO_2 estimated from (DIC, TA)

diff (pCO_2 – pCO_2 (DIC, TA)) ~ 4.4 µatm

(uncertainty pCO_2(DIC,TA) ~ 5 µatm)

1995-1997 (Hood and Merlivat 2001)

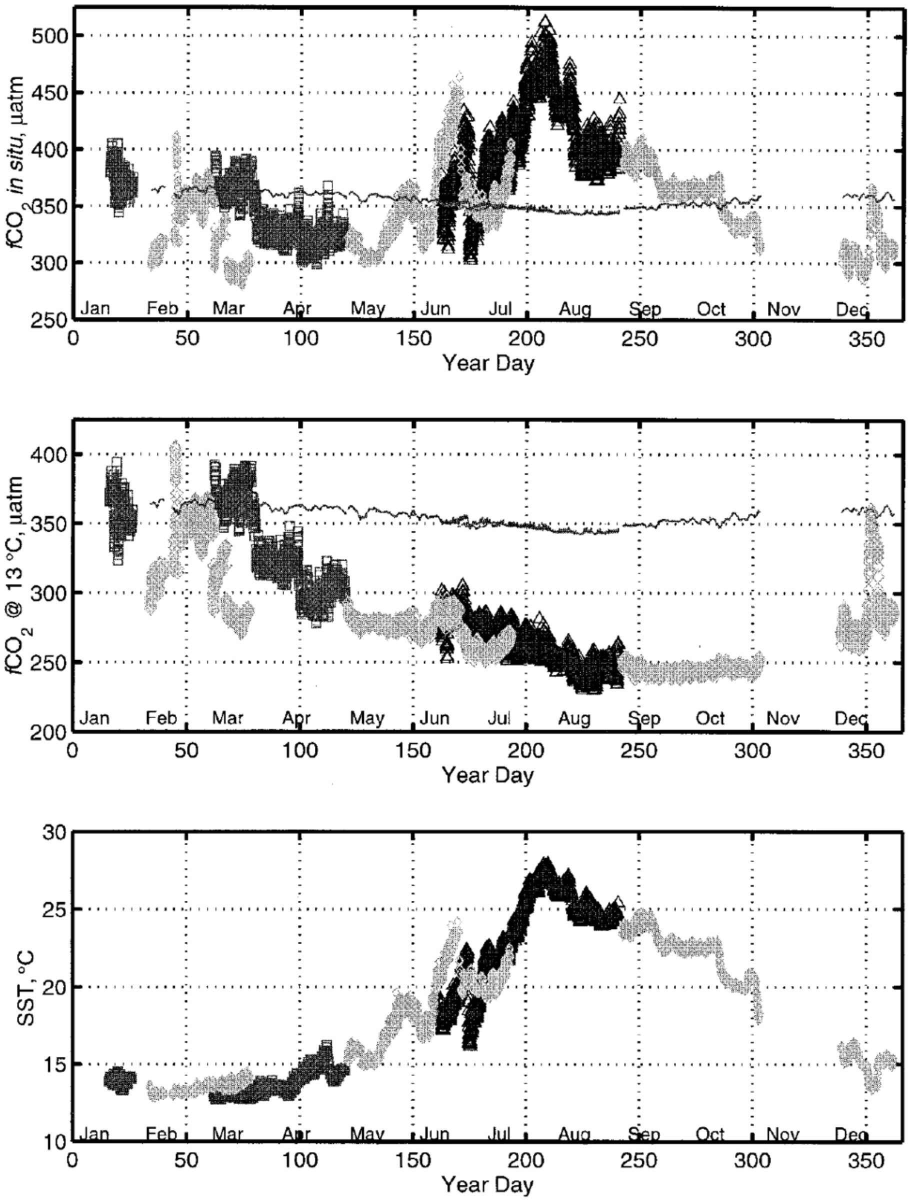
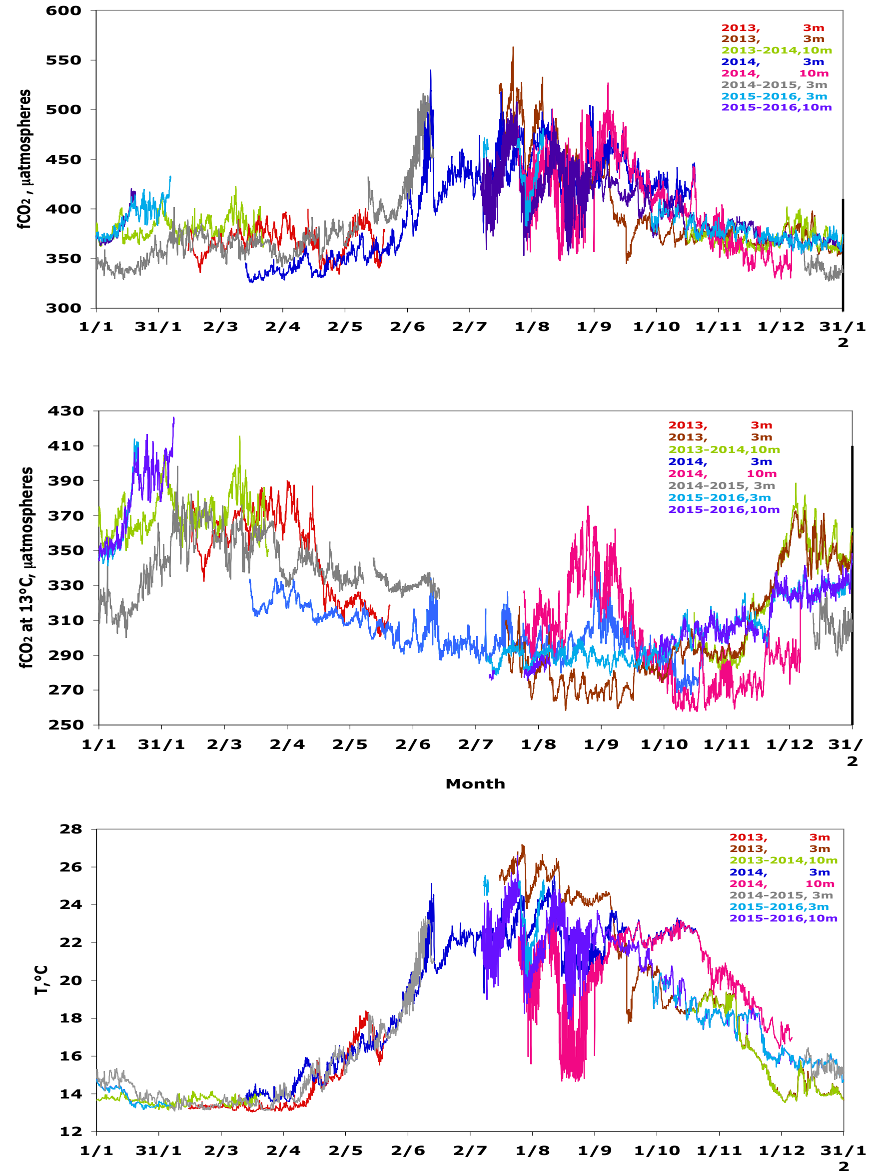


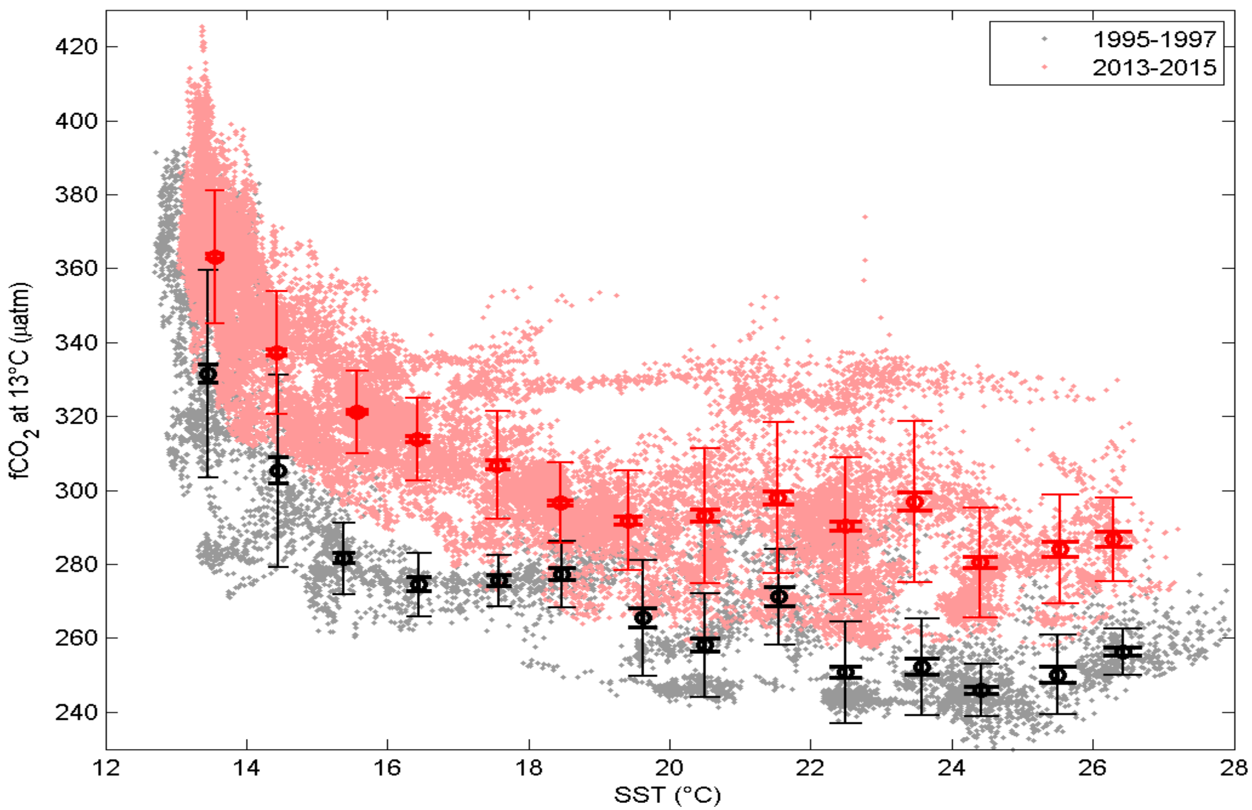
Figure 4. (a) fCO_2 data from all three years; 1995 = dark triangles, 1996 = medium gray squares, and 1997 = light gray diamonds. (b) Temperature-normalized fCO_2 data from all three years; symbols are the same as for (a). (c) Sea-surface temperature data from all three years.

2013-2015 (this study)



remove the 10m depth data during summer not representative of the surface because of vertical stratification

DYFAMED and BIOCAREX CARIOCA data
fCO_2 at 13° C as a function of temperature



18-years variability :

DIC increase :
1.4 mmol/kg/yr

pH decrease:
-2.2+/-0.1 10^{-3}
pHunit/yr

This is ~15% more than the variability expected from atmospheric pCO_2 increase

- Strong interannual variability of frequency and intensity of winter convection events
- Signature of the contribution of the Atlantic Ocean as a source of anthropogenic carbon to the Mediterranean Sea through the strait of Gibraltar.