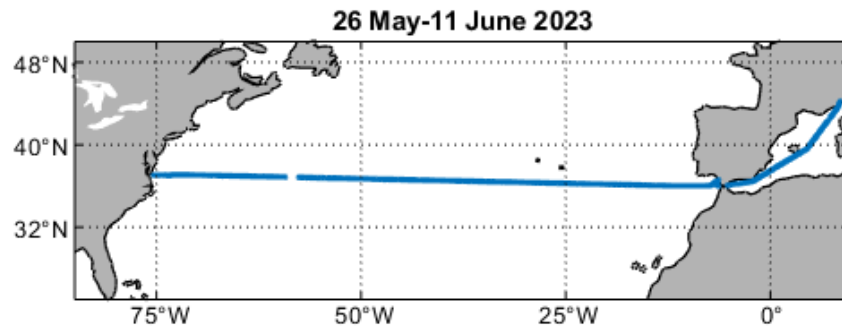


## AX20 Readme File

### Platform Information

In February 2006, IRD installed an instrument to measure CO<sub>2</sub> in surface water on the MN Colibri. In May-June 2023, the vessel sailed from Marseille (France) to Norfolk (USA).



The CO<sub>2</sub> analyser was designed and built by Craig Neil. It is fully automated. On MN Colibri, it is located in the ship's bow thruster space. A Seabird SBE21 thermosalinograph is installed on the same sea water inlet piping. An air inlet is placed on top of the bridge. It allows atmospheric CO<sub>2</sub> measurements in conjunction with surface water CO<sub>2</sub> observations.

### Cruise information

Survey type: VOS line

Vessel Name: MN Colibri

Country vessel: FR

Call sign: FNHO

Expocode: 35MJ20220720

**Period: 26 May-11 June 2023**

**Geographical coverage: English Channel, European coast**

#### **Bounds:**

Westernmost longitude: 75°W

Easternmost longitude: 8°E

Northernmost latitude: 44°N

Southernmost latitude: 36°N

**Class of Data:** Surface ocean carbon dioxide concentrations

### Investigator

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## **System operator & technical support**

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## **CO<sub>2</sub> sensors (xCO<sub>2</sub>)**

The accuracies of all components, when operating optimally, are such that the calculated seawater fCO<sub>2</sub> has an accuracy of 2 µatm or better and the calculated mole fraction of CO<sub>2</sub> in air (xCO<sub>2</sub>) has an accuracy of 0.1 µatm.

## **Infrared Analyzer**

LI-COR model 6262 (February 2006 - present)

[ftp://ftp.licor.com/perm/env/LI-6262/Manual/LI-6262\\_Manual.pdf](ftp://ftp.licor.com/perm/env/LI-6262/Manual/LI-6262_Manual.pdf)

CO<sub>2</sub> resolution: 0.01 µmol/mol

CO<sub>2</sub> accuracy: ± 1 ppm at 350 ppm

Pressure resolution: 0.02 hPa

Internal pressure transducer accuracy: ± 1.2 hPa

(Manufacturer specifications: ±0.1% FS, where FS = 0-1150 hPa)

The general principle of instrumental design can be found in Pierrot et al. (2009). The concentration of CO<sub>2</sub> in the headspace gas was measured using the adsorption of infrared (IR) radiation by the CO<sub>2</sub> molecule. The LI-COR analyzer passed IR radiation through two cells. The reference cell is constantly flushed with a reference gas CO<sub>2</sub>-free. The sample cell is flushed with the gas of interest (standard, outside atmosphere, or headspace gas from equilibration chamber).

The infrared analyzer is calibrated regularly using three standard gases (~250-~500 ppm) from Air Liquide - France, which were calibrated at DT INSU against primary NOAA standards for the high standard and at LSCE for the other two (ICOS Atmospheric Thematic Center).

The exact concentrations of the standards are:

0 ppm (nitrogen gas)

270.55 ± 0.016 ppm

362.63 ± 0.014 ppm

503.83 ± 0.044 ppm

The analyzer was checked by the manufacturer in October 2018.

## **CO<sub>2</sub> in marine air method (xCO<sub>2</sub>)**

Outside air was constantly being pulled (~6 liters/min) from an inlet on the top of the bridge through ~30 m of tubing (1/4" OD Dekabon) to the analytical system. The flushing rate of the LI-COR analyzer during ATM analyses is ~70-150 ml/min.

**Drying:** The effects of water vapor on the sample analyses were kept to a minimum by removing as much water as possible. The water was first condensed out of the sample gas stream by cooling to ~5° C using a thermoelectric device. Then water was further removed using Nafion® gas dryers before reaching the IR analyzer. The counterflow gas in the dryer is pre-dried outside air. Typical water content of the analyzed gas was less than 3 millimoles/mole with approximately 90% of the water being removed.

## **Sampling and equilibrator design**

The seawater inlet is on the sea chest at an approximate depth of 3 meters. Seawater was pushed through a spray head into an equilibration chamber that was fabricated using a filter housing (ColeParmer, U-010509-00). The chamber had a ~0.5 L water reservoir and a ~0.8 L gaseous headspace. Water flow rate was ~2 - 3 L/min. The rate at which the headspace gas recirculated through the analyzer during EQU analyses was ~70 - 150 ml/min.

The equilibration chamber was vented to the surrounding space.

**Drying:** The effects of water vapor on the sample analyses were kept to a minimum by removing as much water as possible. The water was first condensed out of the sample gas stream by cooling to ~5° C using a thermoelectric device. Then water was further removed using Nafion® gas dryers before reaching the IR analyzer. The counterflow gas in the dryer is pre-dried outside air. Typical water content of the analyzed gas was less than 3 millimoles/mole with approximately 90% of the water being removed.

A typical sequence of the continuous analyses was:

STEP	TYPE	REPETITIONS
1	Standards (all)	1
2	ATM	6
3	EQU	90

### **Sea Surface Temperature (SST) and Salinity (SSS)**

SeaBird model SBE-21 (February 2006 - Present)

[http://www.seabird.com/pdf\\_documents/manuals/21\\_026.pdf](http://www.seabird.com/pdf_documents/manuals/21_026.pdf)

Temperature resolution: 0.001°C

Temperature accuracy: ± 0.01°C

Salinity resolution: 0.002 ‰

Seawater samples are taken daily at the thermosalinograph outlet. Samples are analysed at SHOM-France in an OSIL Portasal, and compared to IAPSO Sea Water Standards.

The salinity accuracy is expected to be ± 0.02 ‰

The thermosalinograph is calibrated every 18 months, either at Seabird-USA or at SHOM-France.

The seawater inlet of both CO<sub>2</sub> analyser and TSG is located on the sea chest. The TSG is very close to the hull, the sea water flow rate is 30 l/min. We consider that the temperature inside the TSG is the SST. The warming between the TSG and the CO<sub>2</sub> analyser is 0.2°C ( $T_{\text{equ}} - T_{\text{TSG}}$ ).

### **Equilibrator Temperature ( $T_{\text{equ}}$ )**

Hart model 1521 (April 2007 - present) with a 5610 thermistor probe

[http://www.testequipmentdepot.com/hart/pdfs/1521\\_1522.pdf](http://www.testequipmentdepot.com/hart/pdfs/1521_1522.pdf)

Resolution: 0.001°C

Accuracy: ± 0.025°C

This thermometer was calibrated at SHOM - France in February 2021.

### **Atmospheric Pressure ( $P_{\text{atm}}$ )**

Druck barometer RPT350 (February 2006 - present)

<http://www.ge-mcs.com/en/pressure-and-level/transducerstransmitters/rtp350.html>

Accuracy: ± 0.01 %

The barometric pressure was measured in the bridge, ~20 m above the equilibrator. The Druck barometer is placed in a box, which also contains the GPS and the Iridium transmitter. It was calibrated in August 2019.

### Equilibrator Pressure (Pequ)

The pressure in the equilibrator relative to the bow thruster compartment was measured with a Setra model 239 differential barometer. The LI-COR barometer measured the barometric pressure of the compartment.

Setra model 239, differential pressure (February 2006 - present)

[http://www.setra.com/ProductDetails/model\\_239.htm](http://www.setra.com/ProductDetails/model_239.htm)

Resolution: 0.01 hPa

Accuracy:  $\pm 0.052$  hPa

(manufacturer specifications:  $\pm 0.14\%$  FS, where FS =  $\pm 7.5$  inches WC)

The absolute pressure of the equilibrator headspace reported in data files is the sum of the infrared analyzer pressure and the differential pressure from the pressure transducer attached to the equilibrator.

### Variables info

Column header	Explanation
yy	Year UTC date
mm	Month
dd	Day
hh	Hours UTC time
mn	Minutes
ss	Seconds
day	Decimal year day
Lon	Longitude in decimal degrees (negative values in west)
Lat	Latitude in decimal degrees (negative values in southern hemisphere)
sst	Temperature from the ship's thermosalinograph ( $^{\circ}\text{C}$ )
sss	Salinity from the ship's thermosalinograph (psu)
Patm	Atmospheric pressure in millibar
Tequ	Equilibrator temperature ( $^{\circ}\text{C}$ )
xCO2	Mole fraction of CO <sub>2</sub> (dry) in air or equilibrated air (ppm)
H2Omm	Water content of Licor in mmol/mol
Pequ	Pressure in equilibrator (mbar)
fCO2sw	Fugacity in CO <sub>2</sub> in seawater ( $\mu\text{atm}$ )

### CALCULATIONS:

Mixing ratios of dried equilibrated headspace and air, corrected from the Licor drift (xCO<sub>2</sub>), are converted to fugacity of CO<sub>2</sub> in surface seawater and water saturated air in order to determine the fCO<sub>2</sub>.

For ambient air and equilibrator headspace the fCO<sub>2a</sub>, or fCO<sub>2eq</sub> is calculated assuming 100% water vapor content:

$$f_{\text{CO2eq}} = x_{\text{CO2eq}} (P - p_{\text{H2O}}) \exp(B11 + 2 \delta_{12}) P/RT$$

where  $f_{\text{CO2eq}}$  is the fugacity in the equilibrator,  $p_{\text{H2O}}$  is the water vapor pressure at the sea surface temperature,  $P$  is the atmospheric pressure (in atm),  $T$  is the SST or equilibrator temperature (in K) and  $R$  is the ideal gas constant ( $82.057 \text{ cm}^3 \cdot \text{atm} \cdot \text{deg}^{-1} \cdot \text{mol}^{-1}$ ). The exponential term is the fugacity correction where  $B11$  is the second virial coefficient of pure  $\text{CO}_2$

$$B11 = -1636.75 + 12.0408 T - 0.032795 T^2 + 3.16528 \times 10^{-5} T^3$$

and

$$\delta_{12} = 57.7 - 0.118 T$$

is the correction for an air- $\text{CO}_2$  mixture in units of  $\text{cm}^3 \cdot \text{mol}^{-1}$  (Weiss, 1974).

The calculation for the fugacity at SST involves a temperature correction term for the change of  $f_{\text{CO}_2}$  due to changes in water temperature which when the water passes through the pump and through the rubber tubing within the ship. The water in the equilibrator is typically  $0.2^\circ\text{C}$  warmer than sea surface temperature.

The empirical temperature correction from equilibrator temperature to SST was:

$$f_{\text{CO}_2}(\text{SST}) = f_{\text{CO}_2}(\text{eq}) \exp(-0.0423 (T_{\text{eq}} - \text{SST}))$$

where SST is the sea surface temperature and  $T_{\text{eq}}$  is the equilibrator temperature in  $^\circ\text{C}$ .

#### METHOD REFERENCES:

- Pierrot, D., C. Neill, K. Sullivan, R. Castle, R. Wanninkhof, H. Luger, T. Johannessen, A. Olsen, R. A. Feely, and C. E. Cosca (2009). Recommendations for autonomous underway  $p\text{CO}_2$  measuring systems and data-reduction routines. *Deep Sea Research II*, 56: 512-522.
- Weiss, R. F. (1974). Carbon dioxide in water and seawater: the solubility of a non-ideal gas. *Mar. Chem.* 2: 203-215.