Autonomous pCO_2 measurements in seawater using SAMI-CO_2 (Submersible Autonomous Moored Instrument) on the Astan buoy system in the Western Channel, off Roscoff.

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The actual development of monitoring networks, in coastal areas, provides to the scientific community platforms to deploy and test new sensors. In 2007, the Marine Chemistry team, in Roscoff equipped the cardinal buoy of opportunity ASTAN (picture 1) (Western Channel) from the French "Maritime aids to navigation and lighthouse Authorities" with a full CTD system (temperature, salinity, D.O., fluorescence) and atmospheric sensors. Cycles measurements occur every 30 minutes. To complete the existing system, we installed in 2015 **a pCO_2 sensor** from Sunburst Sensors LLC (picture 2). This sensor uses indicator-based spectrophotometric method to measure the environment pCO_2 variations by diffusion through a membrane.

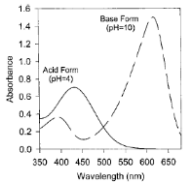
Principle :

The SAMI pCO_2 analysis is based on the colometric changes of a pH sensitive indicator solution (Bromothymol Blue). Aqueous carbon dioxide in seawater diffuses across the silicon membrane equilibrator (Fig. 2) and modifies the equilibrated indicator solution : $HI^- \longleftrightarrow H^+ + I^{2-}$ (Ka') where HI^- and I^{2-} are the protonated and unprotonated forms of the diprotic indicator, Ka' the apparent indicator equilibrium constant. The absorbance measurements are made at the absorbance maxima of HI^- (434 nm) and I^{2-} (620 nm) (Fig. 1).

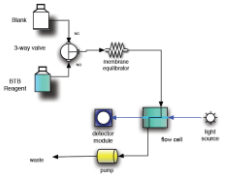
$$pH = pKa' + \log([I^{2-}]/[HI^-]) \quad \text{with} \quad [I^{2-}]/[HI^-] = \frac{A_R - \frac{\varepsilon 620a}{\varepsilon 434a}}{\frac{\varepsilon 620b}{\varepsilon 434a} - A_R * \frac{\varepsilon 434b}{\varepsilon 434a}}$$

, $A_R = A_{620}/A_{434}$ and ε's are ratios of the HI^- and I^{2-} molar absorptivities.

The instrument response $RCO_2 = -\log\left(\frac{A_R - \frac{\varepsilon 620a}{\varepsilon 434a}}{\frac{\varepsilon 620b}{\varepsilon 434a} - A_R * \frac{\varepsilon 434b}{\varepsilon 434a}}\right) = pKa' - pH$. The response RCO_2 is therefore only dependent upon the molar absorptivities (ε's) and absorbance ratio A_R. To calculate A_R, the optical absorbances at 434 and 620 nm are corrected by regular measurements of a blank solution (de-ionized water) at 740 nm.



Fig, 1 : Optical spectrum of bromothymol blue



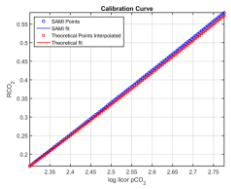
Fig, 2 : SAMI system diagram

Picture 1 : Astan Buoy, off Roscoff - (© W. Thomas)

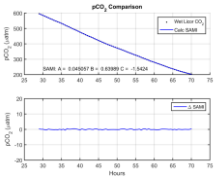
Picture 2 : SAMI installation under Astan Buoy - (© W. Thomas)

Calibration :

The SAMI response (RCO_2) is determined using a calibrated Li-COR (NDIR) CO_2 analyzer. Variable CO_2 gas concentrations are monitored in a thermostated chamber. The SAMI and NDIR data are combined to give a second-order polynomial calibration curve. $RCO_2 = a(\log pCO_2)^2 + b(\log pCO_2) + c$ (Fig.3). A temperature coefficient is also determined to correct the pCO_2 value at temperaure differing from the calibration temperature. Then, sensor values are compared to measurements in a bath using again the Li-COR (NDIR) CO_2 analyzer (Fig.4).



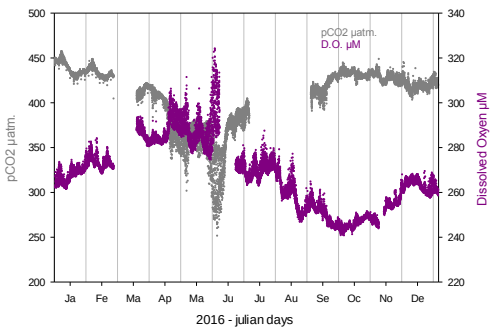
Fig, 3 : SAMI calibration curves



Fig, 4 : Comparison with Li-COR CO_2 analyzer

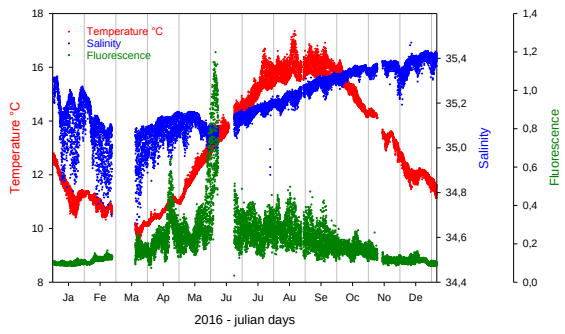
2016 - RESULTS

Seasonnal variability of pCO_2 and dissolved oxygen (D.O.)
Astan Buoy - 2016



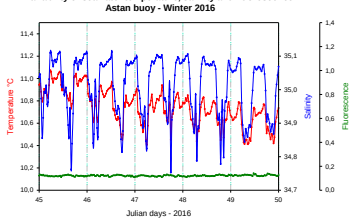
Fig, 5 : 2016 : pCO2 and D.O. variability

Seasonnal variability of seawater temperature, salinity and fluorescence.
Astan Buoy - 2016



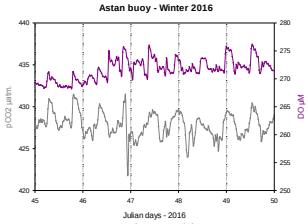
Fig, 6 : 2016 seawater temperature, salinity and fluorescence variability

Variability of seawater temperature, salinity and fluorescence.
Astan buoy - Winter 2016



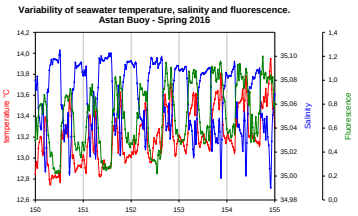
Fig, 10 : Winter seawater temperature, salinity and fluorescence variability

Variability of pCO_2 and dissolved oxygen (D.O.)
Astan buoy - Winter 2016



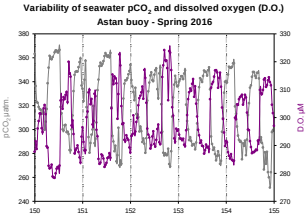
Fig, 7 : Winter pCO_2 and D.O. variability

Variability of seawater temperature, salinity and fluorescence.
Astan Buoy - Spring 2016



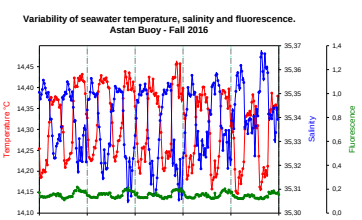
Fig, 11 : Spring seawater temperature, salinity and fluorescence variability

Variability of seawater pCO_2 and dissolved oxygen (D.O.)
Astan buoy - Spring 2016



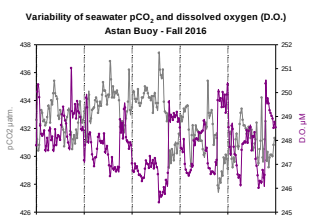
Fig, 8 : Spring pCO_2 and D.O. variability

Variability of seawater temperature, salinity and fluorescence.
Astan Buoy - Fall 2016



Fig, 12 : Fall seawater temperature, salinity and fluorescence variability

Variability of seawater pCO_2 and dissolved oxygen (D.O.)
Astan Buoy - Fall 2016



Fig, 9 : Fall pCO_2 and D.O. variability

Conclusion : Results obtained with SAMI and the other sensors highlight the dynamiscs of this ecosystem (Fig.5 to 12). The seasonal variability of the biogeochemical parameters of the coastal area is well captured by the system. SAMI allows to measure the amounts of pCO_2 of the natural environment which behaves like source or sink of carbon depending on the seasons (solubility or/and biological pumps). We can also notice the strong daily variability of the parameters influenced by the tidal currents .