HIGH FREQUENCY MONITORING OF pCO_2 AND RELATED PARAMETERS USING A CARIOCA SENSOR IN A TEMPERATE COASTAL ECOSYSTEM (2003-2009)

Bozec, Y.[1,2], L. Merlivat[3], L. Beaumont[4], T. Danguy[4], A. Guillot[5], M. Répécaud[6], E. Grossteffan[7], E. Bucciarelli[8], J. Guillou[8], S. Blain[9], P. Tréguer[8]

[1]CNRS, UMR 7144, Equipe Chimie Marine, Station Biologique de Roscoff, Place Georges Teissier BP74, 29682 Roscoff, France, Email : bozec@sb-roscoff.fr
[2]UPMC Univ. Paris 06, UMR 7144, Adaptation et Diversité en Milieu Marin, Station Biologique de Roscoff, 29682 Roscoff, France
[3]LOCEAN, Univ. Paris 6, 75252 Paris Cedex 05, Paris, France,
[4]Division Technique INSU-CNRS, 92195 Meudon cedex, France
[5]Division Technique INSU-CNRS, 29280 Plouzané, France
[6]IFREMER, Centre de Brest, 29280 Plouzané, France
[7]UMS 3113 CNRS-UBO, Institut Universitaire Européen de la Mer (IUEM), 29280 Plouzané, France
[8]UMR 6539 CNRS-UBO, IUEM, 29280 Plouzané, France
[9]UMR 7621 CNRS-UPMC, Observatoire Océanologique de Banyuls sur Mer, 66651 Banyuls sur mer, France

ABSTRACT

High-frequency pCO_2 and ancillary data were recorded for 6 years during the first deployment of a CARIOCA sensor in the surface waters of a temperate coastal ecosystem, the Bay of Brest, which is impacted by both coastal and oceanic variability. Biological processes (e.g. photosynthesis/respiration) were the main driver of seasonal and diurnal pCO_2 dynamics throughout six years of observations. The amplitudes of diurnal pCO_2 variations represented 10 to 60% of the pCO_2 drawdown observed each year during spring. Sub-daily variations of pCO_2 were therefore extremely relevant for annual estimates of air-sea CO_2 fluxes. The annual emissions of CO_2 from the surface waters to the atmosphere ($+1.4 \pm 0.4$ mol m^{-2} yr^{-1}) were similar to those observed in temperate macrotidal outer-estuarine plumes with comparable salinity range.

1. INTRODUCTION

The constraint of air–sea CO_2 fluxes and their variability at various time and spatial levels remain a central task in global carbon and climate studies. In the past decade, the coastal oceans have been the focus of several studies highlighting the key role of these ecosystems in the global budget of air-sea CO_2 fluxes [1,2,3]. In these extremely heterogeneous and dynamic ecosystems, the direction and magnitude of these fluxes present much larger gradients than in the open ocean, which make coastal ecosystems relevant for global estimates of air-sea CO_2 fluxes. The spatial variability is large from one ecosystem to the other and [4] recently proposed to classify continental shelves as sinks and near-shore ecosystems as sources of atmospheric CO_2. This hypothesis is based on several studies, mainly based on shipboard cruises that inferred air-sea CO_2 fluxes at seasonal levels in diverse regions of the world Ocean (see [4] and references therein). However, inter-annual variations of air-sea CO_2 fluxes in the coastal ocean are virtually unknown. Moreover, uncertainty in the global estimate of these fluxes would be reduced by better constraining variations due to processes occurring at hourly to daily scales (diel biological cycles, tides…).

Sensors allowing time-series measurements of partial pressure of CO_2 (pCO_2) and related biogeochemical parameters at high frequency in the coastal ocean are needed to reduce the uncertainty on global air-sea CO_2 fluxes estimates. Simultaneous measurements of pCO_2 and dissolved O_2 (O_2) with synoptic datasets of related physical and biogeochemical parameters are effective tools to unravel the impact of water temperature, tides, respiration/photosynthesis, calcification/dissolution of $CaCO_3$ on the variability of air-sea CO_2 fluxes at scales going from daily [5,6,7,8,9,10] to inter-annual levels. The CARbon Interface Ocean Atmosphere (CARIOCA) sensor was originally developed for long term and high frequency measurements of pCO_2 in open ocean surface waters [11]. CARIOCA measurements provide very useful in-situ estimates of ocean biological production rates [12] and can be excellent tools for investigating the high variability and the evolution of seawater surface pCO_2 in coastal environments.

Here we present high-frequency pCO_2 and ancillary data recorded for 6 years during the first

deployment of a CARIOCA sensor on a MAREL buoy equipped with 6 other biogeochemical sensors in the surface waters of a temperate coastal ecosystem, the Bay of Brest, which is impacted by both coastal and oceanic variability.

2. STUDY SITE AND METHODS

The Bay of Brest is a shallow, semi enclosed ecosystem, located at the extreme West of France in Brittany. The hydrology of the bay is controlled by water exchanges with the Atlantic Ocean, through a narrow strait (2 km wide), and influenced by the moderate input of 2 rivers (Aulne and Elorn, average annual flow 21 and 5 m^3s^{-1}, respectively). The Bay waters remain mainly oceanic throughout the year; the salinity varies little from 34 to 35.5, except during short winter floods. In this shallow macrotidal system (maximum tidal amplitude 8 m, tide periodicity: 12 h 15 min and 14 d, maximum tidal currents 2.6 ms^{-1}), tidal currents and wind ensure that waters are well mixed throughout the year.

The automated MAREL buoy is situated at the entrance of the bay (48°21'N; 4°33'W) and record T, S, O_2, turbidity, Chl *a*, pH at 20 minutes intervals (see details in [13]). The buoy is equipped with a CARbon Interface Ocean Atmosphere (CARIOCA) sensor for high frequency (hourly) measurements of pCO_2 (Collaboration Technical division INSU). The sampling site is situated at the fixed station Brest_SOMLIT (National Network for Observation of the Coastal Zone) where 12 biogeochemical parameters (e.g. S, T, O_2, Chl *a*…) are measured weekly (http://www.domino.u-bordeaux.fr/somlit_national/).

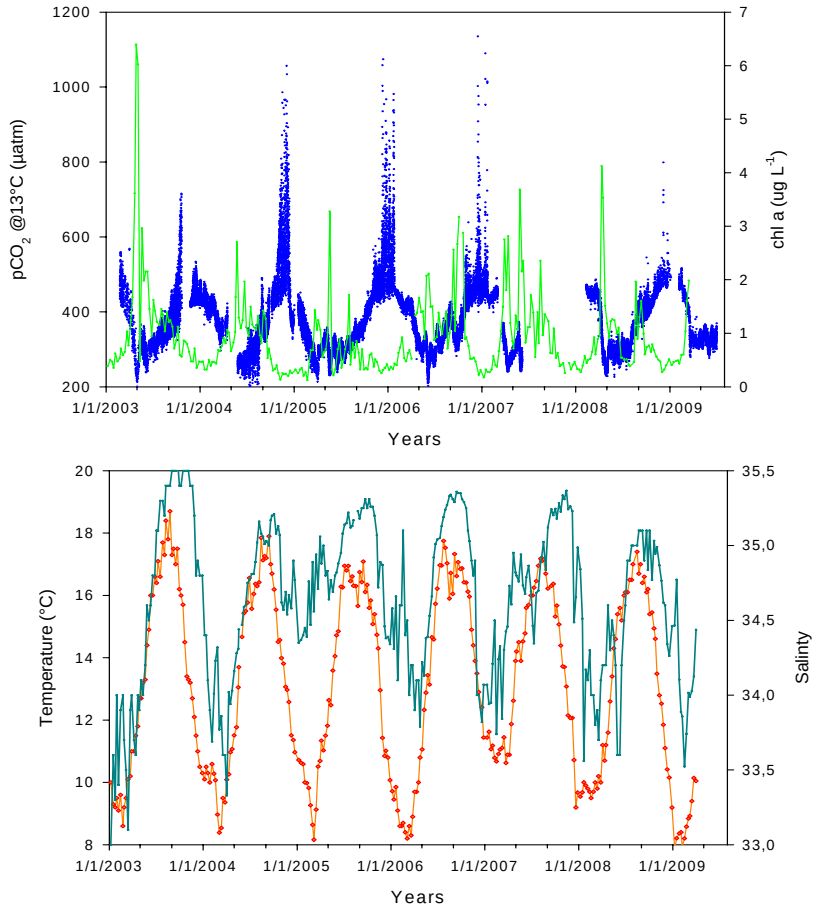

Figure 1: Surface waters evolution of pCO_2 normalized at the average temperature of 13°C (pCO_2@13°C, blue, hourly frequency) and concentrations of Chl a (green) (A), salinity (cygan) and temperature (red) (B) (weekly frequency).

3. RESULTS AND DISCUSSION

3.1. Dynamics of pCO_2 in surface waters at inter-seasonal to inter-annual levels

The seasonal variations of pCO_2 were rather typical of temperate coastal ecosystems in northern Europe with a clear drawdown of pCO_2 occurring during spring: A sudden decrease of 200 µatm (usually from an average value of 430 to 230 µatm) was for example observed within one month (April) in 2003, 2005 and 2008. This large drawdown of pCO_2 was followed by a slow increase of pCO_2 values during the following summer and late fall where pCO_2 values were usually back to an average

of 430 µatm before reaching maximum values of 600-800 µatm during winter months. The clear negative correlations of pCO_2 normalized at an average temperature of 13°C versus Chl *a* concentrations (Fig. 1) and dissolved oxygen (O_2) (not shown) suggested a strong control of the pCO_2 variations by biological processes (i.e. photosynthesis/respiration).

To estimate the impact of thermodynamics (T) versus biological processes (B) on the pCO_2 variations, we used the method of [14] over each annual cycle during the year 2003, 2004, 2005 and 2006. The T/B ratios <1 (0.49, 0.44, 0.38, 0.55, respectively) confirmed that the main driver of the pCO_2 dynamic in the Bay were the biological processes, which dominated significantly thermodynamics effects each year. For example, the temperature raise occurring during spring and summer months was responsible for an increase of pCO_2 values of ≈80 µatm whereas biological drawdown was in average 250 µatm during those months. As mentioned by [15,16], the method proposed by [14] can be a reasonable approach to assess the qualitative relative importance of temperature and biological processes on the pCO_2 dynamics in several coastal ecosystems. However, besides temperature and biology other physical/chemical processes can significantly affect the pCO_2 dynamics: freshwater discharge, tides (i.e. exchange between different water masses), sediment/water column exchanges, variations of Total Alkalinity (TAlk) and air-sea CO_2 fluxes. In the case of the macrotidal bay of Brest, vertical and horizontal redistribution of suspended material is usually strong periodically, during spring tides, and/or aperiodically especially during fall and winter storms. The large increase of pCO_2 observed during winter months is in part due to respiration of this resuspended organic matter produced during the spring period (as seen from the negative-correlation of particular organic Carbon (POC) vs pCO_2, not shown) but also to a larger inflow of freshwater with high pCO_2 content from the Aulne and Elorn rivers (salinity drawdown of 35.5 to 33.5, (Fig. 1)) from December to February.

On an inter-annual level, pCO_2 dynamics were rather similar, the pattern described above occurring every year with similar magnitude and few sudden events occurring at specific years. For example, during the late summer 2006, a bloom, characterised by an increase in Chl *a* concentrations of 3.15 µg L^{-1}, similar to those usually encountered during spring blooms, occurred and induced a drawdown of 100 µatm pCO_2 within a month. These types of sudden events can only be captured by long-term high frequency measurements thus reducing the uncertainty on global air-sea CO_2 fluxes estimates from one year to the other.

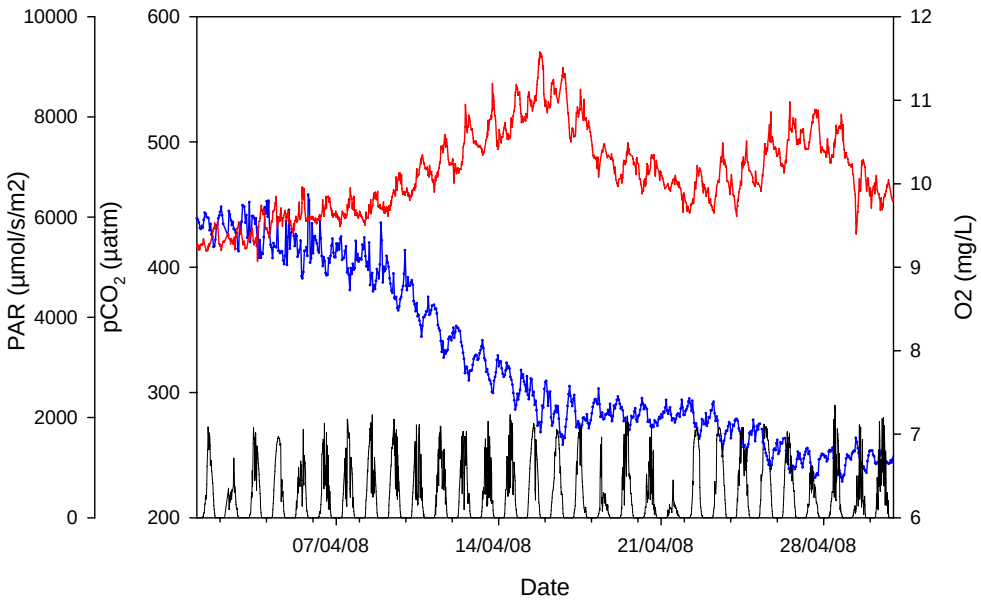

Figure 2 : Diurnal variations of pCO_2 (blue), O_2 (red) and PAR (black) during a spring bloom (April 2008) measured by the MAREL-Iroise buoy' and CARIOCA' sensors at a frequency of 60, 30 and 30 minutes, respectively.

3.2. Dynamics of pCO_2 in surface waters at sub-daily to weekly levels

As discussed in the previous section, biological uptake of pCO_2 via photosynthesis induced a pCO_2 drawdown of approximately 100, 75 and 200 µatm during April 2006, 2007 and 2008, respectively (with concomitant increase in dissolved oxygen of 0.7, 1.0 and 1.9 mg L^{-1}, respectively). During these three periods, we examined the relationship

between pCO_2, dissolved O_2 and the solar photosynthetically available radiation (PAR) to determine the impacts of the diel biological cycle, tides and freshwater inputs on pCO_2 dynamics at sub-daily to weekly levels. During all periods, pCO_2 and dissolved O_2 showed a clear negative correlation (Fig. 2). Drawdowns of pCO_2 ranging from 20 to 70 µatm were concomitant with increases of dissolved O_2 concentrations ranging from 0.3 to 0.7 mg L^{-1} and maximum PAR values (Fig. 2). Minimum pCO_2 and maximum O_2 values were observed at dusk whereas maximum pCO_2 and minimum O_2 values were observed at dawn. These variations were also slightly impacted by tide heights with slight increase in pCO_2 of approximately 5 µatm occurring during the night at low tide.

These observations revealed that the diel biological cycles were the main mechanisms controlling the pCO_2 diurnal variations during spring months, whereas no clear diurnal cycles have yet been found for the other seasons. The amplitude of diurnal pCO_2 variations represented 10% to 60% of the total pCO_2 drawdown occurring each year during the spring season because of primary production (Fig. 2). These results highlight the significance of diurnal variations of pCO_2 in estimates of air-sea CO_2 fluxes.

3.3. Estimation of air-sea CO_2 fluxes

For calculations of air-sea CO_2 fluxes, we used hourly average wind speed data from the Royal Netherlands Meteorological Institute for the area and atmospheric pCO_2 measured at the Mace Head station (Ireland) of the RAMCES network (Observatory Network of Green House gases). As discussed above, during the spring and summer periods, high biological activity (autotrophy) maintains low pCO_2 values in the surface waters of the bay inducing absorption of CO_2 from the atmosphere each year with monthly flows ranging from 0.15 mmol to 0.6 m^{-2} $month^{-1}$. During fall and winter, high wind speeds, associated with high CO_2 over saturation in the surface waters (from heterotrophic processes and freshwater inputs with higher pCO_2 content) are responsible for a strong degassing of CO_2 to the atmosphere with fluxes ranging from 0.1 to 0.9 mmol m^{-2} $month^{-1}$. We computed annual air-sea fluxes of CO_2 for the years 2003, 2004, 2005 and 2006 for which we had the most extensive datasets of pCO_2. Annual fluxes were remarkably constant with values of 1.6 (± 0.4), 1.5 (± 0.4), 0.8 (± 0.3) and 1.6 (± 0.2) mol m^{-2} yr^{-1}, respectively.

4. CONCLUSION

In the Bay of Brest, a macrotidal temperate coastal ecosystem, the biological processes (e.g. photosynthesis/respiration) were the main driver of seasonal and diurnal pCO_2 dynamics throughout six years of observations. Our study showed that the amplitudes of diurnal pCO_2 variations represented 10 to 60% of the pCO_2 drawdown observed each year during spring. Sub-daily variations of pCO_2 were therefore extremely relevant for annual estimates of CO_2 air-sea fluxes. The annual emissions of CO_2 from the surface waters to the atmosphere (+1.4 ± 0.4 mol m^{-2} yr^{-1}) were similar to those observed in macrotidal outer-estuarine plumes [17] with comparable salinity range. Our results provided one of the rare estimation of inter-annual variability of air-sea CO_2 fluxes based on high frequency measurements in a coastal ecosystem. The impacts of biogeochemical processes on air-sea CO_2 fluxes at different temporal scales could thus be identified rigorously. Further investigations will rely on additional sampling of the CO_2 system parameters (alkalinity, DIC) and assessment of the spatial variability of pCO_2 in the bay. Also, long-term records of these CO_2 systems parameters will improve our biogeochemical understanding of acidification in coastal environments surface waters.

5. ACKNOWLEDGEMENTS

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