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### Marine Chemistry



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# Diurnal to inter-annual dynamics of pCO<sub>2</sub> recorded by a CARIOCA sensor in a temperate coastal ecosystem (2003–2009)

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#### A R T I C L E I N F O

Article history: Received 28 June 2010 Received in revised form 7 February 2011 Accepted 17 March 2011 Available online 23 March 2011

Keywords: High-frequency sensors Air-sea CO<sub>2</sub> exchange Daily to inter-annual scale Carbon cycle Coastal ecosystems (47-49°N; 4-5.5°W)

#### $A \hspace{0.1in} B \hspace{0.1in} S \hspace{0.1in} T \hspace{0.1in} R \hspace{0.1in} A \hspace{0.1in} C \hspace{0.1in} T$

High-frequency pCO<sub>2</sub> and ancillary data were recorded for seven years during the first deployment of a CARbon Interface OCean Atmosphere (CARIOCA) sensor in the surface waters of a temperate coastal ecosystem, the Bay of Brest, which is impacted by both coastal (via estuaries) and oceanic (North Atlantic via the Iroise Sea) water inputs. The CARIOCA sensor proved to be an excellent tool to constrain the high pCO<sub>2</sub> variability in such dynamic coastal ecosystem. Biological processes (e.g. pelagic photosynthesis/respiration) were the main drivers of the seasonal and diurnal pCO<sub>2</sub> dynamics throughout seven years of observations. Autotrophic processes were responsible for abrupt pCO<sub>2</sub> drawdown of 100 to 200 µatm in spring. During the spring bloom, diurnal variations were driven by diel biological cycle. The average daily drawdown due to autotrophy (observed during highest daily PAR) was equivalent to 10 to 60% of the total pCO<sub>2</sub> drawdown observed every year during the spring season. From late summer to fall, heterotrophic processes increased pCO<sub>2</sub> in the surface water of the Bay back to the pre-bloom level. The average daily increase due to heterotrophy (observed during lowest daily PAR) corresponded to 10 to 70% of the total pCO<sub>2</sub> increase observed every year during the late summer to fall period. Air-sea CO<sub>2</sub> fluxes estimates based on hourly, daily and monthly calculations showed that careful consideration of the diurnal variability was needed to accurately estimate air-sea CO<sub>2</sub> fluxes in the Bay of Brest. Sampling only during daytime or night-time would induce 8 to 36% error on monthly air-sea CO<sub>2</sub> fluxes. This would in turn reverse the direction of the fluxes at annual level for the Bay. The annual emissions of CO<sub>2</sub> from the surface waters of the Bay to the atmosphere showed relatively low inter-annual variations with an average of  $+0.7\pm0.4$  mol Cm $^{-2}$ yr $^{-1}$  computed for the study period. Further, air-sea CO<sub>2</sub> fluxes computed for the adjacent inner-estuaries and Iroise Sea for an annual cycle were  $+\,17\pm3$  mol C  $m^{-2}yr^{-1}$  and  $-\,0.2\pm0.2$  mol C  $m^{-2}yr^{-1}$  , respectively. The spatial gradient showed a clear pattern from strong source to sink of CO<sub>2</sub>, from the inner-estuaries to the open oceanic waters of the North Atlantic. We suggest that semi-enclosed Bays act as buffers for sea to air emissions of CO<sub>2</sub> from inner estuaries to adjacent costal seas.

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#### 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. Over 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 (Borges et al., 2005; Cai et al., 2006; Thomas et al., 2004). In these extremely

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heterogeneous and dynamic coastal 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<sub>2</sub> fluxes despite their relatively small surface area (7% of the total ocean surface area). The spatial variability in airsea CO<sub>2</sub> fluxes is large from one ecosystem to the other and Chen and Borges (2009) recently proposed to classify continental shelves as sinks and near-shore ecosystems as sources of atmospheric CO<sub>2</sub>. This hypothesis is based on several studies, mainly relying on shipboard cruises that inferred air-sea CO<sub>2</sub> fluxes at seasonal levels in diverse regions of the world Ocean (see Chen and Borges (2009) and references therein).

Recently, Borges et al. (2010) pointed out the need for a global sea surface carbon observing system to unravel inorganic carbon dynamics in coastal ecosystems. Such an observing system would rely on Voluntary Observing Ship (VOS) and time-series measurements of the different parameters of the  $CO_2$  system in seawater for various coastal ecosystems. In this respect, the global estimate and the dynamics of air-sea  $CO_2$  fluxes in costal ecosystems would be improved by better constraining variations due to processes occurring at daily to inter-annual scales. Yet, data on the inter-annual variations of air-sea  $CO_2$  fluxes in the coastal ocean are very limited (Borges et al., 2008; Sakamoto et al., 2008). Similarly, comprehensive short scale dynamics of p $CO_2$  have been reported in very few coastal ecosystems (Borges and Frankignoulle, 1999; Yates et al., 2007; Dai et al., 2009; Nemoto et al., 2009).

Sensors allowing time-series measurements of partial pressure of  $CO_2$  (p $CO_2$ ) and dissolved  $O_2$  concentration ( $O_2$ ) with synoptic datasets of related physical and biological parameters (e.g. Temperature (T), Salinity (S), Photosynthetically Available Radiation (PAR), Fluorescence converted to Chlorophyll a (Chl a)) are effective tools to unravel the impact of water temperature, tides, photosynthesis/ respiration, calcification/dissolution of CaCO<sub>3</sub> on the variability of airsea CO<sub>2</sub> fluxes at scales going from daily to inter-annual levels (Zhai et al., 2009). In this context, the CARbon Interface Ocean Atmosphere (CARIOCA) sensor was originally developed for long term and high frequency measurements of pCO<sub>2</sub> in open ocean surface waters (Merlivat and Brault, 1995). Recently, CARIOCA measurements provided in-situ estimates of ocean biological production rates (Boutin and Merlivat, 2009). Alternatively, CARIOCA sensors can be excellent tools for investigating the high variability and the evolution of seawater surface pCO<sub>2</sub> in coastal environments.

Here we present high-frequency pCO<sub>2</sub> and ancillary data recorded for 7 years during the first deployment of a CARIOCA sensor on an automated moored system (MAREL-Iroise buoy) equipped with 5 other sensors (for T, S, O<sub>2</sub>, PAR, fluorescence acquisition) in the surface waters of a temperate coastal ecosystem, the Bay of Brest. This Bay is impacted by both coastal (Aulne and Elorn estuaries) and oceanic water inputs (North Atlantic through the Iroise Sea). The MAREL-Iroise buoy is located off the SOMLIT-Brest site of observation where additional weekly samplings for the above 5 parameters were performed. These extensive datasets were used to compare weekly vs high-frequency measurements of these parameters. More specifically, we focus on processes driving the  $pCO_2$  dynamics at sub-daily to inter-annual scales. Finally, based on complementary seasonal pCO<sub>2</sub> datasets acquired in the adjacent estuaries and Iroise Sea over a full annual cycle, we discuss the spatial variability of air-sea CO<sub>2</sub> fluxes from the inner-Bay to the outer shelf.

#### 2. Material and methods

#### 2.1. Study site

The Bay of Brest is a 180 km<sup>2</sup> semi enclosed ecosystem, located at the extreme West of Europe in Brittany, France (Fig. 1). The hydrology of the Bay is controlled by water exchanges with the Atlantic Ocean,



**Fig. 1.** Map of the study area with the location of the CARIOCA sensor installed on the MAREL-Iroise buoy, which is situated 100 m off the SOMLIT-Brest pier where weekly samples were collected. Also indicated are the two main estuaries Elorn and Aulne surrounding the Bay of Brest as well as the Iroise Sea, a marginal Sea on the continental shelf of the North Atlantic. The main track of the seasonal transects (---) made from the CARIOCA site to the adjacent surface waters of the Iroise Sea as well as in the Aulne and Elorn estuaries (o) are indicated.

through a 1.8 km wide strait connected to the Iroise Sea, and influenced by inputs of two main estuaries (namely Aulne and Elorn). The Aulne and Elorn estuaries comprise 80% of total freshwater inputs with average annual flows of 21 and 5 m<sup>3</sup>s<sup>-1</sup>, respectively. The Bay is a shallow basin with 50% of its surface shallower than 5 m, and only 13% (mainly the fairways of the main rivers and the main strait) more than 20 m deep (average depth 8 m) (Chauvaud et al., 2000). In this shallow macrotidal system (maximum tidal amplitude 8 m, tide periodicity: 12 h 15 min and 14 days, maximum tidal currents 2.6 ms<sup>-1</sup>), tidal currents and wind ensure that waters are well mixed throughout the year. Tidal variation during spring tide represents an oscillating volume of 40% of the high tide volume in the Bay. Between 1/35 and 1/25 of the Bay volume is renewed at each daily tide (Del Amo et al., 1997). The Bay waters remain mainly oceanic throughout the year with salinity values of 34.5–35.5 from spring to early fall. During fall and winter, average salinity range from 33.5 to 34.5 except during short floods, which may decrease the salinity down to minima of 26-28.

Previous studies of the chemical and biological properties of the Bay by Del Amo et al. (1997) showed that the surface waters of the Bay are characterized by phytoplankton blooms related to nutrients availability throughout the year. During winter, because of insufficient PAR, the stocks of nutrients are almost not consumed and the nitrate excess is usually exported to the adjacent ocean. From mid-February to October the surface waters of the Bay are characterized by a succession of phytoplankton blooms of different intensity: the winter-spring transition period (mid-February to early April) is usually marked by increasing Chl a concentrations. The spring period (April-May) is dominated by diatoms blooms, which usually developed under high initial nutrient concentrations. The collapse of the spring bloom by mid-May is usually followed by successive phytoplankton developments of secondary blooms during summer and early fall. Those secondary blooms develop under-lower nutrient concentrations, mostly originating from nutrient recycling. Recently, Beucher et al. (2004) showed that a possible shift from diatoms to dinoflagellates dominance might have occurred in the past ten years during these secondary blooms. The fall/ winter period is the period of lowest phytoplankton biomass activity and is characterized by heterotrophic processes and larger freshwater inputs from the two surrounding estuaries.

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