ABSTRACT

High-frequency pCO₂ 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 pCO₂ dynamics throughout six years of observations. The amplitudes of diurnal pCO₂ variations represented 10 to 60% of the pCO₂ drawdown observed each year during spring. Sub-daily variations of pCO₂ were therefore extremely relevant for annual estimates of air-sea CO₂ fluxes. The annual emissions of CO₂ from the surface waters to the atmosphere (+1.4 ± 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 CO₂ 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 CO₂ 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 CO₂ 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 CO₂. This hypothesis is based on several studies, mainly based on shipboard cruises that inferred air-sea CO₂ fluxes at seasonal levels in diverse regions of the world Ocean (see [4] and references therein). However, inter-annual variations of air-sea CO₂ 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 CO₂ (pCO₂) and related biogeochemical parameters at high frequency in the coastal ocean are needed to reduce the uncertainty on global air-sea CO₂ fluxes estimates. Simultaneous measurements of pCO₂ and dissolved O₂ (O₂) 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 CaCO₃ on the variability of air-sea CO₂ 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 pCO₂ 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 pCO₂ in coastal environments.

Here we present high-frequency pCO₂ 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$^3$s$^{-1}$, 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/).

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 pCO₂ normalized at an average temperature of 13°C versus Chl a concentrations (Fig. 1) and dissolved oxygen (O₂) (not shown) suggested a strong control of the pCO₂ variations by biological processes (i.e. photosynthesis/respiration).

To estimate the impact of thermodynamics (T) versus biological processes (B) on the pCO₂ 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 pCO₂ 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 pCO₂ 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 pCO₂ dynamics in several coastal ecosystems. However, besides temperature and biology other physical/chemical processes can significantly affect the pCO₂ dynamics: freshwater discharge, tides (i.e. exchange between different water masses), sediment/water column exchanges, variations of Total Alkalinity (TAlk) and air-sea CO₂ 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 pCO₂ 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 pCO₂, not shown) but also to a larger inflow of freshwater with high pCO₂ 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, pCO₂ 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 pCO₂ 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 CO₂ fluxes estimates from one year to the other.

3.2. Dynamics of pCO₂ in surface waters at sub-daily to weekly levels

As discussed in the previous section, biological uptake of pCO₂ via photosynthesis induced a pCO₂ 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 pCO₂, dissolved O₂ and the solar photosynthetically available radiation (PAR) to determine the impacts of the diel biological cycle, tides and freshwater inputs on pCO₂ dynamics at sub-daily to weekly levels. During all periods, pCO₂ and dissolved O₂ showed a clear negative correlation (Fig. 2). Drawdowns of pCO₂ ranging from 20 to 70 µatm were concomitant with increases of dissolved O₂ concentrations ranging from 0.3 to 0.7 mg L⁻¹ and maximum PAR values (Fig. 2). Minimum pCO₂ and maximum O₂ values were observed at dusk whereas maximum pCO₂ and minimum O₂ values were observed at dawn. These variations were also slightly impacted by tide heights with slight increase in pCO₂ 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 pCO₂ diurnal variations during spring months, whereas no clear diurnal cycles have yet been found for the other seasons. The amplitude of diurnal pCO₂ variations represented 10% to 60% of the total pCO₂ drawdown occurring each year during the spring season because of primary production (Fig. 2). These results highlight the significance of diurnal variations of pCO₂ in estimates of air-sea CO₂ fluxes.

3.3. Estimation of air-sea CO₂ fluxes

For calculations of air-sea CO₂ fluxes, we used hourly average wind speed data from the Royal Netherlands Meteorological Institute for the area and atmospheric pCO₂ 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 pCO₂ values in the surface waters of the bay inducing absorption of CO₂ from the atmosphere each year with monthly flows ranging from 0.15 mmol to 0.6 m²·month⁻¹. During fall and winter, high wind speeds, associated with high CO₂ over saturation in the surface waters (from heterotrophic processes and freshwater inputs with higher pCO₂ content) are responsible for a strong degassing of CO₂ to the atmosphere with fluxes ranging from 0.1 to 0.9 mmol m⁻²·month⁻¹. We computed annual air-sea fluxes of CO₂ for the years 2003, 2004, 2005 and 2006 for which we had the most extensive datasets of pCO₂. 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 pCO₂ dynamics throughout six years of observations. Our study showed that the amplitudes of diurnal pCO₂ variations represented 10 to 60% of the pCO₂ drawdown observed each year during spring. Sub-daily variations of pCO₂ were therefore extremely relevant for annual estimates of CO₂ air-sea fluxes. The annual emissions of CO₂ 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 CO₂ fluxes based on high frequency measurements in a coastal ecosystem. The impacts of biogeochemical processes on air-sea CO₂ fluxes at different temporal scales could thus be identified rigorously. Further investigations will rely on additional sampling of the CO₂ system parameters (alkalinity, DIC) and assessment of the spatial variability of pCO₂ in the bay. Also, long-term records of these CO₂ systems parameters will improve our biogeochemical understanding of acidification in coastal environments surface waters.

5. ACKNOWLEDGEMENTS

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6. REFERENCES


