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Air-sea CO_2 fluxes measured by eddy covariance in a coastal station in Baja California, México

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Abstract. The influence of wave-associated parameters controlling turbulent CO_2 fluxes through the air–sea water interface is evaluated in a coastal region. The study area, located within the Todos Santos Bay, Baja California, México, was found to be a weak sink of CO_2 with a mean flux of -1.32 μmol m^{-2}s^{-1}. The low correlation found between flux and wind speed ($r = 0.09$), suggests that the influence of other forcing mechanisms, besides wind, is important for gas transfer modulation through the sea surface, at least for the conditions found in this study. In addition, the results suggest that for short periods where an intensification of the wave conditions occurs, a CO_2 flux response increases the transport of gas to the ocean.

1. Introduction

Gas transfer at the sea surface is one of the most important factors regarding global climate and long-term climate changes. Despite its importance, there is still great uncertainty in how to parametrize these processes in order to include them in global climate models; this uncertainty exposes the need to increase our knowledge of gas transfer controlling mechanisms. Recently, the importance of carbon fluxes in the coastal zone have been recognized as a major piece of the global carbon cycle [1]; yet estimates of CO_2 fluxes in the coastal zone are not well constrained; a wide range of values has been reported in the literature [2]. It is therefore essential to understand and accurately account for the factors regulating these fluxes in order to accurately estimate their contribution to the ocean and to the global carbon budget [3].

Under calm conditions, gas exchange through the ocean surface occurs by molecular diffusivity due to the difference in gas concentrations between air and water phases. Some studies, however (see e.g., [4],[5],[6],[7]), have shown that turbulent processes in the atmospheric and oceanic boundary layers tend to enhance the efficiency of gas transfer by modifying the behavior of the diffusive layer. This efficiency can be represented by a resistance of the surface and expressed by a transfer velocity. Thus, air-sea CO_2 exchange can be parametrized as,

$$F_{CO_2} = k_{CO_2} K(\Delta pCO_2) \tag{1}$$

where F_{CO_2} is the air-sea flux, k_{CO_2} is the transfer velocity, K is the solubility of CO_2 and ΔpCO_2 is the difference between the partial pressure of CO_2 in the water and in the atmosphere [8].

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Usually, K and ΔpCO_2 can be determined with precision; it is in the expression of k_{CO_2} where we find the greatest uncertainty when estimating F_{CO_2} [9]. In the ocean, k is commonly expressed as a wind speed function, but it is well known that many other processes including a variety of physical and biogechemical factors can be important when estimating gas fluxes through the sea surface. Further efforts have to be made to understand and include the physical forcings in these parameterizations to achieve closure of the global carbon budget; furthermore, a reduction of the uncertainties in the coastal ocean flux estimates is necessary to be able to extrapolate our understanding of carbon dynamics from local to global scales [3].

The coastal ocean covers only 7% of the total ocean surface [10] but is responsible for up to 30% of the oceanic primary production, 30% to 50% of inorganic carbon and close to 80% of organic carbon burial in sediments [11]. These characteristics, in addition to the physical processes, make the coastal regions very active and heterogeneous ecosystems. The fluxes in these areas are not well represented by the mentioned parametrizations and the lack of high spatial and temporal resolution data hinders the inclusion of the global coastal regions in climate models and leaves open the question of whether these regions are sinks or sources of CO_2.

Previously, Reimer *et al.* [12] compared the CO_2 fluxes at two sites in Todos Santos Bay (TSB), reporting larger fluxes in the intertidal zone than in a site $\sim$ 3 km offshore. Though they carried out different techniques at the two measurement sites, and direct measurements were made only in the intertidal zone, they attribute the differences in the estimated fluxes to the characteristics of the physical forcings at each site.

In this study we present the results of a continuous measurement campaign from which we obtained a full year of high quality data for air-sea CO_2 fluxes in a coastal region. Based on this information we aim to evaluate the influence of wave-associated parameters as controlling mechanisms on turbulent CO_2 fluxes through the air-sea interface. CO_2 and H_2O fluxes were estimated using the eddy covariance method, described in section 2; the main results of this work are presented in section 3, where the relationship between the fluxes and physical parameters such as wind and the wave field is discussed; and in section 5, conclusions and plans for future work are presented.

2. Data and methods

Todos Santos Bay is a small bay ($\sim$ 180 km^2) in the Baja California west coast, approximately 100 km south of the Mexican–U.S. border. The basin is connected to the Pacific Ocean through two segments to the north and south of Todos Santos Island (TSI). The bay has a depth of 50 m in about 80% of its area [13]. TSB lies in a region where upwelling occurs year round, with March–August the months of strongest and more sustained events [14]. The California Current has a strong influence on the thermohaline characteristics of TSB. A sea–land breeze system [15] is one of the main characteristics of TSB, with strong winds from the sea during the day and lower intensities from land during the night.

The study area, known as Punta Morro, is located at the northwest of TSB (figure 1), where direct measurements of CO_2 and water vapor were carried out in a coastal station from May 2014 to April 2015. The measurement tower (figure 2), located on the shoreline at $31°51'41''$N, $116°40'07''$W, was instrumented with two open-path gas analyzers (LI-7500, LI-COR Biosciences) and a sonic anemometer (R3-100 Professional 3D Anemometer, Gill Instruments), all at a height of 13 m above the mean sea level, with a sampling rate of 20 Hz and, given the accessibility of the place, all were powered directly from the electrical network. We only use data retrieved from one of the two gas analyzers because of one instrument failure. In order to reduce the optical contamination, a cleaning system was installed in the functional gas analyzer. Hourly wave data were recorded at 2 Hz using an acoustic Doppler current profiler (Workhorse Sentinel ADCP, Teledyne RD Instruments) deployed at a depth of 10 m and 350 m away from the tower at $31°51'39.6''$N, $116°40'20.28''$W.

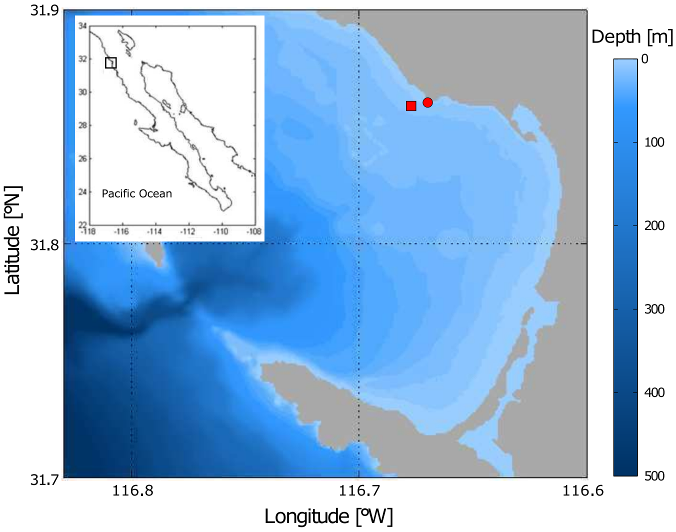

Figure 1. Map of the study site at Todos Santos Bay, Baja California, México. The symbols show the location of the ADCP (■) and the measurement tower (●).

Figure 2. Measurement tower located on the shoreline and instrumented with a sonic anemometer and two open-path gas analyzers.

The CO_2 and water vapor fluxes (hereinafter FCO_2 and FH_2O, respectively) were estimated using the eddy covariance (EC) method [16], which has become the primary method for the estimation of turbulent fluxes in terrestrial and coastal applications. Estimating gas fluxes through EC in the coastal zone allows several timescales to be included in the estimation and resolution of the temporal variability induced by the tidal, diurnal and seasonal cycles [10]. On the other hand, the method is challenging and several corrections are needed to accomplish the physical and theoretical requirements [16]. The EC technique is a non-invasive method that allows gas flux estimations based on measurements of the covariance between fluctuations in the vertical wind velocity and the gas mixing ratio with a high temporal resolution [17]. The general equation describing the flux (F) is:

$$F = \overline{\rho_a w' s'} \tag{2}$$

where ρ_a is the air density [kg m^{-3}], w is the vertical component of the wind speed [m s^{-1}] and s is the mixing ratio of CO_2 and water vapor, with the primes indicating that these values are the fluctuation about their respective means and the overbar indicating the temporal average.

For this study and based on a co-spectral analysis, the averaging period was chosen to be 15 min for the flux estimation and the turbulent fluctuations were obtained through Reynold's decomposition. Quality control procedures were applied to the data before estimating the fluxes. These include de-spiking [18], coordinate rotation [19], sonic corrections [20], atmospheric stability analysis and estimation of mixing ratios as proposed by Sahlée *et al.* [21] to discard the effect of temperature and moisture fluctuations in the FCO_2 estimations. Only on-shore wind directions were taken into account.

The estimated fluxes through the EC method are representative of a certain area, referred to as the footprint; this area depends on parameters such as sensor height, sea surface roughness, atmospheric stability and wind speed. Here we estimated the footprint following Kormann and Meixner [22] and found that in 60% of the cases, under neutral atmospheric conditions, 70%

of the total FCO_2 occurred between the shoreline and 400 m offshore in the predominant wind direction; under unstable conditions (27% of the cases) 45% of the total flux came from the same area close to the shore. On the other hand, the footprint values found under stable conditions were too large (several kilometres) and the FCO_2 under these conditions ($z/L > 1$) were not taken into account.

Applying the SWAN wave model (see [23] and [24]) and considering the directional wave spectrum from the ADCP as a boundary condition, we simulate the wave field over the area covering from the measurement tower to the ADCP (350 m offshore) location. In addition to the integral parameters obtained, the wave steepness and the energy dissipation due to wave breaking were estimated.

3. Results

Wind speed conditions were low to moderate during the entire year with an average value of 4 m s^{-1} and oncoming predominantly from the northwest (figure 3), which is known to induce upwelling [12],[25]. The maximum significant wave height (H_s) recorded was 2.7 m and the average value for the whole year was 0.8 m with the prevailing direction from the southwest due to depth refraction. The description of the environmental parameters is shown in table 1.

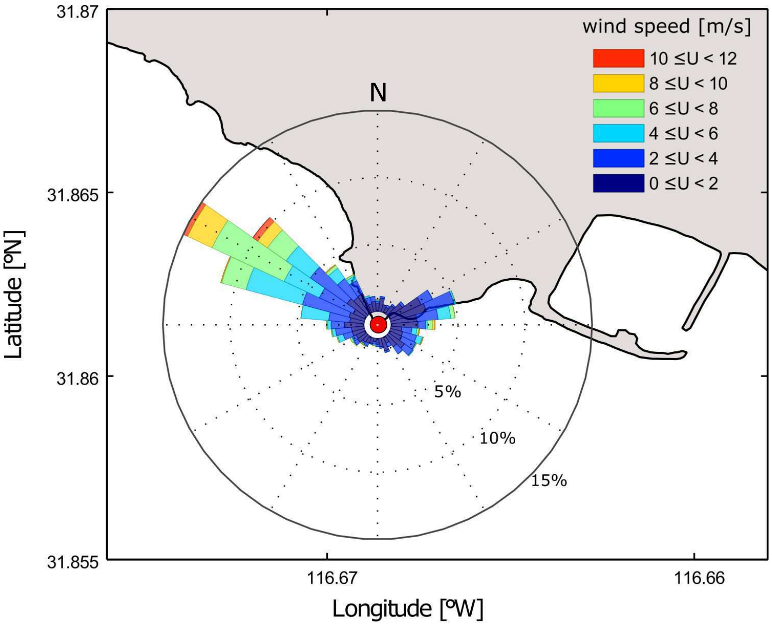

Figure 3. Wind rose at Punta Morro station. The bars indicate the oncoming wind direction, the colors the wind speed and the concentric circles indicate the frequency of occurrence of the data.

Table 1. Environmental parameters measured at Punta Morro from May 2014 to April 2015.

Parameter	Mean ± STD	Min.–Max.	Direction
Wind speed [m s^{-1}]	4.02 ± 2.48	$0.06 - 11.78$	NW
H_s [m]	0.80 ± 0.22	$0.39 - 2.69$	SW
Air Temp. [°C]	20.53 ± 3.59	$8.87 - 32.69$	–
Water Temp. [°C]	16.77 ± 1.78	$12.56 - 21.75$	–
CO_2 conc. [mmol/m^3]	12.58 ± 2.71	$6.55 - 19.43$	–
H_2O conc. [mmol/m^3]	804.41 ± 503.04	$0.66 - 2488.3$	–

The study area was found to be a weak sink of CO_2 during the whole period, with a mean flux and standard deviation of -1.32 ± 8.94 μmol m^{-2}s^{-1}. The estimated CO_2 fluxes are in accordance with Liu *et al.* [26] and Borges *et al.* [2], who suggest that on a global scale, coastal regions are weak sinks of carbon. The mean flux and standard deviation found for H_2O were 0.77 ± 1.28 μmol m^{-2}s^{-1}. There is no particular pattern in the behavior of the fluxes, neither for CO_2 or H_2O (figure 4), but a larger scatter of the data is noticeabe during December–April. This behavior is consistent with the increase of significant wave height (figure 5). Nevertheless, the mean values of FCO_2 remain negative and of similar magnitude in both seasons, indicating that the wave field may be having an effect on the transfer but not modifying the average behavior or describing the direction of the flux.

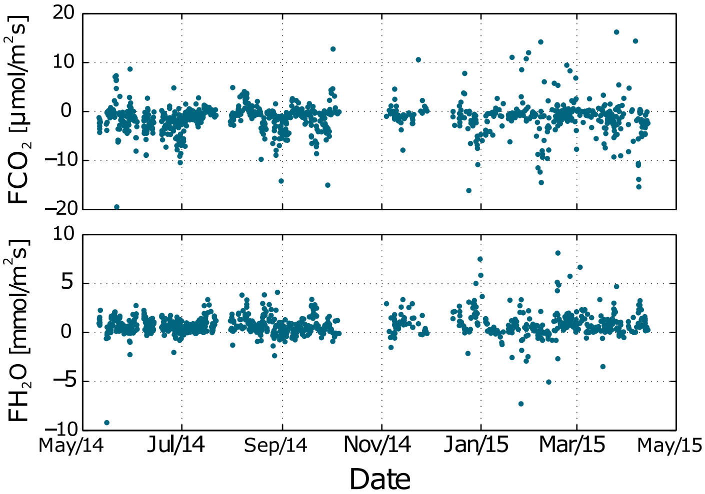

Figure 4. Estimated FCO_2 (upper panel) and FH_2O (lower panel) using 15-min average periods.

Time series of the mean significant wave height, as well as the parameters related to the wave breaking obtained from SWAN model computations are shown in figure 5. An increase of the significant wave height is noticeable for the period October–April with a maximum significant wave height of 2.64 m (figure 5a). This behavior is reflected as an increase in the energy dissipation during that period due to wave breaking (figure 5c), which in coastal regions is known to be the main source of dissipation and for this study was found to be equivalent to the total dissipation. The wave steepness (figure 5b) does not show the same seasonal behavior and maximum values are observed throughout the year, suggesting breaking of smaller waves with less energy dissipation May–October.

To find a relationship between the fluxes and the key physical processes of the region, we represent the fluxes estimated during the entire year as a function of the wind speed and the wave steepness, the latter as an indicative parameter of wave breaking. The results are shown in table 2. The weak correlation between the fluxes and the wind speed suggests that other physical and biological processes may be important factors for gas exchange modulation in coastal waters, but the idea of the wind being a major factor in controlling the fluxes at smaller time scales is not rejected. Similarly, the correlation between fluxes and wave steepness is not enough to establish any relation between both processes and further analysis of the wave field is needed to accomplish a quantitative evaluation of the effect of ocean surface waves on gas exchange in the coastal zone.

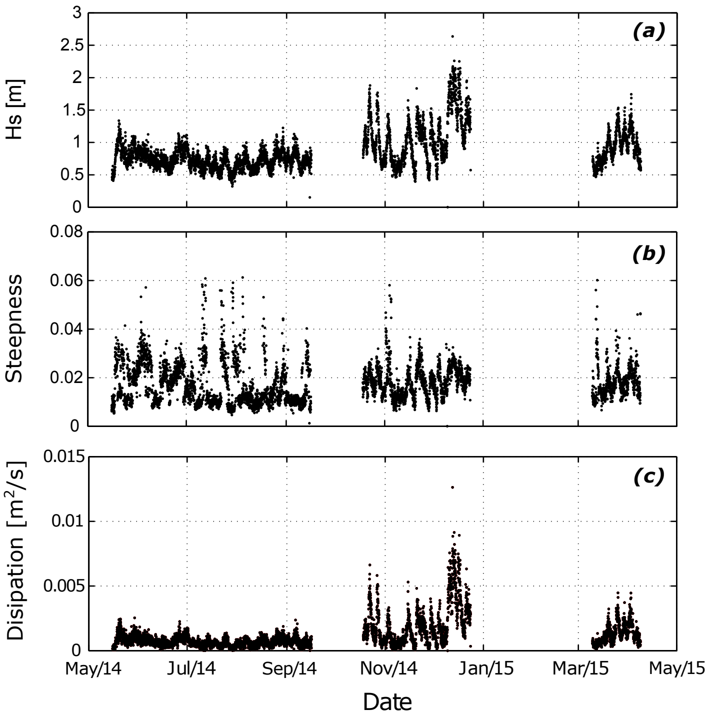

Figure 5. Spatial averages for (*a*) significant wave height (H_s), (*b*) wave steepness obtained as the ratio between H_s and the wavelenght (L), and (*c*) dissipation due to wave breaking.

Table 2. Statistical description of the relationship between fluxes and the physical parameters.

	Correlation (r)	Lower limit*	Upper limit*	p-value**
FCO_2 vs. wind speed	−0.09	−0.15	−0.03	0.0061
FH_2O vs. wind speed	0.32	0.26	0.38	< 0.0001
FCO_2 vs. steepness	−0.16	−0.24	−0.08	0.0002
FH_2O vs. steepness	0.16	0.08	0.24	0.0001

* 95% confidence interval.
** All correlations were statistically significant at $p< 0.05$.

Wave steepness is used as a indicative parameter of wave breaking but in this case we found that it does not explain gas flux behavior. This is because fluxes are not affected directly by the presence of breaking waves but rather by the magnitude of the turbulent processes modifying the air-sea interface at both water and air boundary layers. This explains the low correlation between the fluxes and the wave steepness presented in table 2.

Two 7-day periods with high dissipation rates were selected for further analysis. Good agreement between FCO_2 and the significant wave height was found for these periods with a correlation coefficient of $r = -0.56$ and statistical significance (figure 6).

4. Conclusions

A full year of high-quality coastal CO_2 air–sea flux data are presented. The observation area of TSB was found to be a weak sink of CO_2 for the entire year, based on measurements made between May 2014 and April 2015, with a mean CO_2 flux of -1.32 μmol $m^{-2}s^{-1}$. The low correlation between CO_2 flux and wind speed ($r = -0.09$) suggests that the influence of other forcing mechanisms is important for the transfer modulation through the sea surface, at least for the conditions observed during this study.

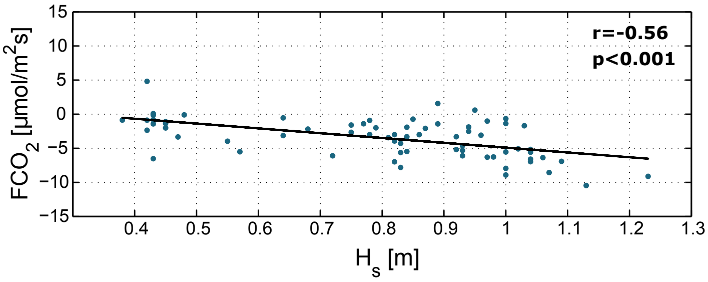

Figure 6. FCO_2 vs. significant wave height (H_s) during two 7-day periods with high dissipation due to wave breaking.

An increase in the wave field was observed for the period December–April, apparently causing scatter in both CO_2 and H_2O fluxes even when no seasonality was found in the flux behavior; this indicates that the wave field may have an effect on gas transfer but did not modify the average behavior.

The dissipation rate caused by the breaking waves was estimated using the SWAN waves model as a measurement of the turbulence caused by the wave field. Good agreement ($r = -0.56$) between the CO_2 flux and significant wave height (H_s) is evident for two periods during which the average dissipation rate increased. The results suggest that for short periods where an intensification of the wave conditions occur, a CO_2 flux response increases the flux into the ocean. This response was not observed for the entire period, which indicates that the effect of other biochemical and physical processes are also important. Further analysis will be needed to better understand the conditions under which the wave field plays a major role in gas flux behavior and to what extent.

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