

**A CO₂ sink in an
eutrophic tropical
coastal embayment**

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A large CO₂ sink enhanced by eutrophication in a tropical coastal embayment (Guanabara Bay, Rio de Janeiro, Brazil)

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Abstract

In contrast to its small surface area, the coastal zone plays a disproportionate role in the global carbon cycle. Carbon production, transformation, emission and burial rates at the land–ocean interface are still poorly known, especially in tropical regions.

5 Surface water $p\text{CO}_2$ and ancillary parameters were monitored during nine field campaigns between April 2013 and April 2014 in Guanabara Bay, a tropical eutrophic to hypertrophic semi-enclosed estuarine embayment surrounded by the city of Rio de Janeiro, SE-Brazil. Water $p\text{CO}_2$ varied between 22 and 3715 ppmv in the Bay showing spatial, diurnal and seasonal trends that mirrored those of dissolved oxygen

10 (DO) and Chlorophyll *a* (Chl *a*). Marked $p\text{CO}_2$ undersaturation was prevalent in the shallow, confined and thermally stratified waters of the upper bay, whereas $p\text{CO}_2$ oversaturation was restricted to sites close to the small river mouths and small sewage channels, which covered only 10% of the bay's area. Substantial daily variations in $p\text{CO}_2$ (up to 395 ppmv between dawn and dusk) were also registered and could

15 be integrated temporally and spatially for the establishment of net diurnal, seasonal and annual CO_2 fluxes. In contrast to other estuaries worldwide, Guanabara Bay behaved as a net sink of atmospheric CO_2 , a property enhanced by the concomitant effects of strong radiation intensity, thermal stratification, and high availability of nutrients, which promotes phytoplankton development and net autotrophy. In the inner

20 part of the bay, the calculated annual CO_2 sink ($-19.6 \text{ mol C m}^2 \text{ yr}^{-1}$) matched the organic carbon burial in the sediments reported in the literature. The carbon sink and autotrophy of Guanabara Bay was driven by planktonic primary production promoted by eutrophication, and by its typology of marine embayment lacking the classical extended estuarine mixing zone, in contrast to river-dominated estuarine systems, which are generally net heterotrophic and CO_2 emitters. Our results show that global

25 CO_2 budgetary assertions still lack information on tropical estuarine embayments and lagoons, which are affected by thermal stratification and eutrophication and behave specifically with respect to atmospheric CO_2 .

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1 Introduction

The rising of atmospheric CO₂ concentration in the last decades has worldwide concern, mainly due to global atmospheric temperature increases (Allen et al., 2009; Matthews et al., 2009) and ocean acidification (Doney et al., 2009). The oceans are known to act as the major sink of atmospheric CO₂, with well quantified air–sea exchange and uptake of excess anthropogenic CO₂ (Takahashi et al., 2002; Sabine et al., 2004; Orr et al., 2005). The coastal ocean, however, is still subject to controversy and poorly understood due to its intrinsic intra- and inter-specific heterogeneity of its typology. The lack of sufficient studies covering the spatial and temporal variability with a common standardized sampling strategy and methodology and the manifold diverse types of ecosystems types (estuaries, deltas, embayments and coastal lagoons) affected by multiple external and internal sources, are some of the reasons for these uncertainties (Gattuso et al., 1998; Borges, 2005; Chen et al., 2013; Cloern et al., 2014). Despite the small surface area of the coastal ocean of around 7% of the global ocean, it exerts a disproportionately large influence upon the carbon cycle, especially on the role of primary production, remineralisation and sedimentation of organic matter (Gattuso et al., 1998; Wollast, 1998). Coastal ecosystems receive material from land via river inputs, submerged groundwater discharge, atmospheric deposition, as well as from the adjacent open ocean. The climatological regime has great influence over these areas, and contributes to the great variability of biogeochemical processes in space and time. In addition, approximately 37% of human population lives within 100 km of coastline (Cohen et al., 2007), making this area of greatest human impact on the marine environment, and suite a lot of anthropogenic perturbations, including intense loading of nutrients, suspended matter, organic and inorganic matter with associated pollutants, and also overfishing, (Bauer et al., 2013).

Several authors have demonstrated that the CO₂ emissions from estuaries are globally significant (Borges and Abril, 2011; Chen et al., 2013). Total ecosystem respiration generally exceeds gross primary production (GPP) in most estuaries

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(Gattuso et al., 1998), which net heterotrophic ecosystems and sources of atmospheric CO₂ (Borges and Abril, 2011; Cloern et al., 2014). LOICZ budgetary assertions of more than 250 estuaries and lagoons have also shown that most of them are heterotrophic or may have a balanced metabolism (Knoppers, 1994; Smith et al., 2010). CO₂ outgassing in major part of the estuaries is supported by the inputs of CO₂-enriched freshwaters, and by the CO₂ generated in the estuarine system itself, planktonic and benthic net heterotrophy and CO₂ advection from saltmarshes and mangroves (e.g. Borges and Abril, 2011; Cai, 2011). On the other hand, low *p*CO₂ waters and autotrophic metabolism has been observed in some estuarine plumes but with small percentage of surface area compared to the freshwater influence (Borges and Abril, 2011). As more systems are being included in the budgeting effort, the global estuarine CO₂ emission estimate at the air–water interface has been declining (Borges and Abril, 2011; Chen et al., 2013). The pioneer estimate of the CO₂ released by estuaries was 0.51 PgCyr⁻¹ (Borges, 2005), whereas the more recent estimate was 0.094 PgCyr⁻¹ (Chen et al., 2013). In fact, first budgets were based on data in systems generally located at temperate regions, being river-dominated, macrotidal and turbid (Borges, 2005; Borges and Abril, 2011). The more recent estimate includes a set of new data from estuaries located at low wind regions and the Arctic Ocean, which contributed to the decrease of the carbon released (Chen et al., 2013). Additionally, Jiang et al. (2008) demonstrated that *p*CO₂ can be significantly lower in marine-dominated estuaries than river-dominated, and according to Maher and Eyre (2012) marine dominated estuaries with low freshwater influences can be CO₂ sink.

In tropical regions, the spatial coverage of CO₂ fluxes of estuaries is still incipient. But, the few available studies also suggested that the tropical estuaries seem to be sources of carbon to the atmosphere (Souza et al., 2009; Sarma et al., 2012; Araujo et al., 2014), except for one lagoon (Koné et al., 2009) and the Amazon River plume (Körtzinger, 2003) which acted as sinks. Also, most studies are potentially biased by the lack of information on the diurnal variations of CO₂, which corresponds to a crucial

component of mass balance calculations (Borges and Frankignoulle, 1999; Zhang et al., 2013; Maher et al., 2015).

The CO₂ budgets of coastal ecosystems may also be altered by eutrophication generated by the anthropogenic nutrient inputs from sewage and fertilizer usage in agriculture, which has become a widespread water quality issue (Nixon, 1995; Cloern, 2001). The consequences of eutrophication, like the development of excessive algal blooms, toxic algae, loss of submerged aquatic vegetation and increase of hypoxia and anoxia, has been well documented (Bricker et al., 2003; Rabalais et al., 2009). However, the influence of eutrophication per se on the CO₂ budgets is poorly documented. In fact, the response of estuarine metabolism to eutrophication seems to be type-specific. Some papers discussed that eutrophication can amplify autotrophy and favour CO₂ uptake (Gypens et al., 2009), while others show that eutrophication can reinforce heterotrophy and CO₂ degassing (Sarma et al., 2012; Chou et al., 2013; Wallace et al., 2014).

The present study addresses the question whether a tropical, marine-dominated, and eutrophic estuarine system Guanabara Bay (SE-Brazil) is a sink or a source of atmospheric CO₂. The bay, surrounded by the City of Rio de Janeiro, is the second largest Brazilian estuarine embayment (Kjerfve et al., 1997). The system is one of the most degraded estuaries worldwide. The waters of Guanabara are eutrophic to hypertrophic and, as such, provide ideal conditions to assess the response of aquatic CO₂ metabolism under marked eutrophication. CO₂ fluxes at the air–water interface of Guanabara Bay were estimated with continuous monitoring of surface water pCO₂, taking into account different temporal (daily and seasonal) and spatial scales. Our results show a very different behaviour in terms of carbon cycling of Guanabara Bay compared to previously documented estuaries, with extreme low values of pCO₂ and a net uptake of atmospheric CO₂ annually.

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2 Material and methods

2.1 Study site

Guanabara Bay (22°41'–22°58' S and 43°02'–43°18' W) is located at the SE-Brazil coast, SW-Atlantic, and embedded within the metropolitan area of Rio de Janeiro, the second most densely populated region of the Brazilian Coast (Fig. 1). The bay has a surface area of 384 km², a mean depth of about 5.7 m, and a volume of 1870 × 10⁶ m³. The main subaqueous channel runs from the bay's 1.8 km wide entrance with depths varying from 25 to 50 m up to 6 km inwards and along 24 km to the upper 20 km wide bay, with depths down to about 2–3 m. The lateral portions of the bay are spiked by small bays, with depths of 2 m. It is a partially mixed estuarine embayment (Kjerfve et al., 1997), being moderately stratified in wintertime, but can become highly stratified in summertime due to concomitant effects of sunlight (thermal stratification) and freshwater discharge (haline stratification) mostly in the central and inner regions (Bérgamo, 2010).

The Bay is subject to a semi-diurnal microtidal regime with an annual mean of 0.7 m and spring tides attaining 1.3 m. With the exception of the entrances of small rivers, salinities vary between 25 and 34. The time for renewal of 50% of the total water volume is 11.4 days and water circulation is complex, as currents are modulated by tide and abrupt changes in the geomorphological configuration (Kjerfve et al., 1997). Circulation between the central and upper western regions is hampered by the presence of a large island (Ilha do Governador, Fig. 1). At the bay's mouth, maximum water velocities vary between 0.8 and 1.5 ms⁻¹ and seawater residence time is much shorter than in most inner regions, particularly behind Ilha do Governador, where maximum current velocities are less than 0.3 ms⁻¹ (Kjerfve et al., 1997).

Guanabara Bay is located in the intertropical zone and its climate is characterized by a diversity of both the annual temperature and precipitation regimes. The weather is tropical humid (Bidone and Lacerda, 2004), with a warm and wet summer in October–March, and a cooler and drier winter in April–November. The most frequent winds in

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the bay from the N and NE in spring and summer, with monthly average velocity of 5 m s^{-1} . Winds from the S and SE are associated with polar cold weather fronts being more common in autumn and winter (Amarante et al., 2002).

The drainage basin has an area of 4080 km^2 and includes 35 small rivers and streams, 6 of which flow into the upper region of the bay and contribute with up to 85% of the total runoff to the bay. The average annual freshwater water discharge to the bay is $100 \pm 59 \text{ m}^3 \text{ s}^{-1}$ and ranges from around $40 \text{ m}^3 \text{ s}^{-1}$ in winter to $190 \text{ m}^3 \text{ s}^{-1}$ in summer. Annual freshwater discharge is nine times smaller than the bay's volume, which also contributes to the two-layered gravitational circulation (the ebb-flood oscillatory tidal current), resulting in the predominant saline (i.e. polyhaline) character of the waters (Kjerfve et al., 1997).

More than 7 million inhabitants discharge $25 \text{ m}^3 \text{ s}^{-1}$ of untreated domestic wastewaters into the bay (Kjerfve et al., 1997; Bidone and Lacerda, 2004), which contributes to a load of about 465 T day^{-1} of organic matter (FEEMA, 1998). Small channels directly connected to sewage outlets are totally anoxic, but represents only about 3% of the surface area of the Bay. More intense cultural eutrophication since the 50's (Borges et al., 2009) also contributed to hypoxic conditions of bottom waters in some of the more confined lateral and upper regions of the bay (Paranhos et al., 1998; Ribeiro and Kjerfve, 2002). Fluxes of phosphorous are currently 9 times higher than those estimated since the late 1800s (Borges et al., 2009). According to Godoy et al. (1998), sedimentation rates have increased up to 14 times over the last 50 years, in parallel with a 10-fold increase in the flux of organic matter to the sediments (Carreira et al., 2002).

In this study, five sectors were defined for the treatment, computations and interpretation of the data (Fig. 1): sector one (S1) corresponds to the region up to 3 km inwards from the narrow and deeper tidal channel, is characterized by a maximum of seawater exchange, material dispersion and is partially mixed. Sector two (S2), located towards the western part of the bay, is delimited on the north by the Island of "Ilha do Governador", which creates a barrier for direct tidal advection of waters into the upper

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north-western area of the bay. It is one of the most contaminated areas of Guanabara Bay. Sector three (S3) corresponds to the deeper channel which connects S1 (i.e. the bay's outlet to the South Atlantic) with the upper region. Sector four (S4) in the upper northeastern part of the bay, is shallow, moderately impacted and bordered by a 90 km² of mangrove forest and non-urbanized land. Sector five (S5) is the most confined area of the bay, located at the northwest and behind Ilha do Governador. It is shallow, has the longest residence time of waters and also receives significant amounts of sewage waters. The small western channel connecting S2 and S5 was disregarded from our analysis, due to its difficult access and extreme degree of contamination; however, it only covers less than 10 % of the entire bay.

2.2 Sampling strategy

Nine sampling campaigns were performed with a frequency varying between 30 to 45 days from April 2013 to April 2014. Each campaign consisted in continuous measurements of the partial pressure of CO₂ ($p\text{CO}_2$), salinity, temperature, Chl *a*, DO, pH and GPS position, all at a frequency of 1 min. Sub-surface (~ 30 cm) water was pumped alongside the boat. In addition to the spatial screening, the diurnal variations of water $p\text{CO}_2$ were estimated on four occasions within the upper and most eutrophic sectors (S4 and S5) and also once in S1, by performing lateral trajectories forth and back across the sectors from dawn (4:30 a.m.) to afternoon or dusk (at the latest until 9:30 p.m.). Diurnal measurements were made in August 2013 and January, February and April 2014 (S4 and S5) and in S1 in April 2014.

In addition, discrete sampling was performed at 16 to 19 stations along the continuous tracks (Fig. 1), except in December 2013, when only 8 stations could be sampled due to logistical problems. Water samples were collected in sub-surface waters at a ~ 30 cm depth with a Niskin bottle, and then conditioned (i.e. fixed and/or kept on ice in the dark) for further chemical analysis in the laboratory. Vertical profiles of temperature, salinity, fluorescence and DO were performed at all discrete stations with an YSI 6600 V2 multiparameter probe.

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2.3 Analytical procedures

2.3.1 Discrete parameters

Total alkalinity (TA) was determined on 100 mL filtrate from GF/F filtered samples, using the classical Gran (1952) electro-titration method by an automated titration system (Metler Toledo Mod. T50). The reproducibility of TA was $4 \mu\text{mol kg}^{-1}$ ($n = 7$). Measurements were compared to certified reference material (CRM provided by A.G. Dickson from Scripps Institution of Oceanography) and consistent at a maximum precision level of $\pm 7 \mu\text{mol kg}^{-1}$. Dissolved inorganic nitrogen (ammonia, nitrite, and nitrate) and phosphate were quantified as in Grasshof et al. (1999) and Chl *a* as in Strickland and Parsons (1972). Whatman GF/F filters were used for the Chl *a* analyses and the filtrate for the nutrient analyses. All water samples were kept in the dark and on ice during transport to the respective laboratories and nutrient samples and Chl *a* filters kept at -18°C in a freezer prior to analyses.

2.3.2 On-line parameters

Continuous measurement of temperature, salinity, fluorescence and DO were performed with a calibrated YSI 6600 V2 multiparameter probe inserted in a flow-through customized acrylic chamber. The values of the fluorescence sensor were correlated with the discrete analysis of Chl *a* to derive a conversion factor. pH was measured continuously with a pH-meter WTW 3310, equipped with one electrode Sentix 41 also inserted in the chamber, and calibrated according to the National Bureau Standard (NBS Standard). $p\text{CO}_2$ was measured using the marble-type equilibrator method, through which seawater flowed ($1\text{--}2 \text{ L min}^{-1}$) from the top to the bottom of the cylinder filled with marbles and air was pumped upwards (1 L min^{-1}) (Frankignoulle et al., 2001; Abril et al., 2006). The air in the equilibrator was dried before passing to a non-dispersive infrared gas analyser (LICOR[®], Type LI-820) which was calibrated using two gas mixture standards at 0 and 1007 ppmv, and verified with two other

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standards at 400 and 5300 ppmv (White Martins Certified Material, RJ, Brazil). The partial pressure of atmospheric CO₂ was measured in dry air twice a day, at the start and the end of the continuous runs.

Solar radiation, wind velocity (U10), accumulated precipitation and atmospheric temperature were recorded at the two airports of Santos Dumont and Galeão, located in the outer and inner regions of the Bay, respectively (Fig. 1) and were provided by Brazilian Institute of Aerial Space Control (ICEA). The data sets of solar radiation (Rs) were converted into daily-averaged photosynthetically active radiation (PAR) using a conversion factor PAR/Rs of 0.5 (Monteith, 1977).

2.3.3 Calculations

Dissolved inorganic carbon (DIC) was calculated using two different pairs of measured parameters: $p\text{CO}_2/\text{TA}$ and pH/TA using the carbonic acid constants sets proposed by Hansson and Merbach refitted by Dickson and Millero (1987), the borate acidity constant from Lee et al. (2010) and the CO₂ solubility coefficient of Weiss (1974). Calculations were performed in the CO2calc 1.2.9 program (Robbins et al., 2010). Both calculations gave very consistent DIC concentrations at $\pm 6.5 \mu\text{mol kg}^{-1}$. Measured pH (in the field) and the one calculated from the pair $p\text{CO}_2/\text{TA}$ also gave an excellent agreement (slope: 0.9994, $R^2 = 0.97$). The excess of DIC (E-DIC, $\mu\text{mol kg}^{-1}$) was calculated as the difference between the in-situ DIC (DIC in situ $\mu\text{mol kg}^{-1}$) and a theoretical DIC at atmospheric equilibrium (DIC equilibrium $\mu\text{mol kg}^{-1}$) according to Abril et al. (2003). The DIC equilibrium was calculated from observed TA and the atmospheric $p\text{CO}_2$ measured in the Bay. The apparent oxygen utilization (AOU, $\mu\text{mol kg}^{-1}$) was calculated from the temperature, salinity and DO concentrations measured continuously with the probe and the theoretical DO saturation (Benson and Krause, 1984).

Diffusive air–sea CO₂ fluxes were computed from $p\text{CO}_2$ measured in the water and the atmosphere and a gas transfer velocity derived from wind and other physical

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drivers. We used the k -wind parameterization of Raymond and Cole (2001) and Abril et al. (2009), which are gases exchange coefficients specific for estuarine waters. The Raymond and Cole (2001) (RC01) equation is based on the compilation of gas transfer velocities derived from tracers in nine rivers and estuaries, only using wind speed as an entry parameter. The Abril et al. (2009) (A09) relationship is based on chamber flux measurements in seven estuaries, and uses wind speed, estuarine surface area, and water current velocity as entry parameters. The gas transfer coefficients normalized to a Schmidt number of 600 obtained with the two parameterizations were then converted to the gas transfer velocity of CO₂ at in situ temperature and salinity, following the procedure of Jähne et al. (1987). Fluxes were computed for each sector of Guanabara Bay, using water p CO₂ representative for diurnal and seasonal variations.

3 Results

3.1 Climatic, hydrological and biogeochemical conditions

Climatic conditions during the study period followed a classical seasonal trend (Fig. 2), although the sampled summer period (October 2013, December 2013, January 2014, February 2014) was slightly warmer and dryer than the average conditions of the reference period 1951–2010. The two warmest and driest months of January 2014 and February 2014, the air temperature was 2.2 °C higher and precipitation was 75% lower than the averaged reference period of 60 years. In contrast, the sampled winter period (April 2013, July 2013, August 2013, September 2013 and April 2014) had air temperature and precipitation consistent with historical data (Fig. 2). Sector-averaged surface water temperature in Guanabara Bay (Table 1) varied between 23.8 and 26.8 °C and salinity varied between 27.0 and 32.2. In the upper portion of the bay (S4 and S5), salinity decreased in winter and temperature increased in summer with an observed maximum of 33.9 °C. S1, at the entrance of the bay exhibited lowest temperatures and highest salinities, with little seasonal variation. A maximum seasonal amplitude of 3.4

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regions of Guanabara Bay, both for summer and winter conditions. During winter, the water column was well mixed in all sectors. Indeed, temperature and salinity showed little vertical variations during this season (Fig. 3a, c and e). Chl *a* and oxygen profiles were also vertically homogeneous, except in the most confined and shallow S5, where Chl *a* was typically 2.5 times higher in the first two meters compared to the bottom (Fig. 3f). During summer, all sectors showed important thermal and saline stratification (Fig. 3g, i and k), halocline and thermocline being located almost at the same depth. In 20 m deep water columns (S1 and S3; Fig. 3g and i), a ~ 4 m deep surface layer was ~ 2–3 °C warmer and had salinity ~ 1–2 units lower than the bottom layer; in 5 m-deep water column (S5; Fig. 3k), the warmer surface layer was ~ 2 m deep with similar temperature and salinity contrasts between the surface and the bottom. The vertical water profile was also analysed to investigate the diurnal variations of temperature and salinity (Fig. 3k and l). Comparison between daytime and nighttime conditions revealed that stratification was subject to diurnal variations, driven by temperature convection concomitant with a moderate mixing of water currents by microtidal action. Summer stratification of the water column was accompanied by a consistent vertical distribution of Chl *a* and oxygen, with maximum in the surface layers and minimum at the bottom. Note that the salinity varied less than the temperature along the day (> 2 °C of variation in 5 h; Fig. 3k). Stratification apparently favoured phytoplankton development, as Chl *a* concentrations were highest (up to 240 µg L⁻¹) at the surface of the stratified water columns. These physical conditions were largely predominant in summer and in the shallowest, calmest and most confined sectors of the Bay (S4 and S5).

3.3 Spatial screening of pCO₂ in surface waters

Spatial distributions of surface water pCO₂ measured continuously along the trajectories, revealed strong spatial gradients between and/or inside each sector, from over- to under-saturation with respect to the atmosphere (Fig. 4). Temporally and spatially, water pCO₂ was negatively correlated with dissolved oxygen ($R^2 = -0.90$; $n = 179$) and Chl *a* ($R^2 = -0.77$; $n = 185$). S1 presented pCO₂ values close to the

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atmospheric equilibrium, with moderate temporal variation around this average (411 ± 145 ppmv). DO and Chl *a* in S1 were 103 ± 29 % and 19 ± 22 μgL^{-1} , respectively. S2, close to most urbanized area, showed highest heterogeneity, from a maximum $p\text{CO}_2$ value of 3750 ppmv in hypoxic waters (DO = 2 % saturation) at the vicinity of the highly polluted urban channels in January 2014 (Fig. 4g), to strong undersaturation, as low as 50 ppmv in a small and protected embayment (Chl *a* = 212 μgL^{-1}) in January 2014. In S2, the extent of $p\text{CO}_2$ supersaturation apparently induced by the urban sewage loads was favoured by strong rains the day before sampling and low PAR incidence in July, August and September 2013, compared to all the other cruises (Fig. 4). In S3, S4 and S5, which account for 75 % of the surface area of Guanabara Bay, $p\text{CO}_2$ was predominantly below the atmospheric equilibrium, particularly during daytime summer cruises (Fig. 4 and Table 1). Massive phytoplankton blooms were sampled during our survey, characterized by extreme patchiness in summer. For example, an extreme of 22 ppmv of $p\text{CO}_2$, 350 % sat DO and 550 μgL^{-1} Chl *a* was recorded in Feb.2014 in a brown/red bloom. In S3, S4 and S5, water $p\text{CO}_2$ was lower than 150 ppmv around midday at all seasons. These blooms and associated $p\text{CO}_2$ undersaturation occurred in S4 and S5 during winter and progressively spread to the entire bay during summer months (Fig. 4). From September 2013 to February 2014, midday undersaturation was encountered over the whole bay, except the urban impacted S2 (Fig. 4). Finally, some increases in water $p\text{CO}_2$ above the atmospheric equilibrium (up to a maximum of 2200 ppmv) were observed in July 2013, August 2013 and April 2014, in the northeastern part of S4 and S5, related to river plumes. Before reaching the open waters of S4, these riverine plumes flowed across a preserved mangrove area. However, the extent of these small plumes was limited (Fig. 4) and their contribution to the sector CO₂ balance was apparently negligible.

3.4 $p\text{CO}_2$ diurnal variations

The five back and forth tracks revealed important diurnal changes in water $p\text{CO}_2$ in S4 and S5, but not in S1 (Fig. 5). In the latter in February 2014 (Fig. 5d), nighttime

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(early morning) $p\text{CO}_2$ (451 ± 38 ppmv) was not significantly different ($p > 0.001$) from daytime $p\text{CO}_2$ (466 ± 26 ppmv). In contrast, in S4 and S5, rapid and significant decreases in water $p\text{CO}_2$ were recorded in the early hours of the morning, followed by a relative stable undersaturation from 10:00 a.m. to all over the afternoon (Fig. 5).

For instance, in September 2014, $p\text{CO}_2$ decreased from 800 ppmv at 8:30 a.m. to 200 ppmv at 13:40 p.m. at the same geographical location (Fig. 5a). The decrease in water $p\text{CO}_2$ occurred relatively quick on all occasions at around 9:30 a.m., which apparently corresponded to the hour of maximum activation of photosynthetic activity by phytoplankton. 9:30 a.m. was then used as the limit to separate nighttime $p\text{CO}_2$ from daytime $p\text{CO}_2$. In S4 and S5, $p\text{CO}_2$ changes from nighttime to daytime were from 591 ± 231 to 194 ± 114 ppmv in September 2013, from 163 ± 40 to 116 ± 25 ppmv in January 2014, from 346 ± 166 to 146 ± 106 ppmv in February 2014, and from 637 ± 421 to 265 ± 186 ppmv in April 2014. In all these cases, water $p\text{CO}_2$ was significantly higher ($p < 0.001$) before than after 9:30 a.m. Consequently, S4 and S5 shifted from a CO₂ source at nighttime to a CO₂ sink at daytime in September 2013 and April 2014, but remained a CO₂ sink all day and night long in January and February 2014. In addition to these five back and forth tracks described in Fig. 5, we could compare water $p\text{CO}_2$ values measured on the same day in early morning (before 9:30 a.m.) with those measured in late afternoon in S1, S3 and S4. Consequently, our data provided a fairly good indication of the diurnal variability of $p\text{CO}_2$ throughout the entire sampling period, in all sectors, except S2 (Fig. 6).

3.5 Seasonal variations

Despite the significant daily variations, very clear seasonal changes were observed in $p\text{CO}_2$ of surface waters (Fig. 6), with higher values in winter (April 2013, July 2013, August 2013, September 2013 and April 2014) than in summer (October 2013, December 2013, January 2014 and February 2014). Seasonal variation in DO and Chl *a* mirrored the $p\text{CO}_2$ variations, with a maximum phytoplanktonic biomass and oxygen saturation in summer, when $p\text{CO}_2$ was minimum. S1 was a source of

atmospheric CO₂ during winter ($p\text{CO}_2$ of 501 ± 98 ppmv), but a sink during summer ($p\text{CO}_2$ of 304 ± 117 ppmv). S2 presented the highest $p\text{CO}_2$ differences between winter (923 ± 484 ppmv) and summer (423 ± 530 ppmv), with high SD resulting from spatial heterogeneity for both periods (Fig. 4). In S3, S4 and S5, CO₂ undersaturation prevailed along the year, except in winter and night-time, where slight oversaturations occurred. In these three sectors, oxygen remained oversaturated all over the year. Average measured values of $p\text{CO}_2$ for winter and summer respectively, were 353 ± 141 and 194 ± 127 in S3, 380 ± 286 and 203 ± 159 in S4, and 364 ± 343 and 132 ± 74 ppmv in S5. Note that these averages are in its majority based on daytime measurements and that integrated yearly average CO₂ fluxes had to be quantified by accounting for both seasonal and diurnal variations (see following section and discussion).

3.6 Gas transfer velocities and CO₂ fluxes at the air–sea interface

Wind speeds (12 h-averaged) varied between 1.4 and 3.9 ms⁻¹, were significantly higher during summer than during winter ($p < 0.001$) and significantly higher during daytime than during nighttime ($p < 0.001$) (Table 2). Instantaneous wind speed showed some peaks at a maximum of 15 ms⁻¹ during short (< 1 h) events. Wind speeds measured at the meteorological station in the southern part of the Bay were higher (S1, S2 and S3) than those recorded at the station in the northern region (S4 and S5) (Table 2).

Calculated gas transfer velocities averaged over daytime and nighttime periods varied between 3 and 12.2 cm h⁻¹ (Table 2). k_{600} values calculated from the equation of Abril et al. (2009) that accounts for the wind velocity, the fetch effect linked to estuarine size and the current velocity, was systematically higher than those calculated from the relationship of Raymond and Cole (2001), which consists in an exponential function of wind velocity. Average k_{600} values based on 15 min wind speed were not significantly different from k_{600} based on 12 h average wind speed, showing that short storms had negligible impact on daily-integrated gas transfer velocities. CO₂ fluxes were calculated using the measured $p\text{CO}_2$ in each sector during the respective period: summer and

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winter, daytime and night-time. In the absence of data, we interpolated $p\text{CO}_2$ from surrounding areas and/or measurement periods. For S2, the only sector that was not sampled at night, we applied the mean diurnal variations of S1 and S3. Because of the relatively narrow range of k_{600} variation, calculated CO_2 fluxes followed the pattern of surface water $p\text{CO}_2$, and varied between $14.6 \text{ mmol m}^{-2} \text{ h}^{-1}$ in the polluted S2 during winter and nighttime, to $-9.7 \text{ mmol m}^{-2} \text{ h}^{-1}$ in dense phytoplanktonic blooms of S5 during summer and daytime (Table 2). Time-integrated CO_2 fluxes, accounting for seasonal and daily variations, revealed that all sectors except S2 behaved as CO_2 sinks on an annual basis.

4 Discussion

4.1 Estuarine typology: comparing Guanabara Bay with other estuaries

The results of the continuous measurements and the concomitant discrete sampling of water quality parameters, showed that, in terms of CO_2 atmospheric exchange, Guanabara Bay does not follow the patterns of a typical drowned-river valley estuary with a marked longitudinal estuarine gradient between its fresh and marine water end-member sources (Pritchard, 1952). Rather, Guanabara Bay corresponds to a tropical marine dominated system, owing to the small freshwater discharge relative to its water volume and tidal exchange, maintaining 85% of the bay with salinities always higher than 25. Its geomorphological characteristics and rather complex circulation of water masses, makes the application of standard approaches to discern sources or sinks from composite plots between salinity and material concentrations difficult (Bourton and Liss, 1976). Furthermore, Guanabara Bay has been considered as one of the world's most degraded embayment characterized by constant eutrophic to hypertrophic conditions and the frequent occurrence of red tides (Rebello et al., 1988; Villac and Tennenbaum, 2010; Guenther et al., 2012).

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The aquatic CO₂ behavior in Guanabara Bay was different from that in most of documented estuaries worldwide. Indeed, the majority of studies that were conducted in macrotidal, turbid and river-dominated estuaries reveal that these systems are heterotrophic and emit large amounts of CO₂ both in temperate and tropical regions (Frankignoulle et al., 1998; Borges and Abril, 2011; Sarma et al., 2012). These drowned valley, river-dominated, estuaries also exhibited a significant inverse trend between salinity and $p\text{CO}_2$ (Frankignoulle et al., 1998), which was not observed in Guanabara Bay. The absence of a negative relationship between $p\text{CO}_2$ and salinity for the range of 27–32 is in fact more consistent with observations in some estuarine plumes (although less pronounced), where $p\text{CO}_2$ undersaturation and diurnal variations are often reported (Borges and Frankignoulle, 1999, 2002; Dai et al., 2009; Bozec et al., 2011). Therefore, our results in Guanabara Bay are still consistent with the comparative analysis of CO₂ dynamics in river- and marine-dominated estuaries by Jiang et al. (2008). In Guanabara Bay, salinities lower than 27 were confined to the upper region at the mouths of the small rivers in S4 (max. $p\text{CO}_2 = 2222$ ppmv), S5 (max. $p\text{CO}_2 = 2203$ ppmv) and some polluted channels of S2 (max. $p\text{CO}_2 = 3715$ ppmv) (Table 1 and Fig. 4). However, these heterotrophic and strong CO₂ degassing regions are relatively small when compared to the total superficial area. In contrast, $p\text{CO}_2$ in S1, which is directly affected by marine water intrusion, exhibited minor diurnal and seasonal variations oscillating around the atmospheric value of 400 ppmv. But, sectors 3, 4 and 5 as a whole, which cover around 75% of the bay's area, behaved as a CO₂ sink on a yearly basis, with concentrations even down to about 30 ppmv on some occasions (Table 2). These three sectors are subject to weaker currents and higher residence times of water and stratification in shallow depths, favouring CO₂ uptake by phytoplankton primary production and autotrophic metabolism, especially during summer. Indeed, thermal or haline stratification of estuarine waters has been identified as a determinant factor that favours the ecosystem to act as a CO₂ sink (Borges, 2005; Chou et al., 2013). Low $p\text{CO}_2$ concentrations at surface waters were reported for the inner shelf of the Changjiang estuary (Chou

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variance revealing that $p\text{CO}_2$ was well separated and negatively correlated with DO, Chl *a*, temperature, wind velocity and PAR incidence. This correlation suggests a strong external meteorological control on phytoplankton dynamics and, in turn, on the CO₂, DO and Chl *a* spatial and temporal variations. Indeed, the high incident light simultaneously provides energy for phytoplankton growth and favors the development of thermal stratification, particularly in the shallow and less hydrodynamic regions (Fig. 3). In the tropics, high light incidence combined with the presence of nutrients contributes to phytoplankton blooms and CO₂ depletion both directly, by supplying light for photosynthesis, and indirectly by favoring stratification of the water column. It is noteworthy that high wind speed in the region of Guanabara was correlated with high PAR, and consequently, gas exchange was favored during daytime, when CO₂ depletion attained its maximum. In contrast, salinity and the 7 day accumulated precipitation were negatively correlated to the other parameters (Factor 2 = 19 %). This suggests that pulsed inputs of freshwater, typical of tropical storms affects salinity in Guanabara Bay, but has little impact on the intensity of blooms and the CO₂ uptake by the phytoplankton.

Our diurnal measurements along the hypertrophic sectors 4 and 5 also showed marked differences of $p\text{CO}_2$ concentrations between daytime and nighttime. The nighttime $p\text{CO}_2$ values were about 30 % higher than daytime (differing by up to 395). As the PAR incidence increased along the day, the surface $p\text{CO}_2$ decreased due to the enhancement of photosynthesis and rapid formation of thermal stratification (Figs. 3 and 5). Our report of strong diurnal variation in $p\text{CO}_2$ in Guanabara Bay (Fig. 5) reveals how photosynthesis and respiration processes vary temporally, especially in domains with high phytoplankton biomass (indicated by Chl *a* values above 50, sometimes reaching 200 $\mu\text{g L}^{-1}$). In their study of primary production based on oxygen incubations in Guanabara Bay, Rebello et al. (1988) postulated that some intriguing very low rates in Chl *a*-rich samples were due to the occurrence of CO₂ limitation. Indeed, the extremely low values of $p\text{CO}_2$ observed in S5 (ex. 24 ppm or 0.6 $\mu\text{mol kg}^{-1}$ of dissolved CO₂) confirm that CO₂ might be one of the limiting factors for primary production. Some

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diurnal variations of $p\text{CO}_2$ controlled by biological activity have been reported in several other estuarine systems worldwide (Dai et al., 2009; Bozec et al., 2011; Yates et al., 2007; Zhang et al., 2013). In the Bay of Brest, a temperate coastal embayment, the phytoplankton blooms were responsible to 10–60% of the seasonal $p\text{CO}_2$ drawdown observed during spring, equivalent to 100–200 ppmv (Bozec et al., 2011). According to Yates et al. (2007), the diurnal variations in $p\text{CO}_2$ (median of 218 ppmv) in Tampa Bay, a shallow and subtropical estuary were largely influenced by primary productivity and respiration of benthic communities. Also, Zhang et al. (2013) reported diurnal $p\text{CO}_2$ variations mainly controlled by biological activities (maximum 218 ppm in autumn) in a Chinese tropical open bay dominated by fringing reefs; however, calcification was also important driver of diurnal $p\text{CO}_2$ variations in winter. In one suite of different coastal ecosystems in the South China Sea, including inshore and onshore locations, Dai et al. (2009) concluded that temperature was a major driver of $p\text{CO}_2$ diurnal variability in the oligotrophic and offshore regions (10–16 ppmv variations), tidal effects in the nearshore (41–152 ppmv), and biological metabolism in the coral reef system (up to 608 ppmv of diurnal variations). Henceforth, it is clear that diurnal variations must be accounted for in estuarine CO₂ budgets assertions, otherwise, estimates based on daytime $p\text{CO}_2$ measurements only, might shift the conclusions toward an overestimates of the CO₂ sink, or an underestimate of CO₂ source. Further in this paper, we use $p\text{CO}_2$ measurements at different hours of the day and night in order to integrate the diurnal variations.

The temperature vs. biological effect on $p\text{CO}_2$ variations in Guanabara Bay was verified using the Takahashi et al. (2002) approach. The relative importance of the temperature and biological effects can be expressed as a ratio between both the temperature and the biology effect. The biological component is estimated by the seasonal amplitude of the temperature-normalized $p\text{CO}_2$ and the temperature component is characterized by the seasonal amplitude of the annual mean $p\text{CO}_2$ corrected for the seasonal temperature variation. The following equations were applied

(Takahashi et al., 2002):

$$p\text{CO}_2 \text{ at } T_{\text{mean}} = p\text{CO}_{2\text{obs}} \cdot \exp[0.0423(T_{\text{mean}} - T_{\text{obs}})]$$

(variations driven by biological effect); (1)

$$p\text{CO}_2 \text{ at } T_{\text{obs}} = p\text{CO}_{2\text{mean}} \cdot \exp[0.0423(T_{\text{obs}} - T_{\text{mean}})]$$

(variations driven by thermodynamic effect); (2)

where T is the temperature in $^{\circ}\text{C}$, and the subscripts “mean” and “obs” indicate the annual average and observed values, respectively. These equations were applied to summer and winter conditions. The biologic effect on the surface-water $p\text{CO}_2$ ($\Delta p\text{CO}_2$)_{Bio} is represented by the seasonal amplitude of $p\text{CO}_2$ values corrected by the mean annual temperature, ($p\text{CO}_2$ at T_{mean}), using Eq. (1):

$$(\Delta p\text{CO}_2)_{\text{Bio}} = (p\text{CO}_2 \text{ at } T_{\text{mean}})_{\text{max}} - (p\text{CO}_2 \text{ at } T_{\text{mean}})_{\text{min}}; \quad (3)$$

where the subscripts “max” and “min” indicate the seasonal maximum and minimum values. The effect of temperature changes on the mean annual $p\text{CO}_2$ value, ($\Delta p\text{CO}_2$)_{temp}, is represented by the seasonal amplitude of ($p\text{CO}_2$ at T_{obs}) values computed using Eq. (2):

$$(\Delta p\text{CO}_2)_{\text{Temp}} = (p\text{CO}_2 \text{ at } T_{\text{obs}})_{\text{max}} - (p\text{CO}_2 \text{ at } T_{\text{obs}})_{\text{min}}. \quad (4)$$

The contributions of temperature and biological activity for Guanabara Bay were estimated as 33 and 255 ppmv, respectively, showing the strong influence of biological productivity over $p\text{CO}_2$ dynamics on this tropical coastal embayment (ratio of 0.12). Some authors utilized the same approach in other estuarine systems with different dominances between temperature and biological effect (Bozec et al., 2011; Zhang et al., 2012; Hunt et al., 2014). The temperature dominating effect were presented by in Jiaozhou Bay (China Sea), Zhang et al. (2012) obtained $p\text{CO}_2$ variations differences of 93 and 78 ppmv for temperature and biological activity respectively (weak temperature

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prevalence and ratio of 1.19). In the Kennebec Estuary (USA), Hunt et al. (2014) found different ratios according to the salinity zones and showed that, in general, higher ratios prevailed at low salinities (1.9–2.1), with higher temperature control on $p\text{CO}_2$ variations. Bozec et al. (2011), on the other hand, in one inter-annual approach encountered a mean value of 0.49, in the Bay of Brest, a temperate embayment in France, confirming that the biological processes were the main driver of the seasonal $p\text{CO}_2$ dynamic. The ratio for Guanabara Bay is much lower than in all these systems, and also consistent with an atypical CO₂ dynamics.

4.3 Eutrophication and CO₂ dynamics

In several coastal systems worldwide, important CO₂ changes, either increasing or decreasing have been attributed to eutrophication processes (Gypens et al., 2009; Borges and Gypens, 2010; Cai et al., 2011; Sunda and Cai, 2012; Chou et al., 2013). Eutrophication occurs when massive anthropogenic inputs of both organic (mainly domestic) and inorganic (agricultural or industrial) nutrients (sometimes during several decades) have enriched estuarine waters and sediments with bioavailable nitrogen and phosphorus (Rabalais et al., 2009). Increases in $p\text{CO}_2$ have been reported in river-dominated estuaries at the vicinity of megacities (Frankignoulle et al., 1998; Zhai et al., 2007; Sarma et al., 2012). When sewage is discharged in such river-dominated systems, heterotrophy is enhanced and CO₂ outgassing increases (Zhai et al., 2007; Sarma et al., 2012). Indeed, environmental conditions in these turbid estuarine waters strongly limit primary production in favor of heterotrophy. Turbidity, together with stratification, is indeed a key parameter that explains $p\text{CO}_2$ variation in estuaries (Jiang et al., 2008; Borges and Abril, 2011). In Guanabara Bay, sewage also predominates as source of organic nutrients (Bidone and Lacerda, 2004). However, the $p\text{CO}_2$ spatial distribution (Fig. 4) suggests that mineralization of this domestic organic matter occurs predominantly within the sewage network itself and in small rivers and channels and their plumes that represent a small surface area in the Bay. It can be noted for example that $p\text{CO}_2$ oversaturation was more extended in S2 in

August 2013, which corresponds to a sampling just after strong rains on the city of Rio de Janeiro. Mineralization of organic matter in these extremely polluted areas leads to rapid CO₂ (and probably CH₄) outgassing, and concomitantly, contributes to a long-term enrichment of the Bay in bioavailable nitrogen and phosphorus (Paranhos et al., 1998; Ribeiro and Kjerfve, 2002).

Except for these peripheral zones, most sectors of Guanabara Bay experienced massive algal blooms thanks to the optimal conditions for primary production, including nutrient, light, and water column stratification. The driving phytoplankton assemblages of Guanabara Bay are typical for eutrophic to hypertrophic systems, largely dominated by bloom and also red tide forming nanoplankton, filamentous cyanobacteria and some microplankters (Valentin et al., 1999; Santos et al., 2007; Villac and Tennenbaum, 2010). Preliminary investigations of the collected material from this study suggests that cyanobacteria were frequently encountered in S2, S4 and S5, during the 9 sampling periods, and great deal of patchiness was observed with a succession of intense red, brown and/or green colored waters, leading to the marked short spatial variability of pCO₂, DO and Chl *a*. In the waters dominated by phytoplankton blooms the pCO₂ concentrations were always extremely low, and the sink characteristics were prevalent, with high CO₂ uptake and autotrophy characteristics. It has been shown, that during summer the heterotrophic bacterial production (BP) lied within the range of only 0.4–19 % of primary production (PP) at the surface and 5–52 % at the bottom, being nutrient dependent (Guenther et al., 2008). Our spatial and temporal pCO₂ dataset (Fig. 4) also suggests that the most confined part of the inner bay apparently behaved as the “bloom genesis region” that can spread phytoplanktonic production, biomass, and associate CO₂ consumption over the rest of the estuarine system. Indeed, CO₂-depleted waters were confined to S4 and S5 in October 2013, and progressively extended to all sectors (except S2) in January 2014, During this period, conditions became ideal for bloom developments with increasing air and water temperature, and the development of water stratification (Figs. 4 and 6).

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Eutrophication, thus, enhances the low surface $p\text{CO}_2$ concentrations in Guanabara Bay. Phytoplankton uses more nutrients and dissolved CO_2 in the surface waters, and produce larger biomass of organic matter. When this additional material reaches the bottom, the organic matter and associated nutrients are recycled, increasing $p\text{CO}_2$ and decreasing the oxygenation of bottom waters (Fig. 3k and l). Some authors recently discussed the increasing of bottom water acidification enhanced by coastal eutrophication especially in stratified ecosystems (Cai et al., 2011; Sunda and Cai, 2012). It has been shown, that water column stratification and bottom water stagnation enhances the isolation of O_2 and CO_2 in deeper waters and consequently their exchange between bottom and surface waters (Chen et al., 2007). Koné et al. (2009) reported a consistent CO_2 vertical distribution in Aby and Tendo lagoons, in Ivory Coast, where a warmer, fresher, Chl *a*-rich surface layer was depleted in CO_2 and nutrients, whereas a more saline and anoxic bottom layer was enriched in CO_2 and nutrients. Gypens et al. (2009) developed and validated a process-based model in the Scheldt estuary plume, that revealed that eutrophication could make the system shift from a net source of atmospheric CO_2 to a net sink, when anthropogenic nutrient loads increased, stimulating the carbon fixation by autotrophs. Chou et al. (2013) also suggested that human-induced increase in nutrient loading may have stimulated primary production and thus enhanced the CO_2 uptake capacity on the inner shelf off the Changjiang Estuary. Our results reveal that the impact of eutrophication on estuarine systems in terms of CO_2 exchange strongly depends on their typology. Drowned-valley, river-dominated, “funnel-type” estuaries, which are generally light-limited and heterotrophic, respond totally differently from estuarine plumes, marine-dominated lagoons or embayments like Guanabara Bay, where optimal condition for autotrophic primary production occur over large surface areas. These estuarine types are different in their hydrological and geomorphological configuration, availability of light, diversity of primary producer and heterotrophic assemblages, and their response to increasing nutrient loading (Smith et al., 2010; Cloern et al., 2004). Depending on the hydrodynamics, the additional organic carbon produced by enhanced eutrophication

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can be buried, mineralized, and/or exported. In quiescent embayments like Guanabara Bay, long-term burial can be significant (Carreira et al., 2002), resulting in a net uptake and storage of atmospheric carbon within the ecosystem.

4.4 Carbon budgets in Guanabara Bay

5 The spatial and temporal CO₂ fluxes were integrated for the Bay, taking into account the diurnal and seasonal variations of $p\text{CO}_2$, wind speed, and gas exchange coefficients. Efforts were made to sample all the sectors of the bay with different PAR intensities (higher, medium and low intensity, for each sampling day and especially in the more eutrophic waters). Characteristic daytime and nighttime $p\text{CO}_2$ were deduced from
10 the five back and forth observations in S4 and S5, and from the comparison of early morning (before 9:30) $p\text{CO}_2$ data with late afternoon data in S1, S3 and S4. Compared to seasonal changes, diurnal changes were significant, surface $p\text{CO}_2$ sometimes shifted from a sink behavior in the evening to source behavior at the end of the night, or sometimes remained under-saturated all night long (Fig. 6). Except for S2, the more
15 polluted sector, and the only one acting as a CO₂ emitter, our data could be used to integrate diurnal variability of $p\text{CO}_2$ throughout the sampling period (Fig. 6). For S2, the only region that was not sampled during the night, the values of the diurnal differences obtained in S1 and S3 were applied, which seems reasonable, owing to their similar Chl *a* concentrations.

20 Comparing the two k_{600} used for the calculated fluxes, the k_{600} of Abril et al. (2009) can be considered the higher flux estimate, based on chamber measurements in 9 estuarine systems, whereas the k_{600} of Raymond and Cole (2001) provides a more conservative value, based on non-intrusive “tracers only” data. k_{600} values varied from 3 to 12.3 cm h⁻¹, which correspond to wind speed velocities between 1.8 and 3.9 m s⁻¹.
25 Current velocity (few dozen of centimeters per second) contributed to a minor fraction of k_{600} in the Abril et al. (2009) equation. On an annual basis, Guanabara Bay was a net sink of atmospheric CO₂ (year-integrated flux of -13.0 and -19.5 mol C m² yr⁻¹, for

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k_{RC01} and k_{A09} , respectively), but with strong differences at temporal and spatial scales. On a daily basis, summer CO₂ uptake was maximal in S3, S4 and S5, with daily fluxes of -190 , -110 and -170 mmolC m² d⁻¹, respectively), whereas in the winter fluxes decreased to -14 , -30 and $+12$ mmolC m² d⁻¹, respectively (note that S5 changed
 5 form a large sink in summer to a slight source in winter). S1 was a moderate source in winter ($+60$ mmolC m² d⁻¹) and a moderate sink in summer (-90 mmolC m² d⁻¹), as well as on an annual basis (-4.45 molC m² yr⁻¹). In the highly polluted S2 sector, where a large part of the domestic organic matter is apparently respired, a strong annual outgassing occurred ($+213$ mmolC m² d⁻¹). However this region occupies only about
 10 10% of the surface area of the bay. It is interesting to note that at the midday/afternoon periods the winds were stronger than during the night/early-morning periods. This abides to the classical daily wind cycle at coastal regions guided by the thermal difference between the land and the water surface (Amarante et al., 2002), which apparently favors the CO₂ sink. Higher wind speed at daytime at nighttime, and in
 15 summer than in winter (Amarante et al., 2002), also favored the CO₂ uptake.

The sink of CO₂ at air–sea interface showed values very close to the burial rates of organic carbon in the sediments. Carreira et al. (2002) found a 10-fold increase in the flux of organic carbon to the sediments in the last 50 years (maximum of 114 mmolC m⁻² d⁻¹ in the S5). Our annual budget of carbon uptake at the air–water
 20 interface was 105 mmolC m² d⁻¹ for this same region, showing that Guanabara Bay is, in fact, a strong CO₂ sink and have autotrophic metabolism. The autotrophic nature of Guanabara Bay is also indicated by the relationship between autotrophic and heterotrophic communities (Guenther and Valentin, 2008; Guenther et al., 2008). Rebello et al. (1988) estimated phytoplankton primary production rates from monthly
 25 measurements over an annual cycle to vary between 60 to 300 mmolC m⁻² d⁻¹, with highest rates in the lateral and upper regions of the bay. The bacterial production used only a small fraction of the dissolved organic carbon pool, which had a turnover between 23 and 71 days in waters of the Bay. Average net primary production (NPP) was 169 mmolC m⁻² d⁻¹. Comparing with our results, the NPP values are

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clearly identified as the predominant driver of CO₂ dynamics and of carbon balance. Indeed, some other cases of net CO₂ uptake have been reported in some relatively polluted tropical coastal lagoons in Ivory Coast (Koné et al., 2010), in three temperate and marine-dominated Australian estuaries (Maher and Eyre, 2012), in temperate and tropical estuarine plumes either preserved (Körtzinger, 2003) or human-impacted (Cai, 2003; Zhai and Dai, 2009; Bozec et al., 2012), and in some pristine Arctic and sub-Arctic fjords (Rysgaard et al., 2012; Ruiz-Halpern et al., 2010). In contrast, inner and low salinity regions of most river-dominated, drowned valley, “funnel-type” estuaries, which are generally well-mixed and relatively turbid environments, have been documented as heterotrophic and CO₂ emitters under tropical (Araujo et al., 2014), temperate (Frankignoulle et al., 1998) and boreal (Silveneroieen et al., 2008) climates and whatever the anthropogenic pressure (Abril et al., 2003, 2004; Zhai et al., 2007; Borges and Abril, 2011; Cai, 2011; Sarma et al., 2012).

Our findings of a net annual CO₂ sink in Guanabara Bay indicate that more field data are needed in particular in the highly productive tropical coastal ocean, in order to adequately integrate estuarine CO₂ fluxes at the global scale. In Brazil, most previous studies concerned river dominated estuaries, especially along the northern and northeastern coast, which all behave as CO₂ sources (Souza et al., 2009; Araujo et al., 2014; Noriega and Araujo, 2014). In contrast to Guanabara Bay, highest CO₂ fluxes correspond to denser population in the watersheds of these net heterotrophic systems (Noriega et al., 2014). In fact, the Brazilian coast presents several estuarine types (river estuarine deltas, estuaries, lagoons and large embayments) which have very different metabolisms (Bernardes et al., 2012), but where CO₂ fluxes have as yet to established. Large *p*CO₂ temporal variations can be expected for instance in a phytoplankton-dominated coastal lagoon in Brazil that exhibited an annually balanced metabolism, but with seasonal shifts between autotrophic and heterotrophic conditions (Carmouze et al., 1991; Knoppers et al., 1999a, b). Lagoons dominated by macroalgae or microphytobenthos exhibited different metabolic trends, but still with a significant potential for a net uptake of atmospheric CO₂ (Knoppers, 1994). Undersampling

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coastal embayments and lagoons with clear and stratified waters, compared to turbid and well-mixed river-dominated estuaries, would potentially lead to an overestimation of the regional estuarine CO₂ budget. In addition, diurnal variations might impact the net CO₂ budget more significantly in autotrophic systems than in heterotrophic systems, and need to be assessed in the field. Continuous ρCO_2 measurements on autonomous buoys (e.g. Frankignoulle et al., 2003; Bozec et al., 2011) are very promising tools to reach sufficient temporal resolution. We also showed that pCO₂ dynamics were strongly correlated with meteorological conditions. Taking into account that the last projections of Intergovernmental Panel on Climate Change (IPCC) include unequivocal predictions of the climate system warming for the next years (Stocker et al., 2013), the increase of water temperature can reinforce the net sink of Guanabara Bay.

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Table 1. Mean (\pm SD), minimum, maximum and number of observations (N) of the principal physicochemical properties of the waters of Guanabara Bay for the sampling period separated by sectors.

	Sector 1	Sector 2	Sector 3	Sector 4	Sector 5
Temp. (°C)	23.8 \pm 1.7 (21.0–29.3) $N = 1918$	25.5 \pm 2.2 (22.1–32.4) $N = 1047$	25.4 \pm 2.1 (22.1–31.5) $N = 2035$	26.8 \pm 2.6 (22.0–32.3) $N = 1594$	26.7 \pm 2.2 (22.6–33.9) $N = 2397$
Sal.	32.2 \pm 2.1 (25.4–34.9) $N = 1918$	30.3 \pm 2.4 (17.7–33.7) $N = 1047$	29.8 \pm 3.0 (15.1–33.8) $N = 2035$	27.0 \pm 4.3 (14.6–33.2) $N = 1594$	27.2 \pm 3.5 (16.6–32.9) $N = 2397$
DO (%)	103 \pm 29 (48–221) $N = 1918$	97 \pm 59 (2–263) $N = 1047$	138 \pm 51 (56–357) $N = 2035$	142 \pm 62 (30–361) $N = 1594$	160 \pm 69 (46–370) $N = 2397$
$p\text{CO}_2$ (ppmv)	411 \pm 145 (104–747) $N = 1918$	711 \pm 561 (50–3715) $N = 1046$	286 \pm 157 (41–660) $N = 2035$	307 \pm 256 (29–2222) $N = 1594$	272 \pm 293 (22–2203) $N = 2397$
pH (NBS)	8.20 \pm 0.16 (7.90–8.71) $N = 1581$	8.15 \pm 0.32 (7.33–8.96) $N = 910$	8.35 \pm 0.23 (7.88–8.96) $N = 1790$	8.34 \pm 0.29 (7.39–9.01) $N = 1490$	8.44 \pm 0.31 (7.51–9.23) $N = 2225$
TA ($\mu\text{mol kg}^{-1}$)	2240 \pm 92 (1942–2320) $N = 44$	2291 \pm 99 (1890–2488) $N = 32$	2168 \pm 177 (1507–2500) $N = 40$	2045 \pm 369 (2111–3920) $N = 39$	2137 \pm 166 (1479–2314) $N = 53$
DIC ($\mu\text{mol kg}^{-1}$)	1979 \pm 112 (1713–2120) $N = 44$	2037 \pm 258 (1520–2513) $N = 32$	1841 \pm 250 (1328–2286) $N = 32$	1652 \pm 254 (1088–2111) $N = 35$	1752 \pm 256 (1193–2186) $N = 52$
Chl <i>a</i> ($\mu\text{g L}^{-1}$)	19.1 \pm 22.0 (2.0–128.0) $N = 34$	46.2 \pm 51.4 (3.3–212.9) $N = 33$	57.6 \pm 90.0 (1.6–537.2) $N = 33$	69.2 \pm 60.2 (13.1–288.8) $N = 32$	107.7 \pm 101.8 (1.5–822.1) $N = 47$
$\text{NO}_3\text{-N}$ (μM)	3.50 \pm 3.30 (0.13–12.50) $N = 34$	3.72 \pm 4.93 (< LD –18.63) $N = 33$	4.12 \pm 5.27 (0.16–19.12) $N = 32$	2.14 \pm 3.29 (< LD –14.74) $N = 33$	1.92 \pm 2.08 (0.04–9.20) $N = 47$
$\text{NO}_2\text{-N}$ (μM)	1.60 \pm 1.92 (0.05–7.30) $N = 36$	2.59 \pm 2.89 (0.10–10.67) $N = 33$	1.81 \pm 2.58 (< LD –10.79) $N = 33$	1.46 \pm 2.74 (0.03–9.37) $N = 33$	1.71 \pm 1.98 (0.03–7.08) $N = 47$
$\text{NH}_4\text{-N}$ (μM)	8.15 \pm 6.26 (0.09–22.50) $N = 37$	44.9 \pm 25.2 (0.15–94.73) $N = 33$	9.10 \pm 9.48 (0.04–37.95) $N = 33$	4.96 \pm 6.92 (0.04–29.29) $N = 33$	26.82 \pm 27.67 (0.13–130.12) $N = 47$
$\text{PO}_4\text{-P}$ (μM)	1.11 \pm 0.60 (0.11–2.44) $N = 37$	5.28 \pm 3.88 (0.17–20.79) $N = 33$	1.51 \pm 1.07 (0.17–1.10) $N = 33$	1.10 \pm 0.79 (0.03–2.96) $N = 33$	2.23 \pm 2.17 (0.02–8.72) $N = 47$

Table 2. Summary of calculated mean values for wind speed (U_{10}), gas exchange coefficient (k_{600}) and CO_2 fluxes at the air–sea interface in each sectors and entire Guanabara Bay. Diurnal variations (nighttime < 9:30 a.m.; daytime > 9:30 p.m.) seasonal means (winter and summer) and time-integrated values are reported. RC01 are the data calculated according to k_{600} of Raymond and Cole (2001), and A09 are data calculated according to k_{600} of Abril et al. (2009).

			U_{10}	k_{600}		CO_2 Flux	
			(ms^{-1})	(cmh $^{-1}$)		(mmolm $^{-2}$ h $^{-1}$)	
				RC01	A09	RC01	A09
Sector 1 (47 km 2)	Winter	Nighttime	1.8	3.5	7.2	1.59	3.37
		Daytime	2.5	4.7	9.0	1.19	2.33
	Summer	Nighttime	2.5	4.8	9.2	-1.27	-2.35
		Daytime	3.8	8.5	12.3	-3.88	-5.42
	Time-integrated		2.6	5.3	9.4	-0.57	-0.51
Sector 2 (32 km 2)	Winter	Nighttime	1.9	3.7	7.5	7.74	14.61
		Daytime	2.4	4.4	8.8	4.99	10.29
	Summer	Nighttime	2.5	4.8	9.2	1.97	2.87
		Daytime	3.3	6.2	10.9	1.28	2.02
	Time-integrated		2.5	4.7	9.1	4.00	7.44
Sector 3 (96 km 2)	Winter	Nighttime	1.4	3.0	6.1	0.06	0.34
		Daytime	2.6	4.9	9.2	-0.79	-1.53
	Summer	Nighttime	2.8	5.0	9.7	-3.28	-6.37
		Daytime	3.9	8.4	12.2	-6.22	-9.65
	Time-integrated		2.6	5.3	9.3	-2.56	-4.29
Sector 4 (55 km 2)	Winter	Nighttime	1.5	3.2	6.2	-0.33	-0.59
		Daytime	2.3	4.4	7.8	-1.26	-2.00
	Summer	Nighttime	2.1	4.0	7.4	-0.43	-0.76
		Daytime	3.2	6.4	9.9	-5.90	-9.13
	Time-integrated		2.2	4.5	7.8	-1.97	-3.12
Sector 5 (80 km 2)	Winter	Nighttime	1.5	3.2	6.1	3.32	5.88
		Daytime	2.4	4.5	8.0	-2.67	-4.87
	Summer	Nighttime	2.1	4.0	7.4	-3.25	-4.99
		Daytime	3.1	6.0	9.6	-6.21	-9.73
	Time-integrated		2.2	4.4	7.7	-2.20	-3.42
All Bay (310 km 2)	Winter	Nighttime				1.86	3.53
		Daytime				-0.86	-1.32
	Summer	Nighttime				-1.92	-3.45
		Daytime				-5.02	-7.73
	Time-integrated					-1.48	-2.24

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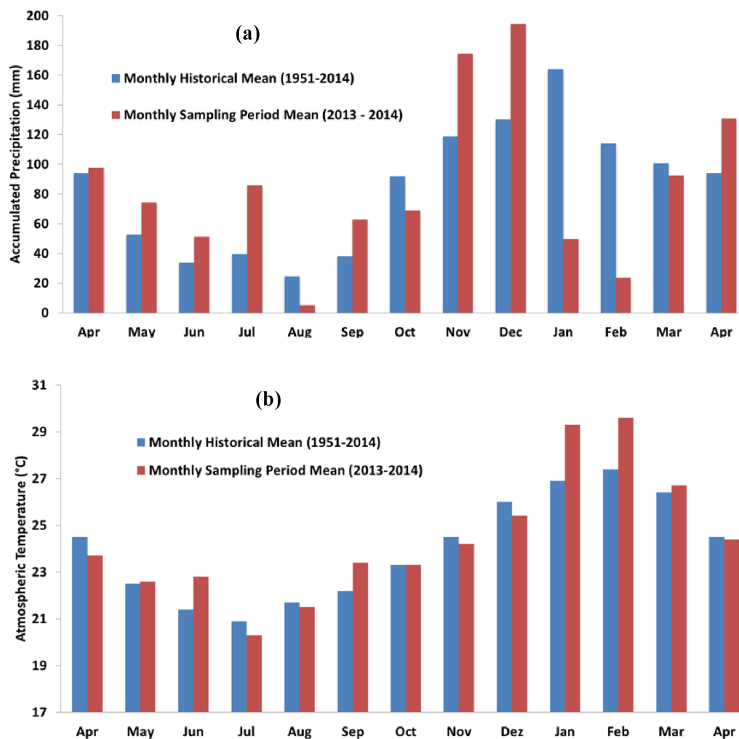


Figure 2. Meteorological conditions during the sampling period (in red) compared with historical values (1951–2014, in blue). **(a)** presents the mensal accumulated precipitation; **(b)** presents the means of mensal atmospheric temperature.

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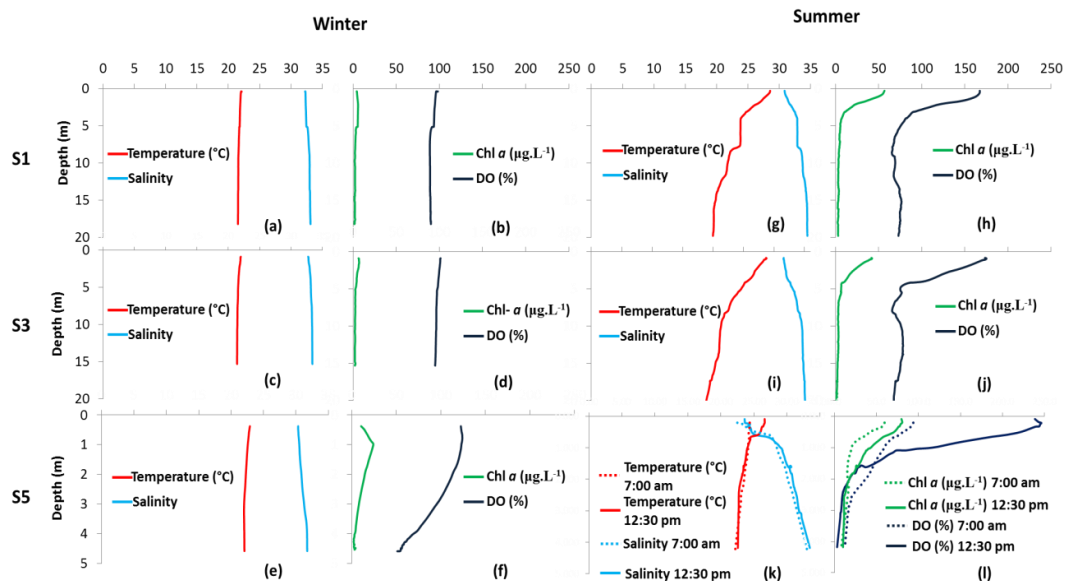


Figure 3. Typical vertical profiles of salinity, temperature, dissolved oxygen (DO) and chlorophyll *a* (Chl *a*) in the water column. Profiles are shown for S1, S3 and S5, in summer and winter conditions. Note the different depth scale for the S5. Dotted line in (k) and (l) shows nighttime profile (7:00 a.m.), whereas full line shows a daytime profile (12:30 p.m.) the same day at the same station.

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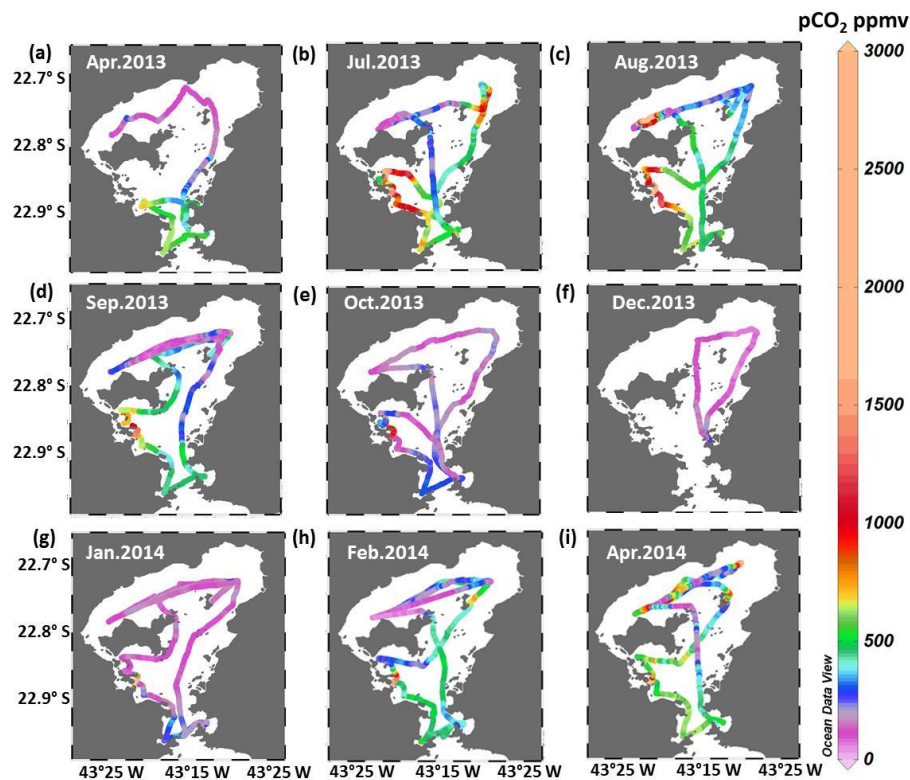


Figure 4. Concentration maps of continuous $p\text{CO}_2$ measurements in superficial waters of Guanabara Bay for all the sampling campaigns.

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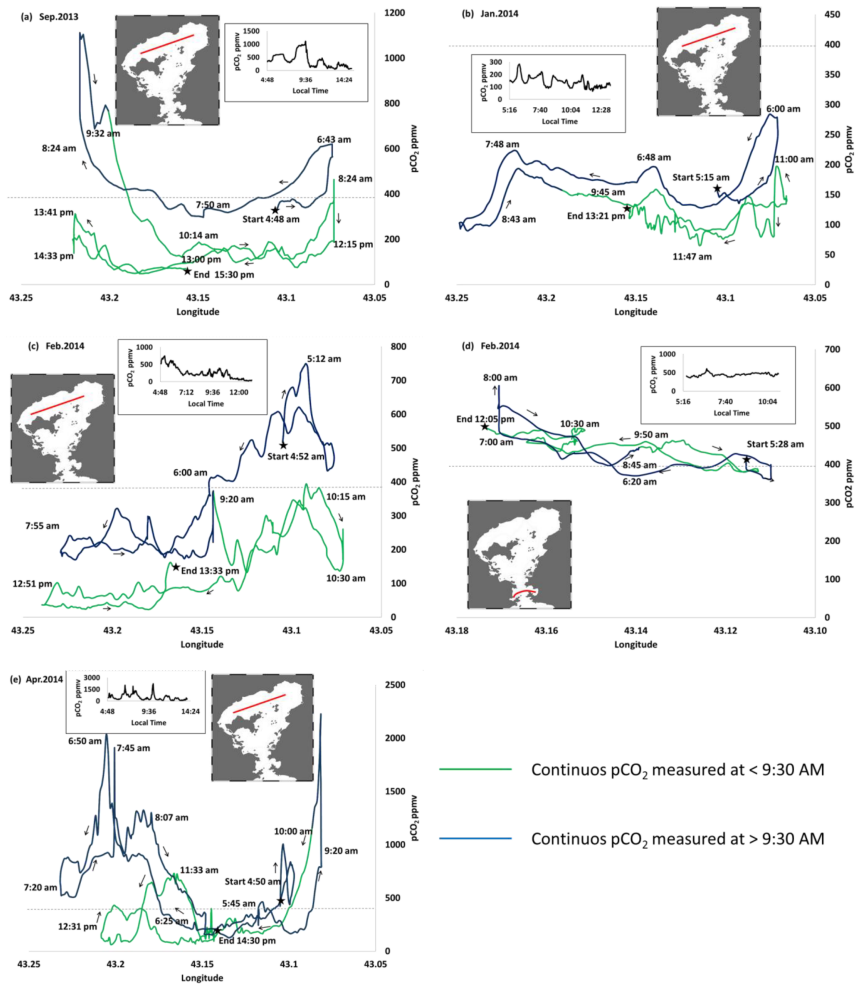


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Figure 5. Diurnal variations of $p\text{CO}_2$ concentrations. The ship back and forth tracks are indicated as red lines in small maps. Arrows show the boat direction and sampling time are indicated along each track. Blue parts of the tracks are considered as nighttime (< 9:30 a.m.) and green parts as daytime (> 9:30 a.m.). Inserted graphs also show the water $p\text{CO}_2$ evolution vs. time. The grey lines indicate the atmospheric $p\text{CO}_2$ (400 ppmv). Note the different $p\text{CO}_2$ scales for each survey.

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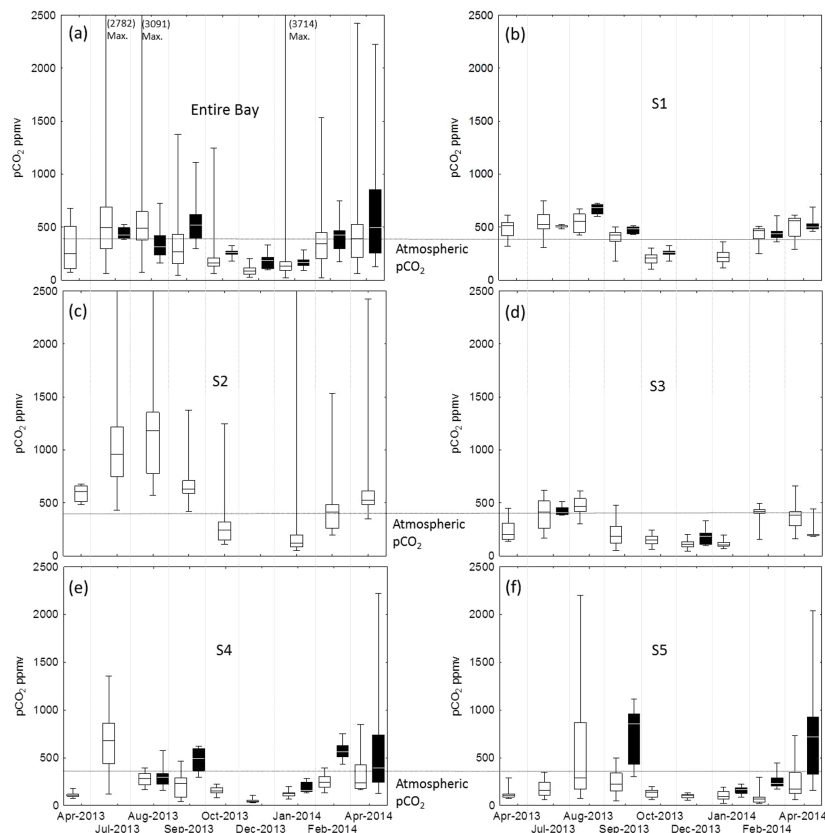


Figure 6. Box plots (maximum, percentile 75%, median, percentile 25% and minimum) of $p\text{CO}_2$ data for all the campaigns (a), and for each individual sectors (b, c, d, e and f). Black box plots represents the nighttime data (< 9:00 a.m.), when available, and white box plots represent daytime data (> 9:30 a.m.).

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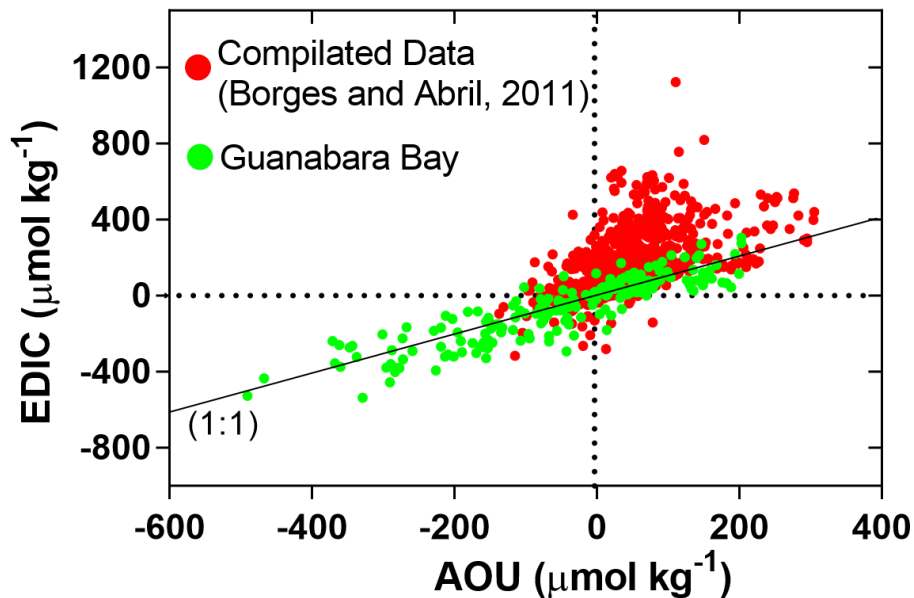


Figure 7. Relationship between the excess dissolved inorganic carbon (E-DIC) and apparent utilization of oxygen (AOU) in Guanabara Bay (green dots) compared to those reported in 24 estuarine environments (red dots, Borges and Abril, 2011).

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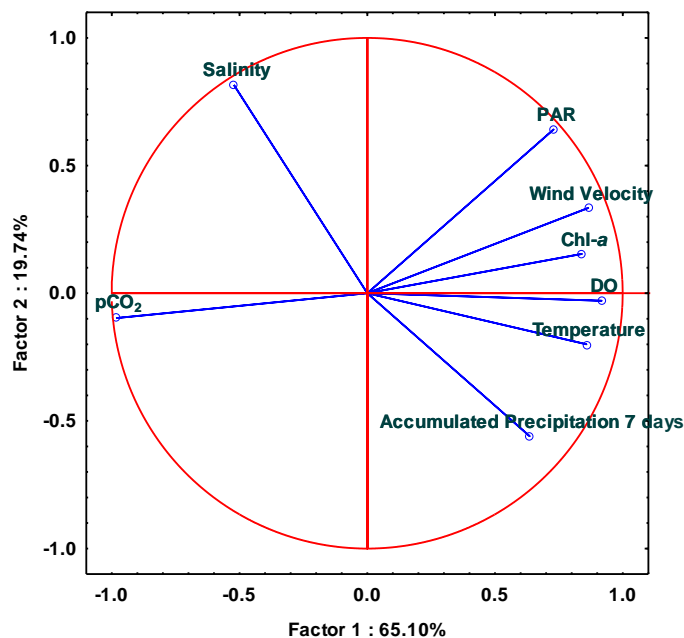


Figure 8. Principal Components Analysis (PCA) based on mean values for each sampling campaign of the physical and biogeochemical properties of the water (temperature, salinity, $p\text{CO}_2$, DO and Chl *a*) and meteorological conditions (wind velocity and accumulated precipitation of 7 days before each survey). The data-set was normalized by z scores.

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