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1 **Eutrophication overcoming carbonate precipitation in a tropical hypersaline coastal lagoon acting as a**  
2 **CO<sub>2</sub> sink (Araruama Lagoon, SE Brazil)**

3

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30 **Abstract**

31 The carbonate chemistry was investigated in the semiarid eutrophic Araruama Lagoon (Brazil), one of the largest  
32 hypersaline coastal lagoons in the world. Spatial surveys during winter and summer periods were performed, in  
33 addition to a diurnal sampling in summer. The hypersaline waters have higher concentrations of total alkalinity  
34 (TA) and dissolved inorganic carbon (DIC) than the seawater that feed the lagoon, due to evaporation. However,  
35 TA and DIC concentrations were lower than those expected from evaporation. Calcium carbonate (CaCO<sub>3</sub>)  
36 precipitation partially explained these deficits. The negative correlation between the partial pressure of CO<sub>2</sub>  
37 (*p*CO<sub>2</sub>) and chlorophyll *a* (Chl *a*) indicated that DIC was also consumed by primary producers. The uptake by  
38 photosynthesis contributes to 57-63% of DIC deviation from evaporation, the remaining credited to CaCO<sub>3</sub>  
39 precipitation. Marked *p*CO<sub>2</sub> undersaturation was prevalent at the innermost region with shallow, confined, and  
40 phytoplankton-dominated waters, with a strong enrichment of heavier carbon isotope ( $\delta^{13}\text{C-DIC}$  up to 5.55‰),  
41 and highest pH. Oversaturation was restricted to an urbanized region, and during night-time. The lagoon behaved  
42 as a marked CO<sub>2</sub> sink during winter (-15.32 to -10.15 mmolC m<sup>-2</sup> d<sup>-1</sup>), a moderate sink during summer (-5.50 to -  
43 4.67 mmolC m<sup>-2</sup> d<sup>-1</sup>), with a net community production (NCP) of 93.7 mmolC m<sup>-2</sup> d<sup>-1</sup> and prevalence of net  
44 autotrophic metabolism. A decoupling between CO<sub>2</sub> and O<sub>2</sub> exchange rate at the air-water interface was  
45 attributed to differences in gas solubility, and high buffering capacity. The carbonate chemistry reveals  
46 simultaneous and antagonistic actions of CaCO<sub>3</sub> precipitation and autotrophic metabolism on CO<sub>2</sub> fluxes, and  
47 could reflect future conditions in populated and semiarid coastal ecosystems worldwide.

48

49 **Key-words:** carbonate chemistry; coastal eutrophication; hypersaline waters; climate change; atmospheric CO<sub>2</sub>  
50 sink

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## 58 **1. Introduction**

59 Carbon is continuously displaced laterally and vertically along the land–ocean aquatic continuum comprising  
60 freshwaters, estuaries, and coastal areas (Regnier et al. 2013). Compared to the open ocean, the coastal ocean  
61 represents an important carbon sink (Cao et al. 2020) and plays a disproportionate role despite its modest surface  
62 area (Gattuso et al. 1998). According to the latest global estimates, estuaries emit  $\sim 0.10 \text{ GtC yr}^{-1}$  of  $\text{CO}_2$  to the  
63 atmosphere (Chen et al. 2013; Laruelle et al., 2013), whereas continental shelf waters absorb  $\sim 0.20 \text{ GtC yr}^{-1}$   
64 (Roobaert et al. 2019); however, these fluxes are still highly uncertain owing to the complexity of processes  
65 involved in these air–sea  $\text{CO}_2$  fluxes (Borges 2005). One of the main issues to be solved is the intrinsic  
66 spatiotemporal variability related to the heterogeneity of coastal ecosystems in different climatic domains  
67 (Borges and Abril 2011). In addition, important temporal variabilities at the tidal, diurnal, seasonal, annual and  
68 inter-annual time scales should be addressed (Borges 2005). Furthermore, anthropogenic impacts of global  
69 change and land and water uses have increased in coastal zones and have modified the biogeochemical cycles,  
70 particularly through nutrient pollution and eutrophication (Howarth et al. 2011). Coastal lagoons cover about  
71 13% of the coastal areas (Kjerfve 1994). They are very productive ecosystems, sustaining high rates of benthic  
72 and/or planktonic primary production (Knoppers et al. 1999; Maher and Eyre 2012). Coastal lagoons present  
73 ideal conditions for human settlement, hosting  $\sim 14.4\%$  of the global population (Kjerfve 1994), but suffering the  
74 increasing symptoms of demographic expansions mainly via urbanization and sewage discharge (Knoppers and  
75 Kjerfve 1999). Few studies have investigated carbonate chemistry dynamics and air–water  $\text{CO}_2$  fluxes in coastal  
76 lagoons. Findings in tropical and subtropical coastal lagoons indicate that they can act both as net  $\text{CO}_2$  sources or  
77 sinks depending on hydrological, chemical, and biological characteristics which are affected by natural and  
78 anthropogenic–derived disturbances, especially the inputs of nutrients and dissolved carbon from the watershed  
79 (Koné et al. 2009; Ribas-Ribas et al. 2011; Ávila-López et al. 2016; Maher et al. 2019). Furthermore, Koné et al.  
80 (2009) postulated that physical settings (mixed *versus* stratified water column) play an important role modulating  
81 air–water  $\text{CO}_2$  fluxes.

82 In productive coastal waters, the carbonate chemistry is strongly influenced by the processes of primary  
83 production and microbial respiration of organic matter (Maher and Eyre 2012; Koné et al. 2009; Maher et al.  
84 2019). In estuarine and coastal ecosystems, the acid–base properties of waters are driven by ecosystem primary

85 production and respiration, CaCO<sub>3</sub> precipitation, CaCO<sub>3</sub> dissolution, air-water CO<sub>2</sub> fluxes and thermodynamic  
86 equilibration during mixing of freshwater with seawater (Cai et al. 2020; Abril et al. 2021). Ecosystems that are  
87 net sinks of CO<sub>2</sub> are generally autotrophic (gross primary production, GPP > community respiration, CR), and  
88 ecosystems that are net sources of CO<sub>2</sub> are generally heterotrophic (GPP < CR) (Borges and Abril 2011).  
89 However, many exceptions exist where autotrophic systems are CO<sub>2</sub> sources and heterotrophic systems are CO<sub>2</sub>  
90 sinks (Borges 2005; Cotovicz et al. 2020; Abril et al. 2021). In addition, the diurnal variability of carbonate  
91 chemistry parameters and associated air-water CO<sub>2</sub> fluxes are significant in productive ecosystem (Cotovicz et  
92 al. 2015). Estuarine systems and near-shore coastal waters are considered as significant sources of CO<sub>2</sub> to the  
93 atmosphere due to their heterotrophic character and inputs of CO<sub>2</sub>-enriched waters from rivers and intertidal  
94 vegetated areas (Cai et al. 1999; Cai et al. 2011; Borges and Abril 2011). However, net uptake of atmospheric  
95 CO<sub>2</sub> has been found in coastal ecosystem located in tropical (Koné et al. 2009; Cotovicz et al. 2015) and  
96 subtropical (Maher and Eyre 2012; Kubo et al. 2017) regions. The sink behavior is often associated to human-  
97 induced coastal eutrophication stimulating high levels of phytoplanktonic primary production (Cotovicz et al.  
98 2015; Kubo et al. 2017). Capture of atmospheric CO<sub>2</sub> also occurs in coastal lagoons as the result of vertical  
99 haline stratification that favors phytoplankton development (Koné et al., 2009). However, the enhancement of  
100 primary production by eutrophication is associated to a concomitant enhancement of respiratory processes and  
101 emissions of CO<sub>2</sub> to the atmosphere (Cai et al. 2011). These processes can be tracked by analyzing the stable  
102 isotope signatures of the DIC ( $\delta^{13}\text{C}$ -DIC) due to the preferential uptake of the lighter stable carbon isotope ( $^{12}\text{C}$ )  
103 during photosynthesis, turning the residual DIC enriched in the heavier carbon isotope ( $^{13}\text{C}$ ) (Mook 2001). For  
104 that reason, the  $\delta^{13}\text{C}$ -DIC of phytoplankton-dominated coastal waters show very positive values (Cotovicz et al.,  
105 2019; 2020). The ecosystem-level responses of carbonate chemistry in face to eutrophication are antagonists and  
106 site-specific exerting both positive and negative feedbacks on the process of coastal and ocean acidification by  
107 increasing or decreasing the aquatic levels of CO<sub>2</sub>.

108 Among tropical lagoons, hypersalinity is a common characteristic in arid and semiarid regions (Kjerfve et al.  
109 1996). The aridity is increasing worldwide as the result of climate change (Huang et al. 2017). Observations and  
110 modelling of future scenarios suggest an increase of evaporation compared to precipitation in arid/semiarid  
111 regions; in other words, arid and semiarid regions tend to be larger and drier (Chou et al. 2009; Huang et al.  
112 2017). Currently, semiarid regions cover ~15 % of the Earth's continental surface (Safriel and Adeel 2005).  
113 However, the area of global drylands will expand ~10 % by 2100, from inland regions to coastal zones (Feng  
114 and Fu 2013). In such ecosystems, the water balance during dry months is normally negative, when the water

115 loss by evaporation exceeds the water inputs by rainfall and riverine contribution. During evaporation of  
116 seawater, the concentration of dissolved salts increases in the remaining water, which become hypersaline (some  
117 authors call this remaining aqueous solution as “brines”; Babel and Schreiber, 2014). The negative water balance  
118 has the potential to change the carbonate chemistry, increasing the concentrations of TA and DIC compared to  
119 the initial concentration of seawater (Golan et al. 2016; Yao and Hu 2017; McCutcheon et al. 2019). If the  
120 weather conditions remain dry and warm and evaporation continues at high rates, salts can precipitate, CaCO<sub>3</sub>  
121 being the first salt to form (Babel and Schreiber 2014). The precipitation of CaCO<sub>3</sub> releases CO<sub>2</sub> in the water,  
122 while TA and DIC are consumed in a ratio of 2:1 for every mole of CaCO<sub>3</sub> precipitated (Dickson 2010). To the  
123 contrary, CaCO<sub>3</sub> dissolution can occur in areas of organic matter degradation, absorbing CO<sub>2</sub> from the water and  
124 releasing TA and DIC (Abril et al. 2003). The CaCO<sub>3</sub> precipitation consumes DIC from the water in the form of  
125 carbonate (CO<sub>3</sub><sup>2-</sup>), which is the DIC form that has the heavier carbon stable isotope signature, turning the  
126 remaining DIC pool slightly depleted in <sup>13</sup>C relative to the initial seawater (Zhang et al. 1995; Isaji et al. 2017).  
127 These increases in TA and DIC concentrations affect the saturation state of CaCO<sub>3</sub> minerals ( $\Omega$ ), the buffering  
128 capacity of the ecosystem, and the air-water CO<sub>2</sub> fluxes (Frankignoulle 1994; Frankignoulle et al. 1994; Egleston  
129 et al. 2010). Hypersalinity may also lead to biological changes in the ecosystem in terms of abundance and  
130 diversity (Breux et al., 2009) and, consequently, changes in the carbonate chemistry. Furthermore, the ongoing  
131 long-term sea-level rise is expected to have a significant impact on the water chemistry of coastal lagoons in  
132 some regions (Anthony et al., 2009), which will interact with the impacts of increasing eutrophication and aridity  
133 in a near future.

134

135 As noted above, eutrophication and hypersalinity drive the carbonate chemistry in specific pathways. The  
136 primary productivity consumes DIC (and CO<sub>2</sub>) from the water, and makes the  $\delta^{13}\text{C}$ -DIC signatures heavier. In  
137 contrast, the CaCO<sub>3</sub> precipitation also consumes DIC (but releases CO<sub>2</sub>), and this process makes the  $\delta^{13}\text{C}$ -DIC  
138 lighter. To our best knowledge, the effects of eutrophication on carbonate chemistry of hypersaline coastal  
139 waters are almost undocumented. Araruama Lagoon, located at the Southeast coast of Brazil, is one of the largest  
140 hypersaline coastal lagoon in the world (Kjerfve et al. 1996). The system has been suffering from increasing  
141 anthropogenic disturbances along and within the watershed, especially urbanization receiving high amounts of  
142 domestic effluents. Here we report on carbonate chemistry in the Araruama Lagoon, were both processes of  
143 primary production and CaCO<sub>3</sub> precipitation are intense and competing. We investigated the main controls on  
144 the air-water CO<sub>2</sub> fluxes and carbonate chemistry considering the spatial and temporal variabilities.

145

## 146 2. Material and Methods

### 147 2.1 Study Area

148 The Araruama Lagoon (Fig. 1), located in the state of Rio de Janeiro (Brazil), is one of the largest permanent  
149 hypersaline lagoon in the world, covering 220 km<sup>2</sup>, and composed of seven elliptical-shaped cells (Kjerfve et al.  
150 1996; Knoppers et al. 1996). The average depth is 3m, with a maximum of 17m in the unique channel that  
151 connects the bay to the ocean. The lagoon is 40km long and 13 km wide at maximum, with a total water volume  
152 of about 0.62 km<sup>3</sup> (Kjerfve et al. 1996). The climate in the region is semiarid, with a mean annual rainfall of 800  
153 mm (Barbière and Monteiro1974). The lagoon exhibits an excess of evaporation compared to precipitation and  
154 drainage from its very small freshwater basin. The lagoon waters are hypersaline (Barbière and Monteiro 1974;  
155 Kjerfve et al. 1996). Historical data indicate that salinity in the lagoon is on average 52 and oscillates seasonally  
156 in response to the balance between evaporation and precipitation (Kjerfve et al. 1996). The wind velocities in the  
157 region are high, with annual averages > 6 m s<sup>-1</sup> (Amarante et al. 2002). The flow of most incoming rivers is quite  
158 low (except during episodes of local heavy rain), with a mean annual surface runoff estimated at about 1 m<sup>3</sup> s<sup>-1</sup>  
159 (Kjerfve et al. 1996). Owing to the restricted connection with the open ocean, the time necessary to renew 50%  
160 of the water in the lagoon with seawater is estimated at about 83 days (Kjerfve et al. 1996).

161 In the 70's-80' years, the embayment was classified as oligotrophic (Knoppers et al. 1996). At that time, studies  
162 have documented blue and crystalline waters with healthy beaches, mangroves, sandbanks and dune areas  
163 (Bertucci et al. 2016). The primary production was dominated by microphytobenthos, which greatly exceeded  
164 the planktonic primary production (Knoppers et al. 1996). However, intensive urbanization in the 80's and 90's,  
165 with absence or inefficient wastewater treatment, have led to a dramatic increase in organic matter and nutrients  
166 concentrations in the lagoon waters and sediments (Moreira-Turcq 2000; Souza et al. 2003). In addition, the  
167 settlement of an industry of carbonates extraction in the lagoon (*Anomalocardia brasiliiana* shells for calcareous  
168 manufacture) in the 60's has increased the sediment remobilization (Kjerfve et al. 1996; Bertucci et al. 2016).  
169 This industry was decommissioned in 2006. All these factors have contributed to environmental degradation,  
170 turning the waters turbid, with an increase of planktonic primary production and a shift from oligotrophic to  
171 mesotrophic / eutrophic conditions (Knoppers et al. 1999; Souza et. al. 2003; Laut et al. 2020).

172

## 173 2.2 Sampling Strategy

174 Two sampling campaigns were conducted in the lagoon, in winter (from 17 to 20 of July-2017) and summer  
175 (from 19 to 22 of February-2018) conditions. The sampling consisted in spatial surveys covering the major area  
176 of the lagoon using a medium-size boat, with continuous real-time measurements and discrete sampling (Fig. 1).  
177 Continuous measurements included partial pressure of CO<sub>2</sub> in the water (*p*CO<sub>2</sub>), pH, salinity, temperature,  
178 dissolved oxygen (DO) concentrations and geographical position. Discrete sampling of surface waters was  
179 performed for determination of TA, stable isotopic composition of DIC ( $\delta^{13}\text{C-DIC}$ ), and photosynthetic pigments  
180 (chlorophyll *a* and pheopigments). During the sampling of February-2018, we also performed a diurnal sampling  
181 at an anchored station located at the central region of the lagoon (Fig. 1), also with continuous measurements and  
182 hourly discrete sampling during 22 hours. We could not achieve a complete 24 hours of diurnal sampling due to  
183 logistical limitations.

### 184 2.2.1 Continuous measurements

185 The continuous measurement system allows real-time (every minute) record of surface water *p*CO<sub>2</sub> and ancillary  
186 parameters (Frankignoulle et al. 2001). A water pump positioned at depth of ~0.2 m supplies water continuously  
187 to an equilibrator system at a rate of ~3L min<sup>-1</sup>. The equilibrator consists of an acrylic cylinder (diameter of 8  
188 cm, height of 100 cm), where the water flows from top to down. Marbles inside the equilibrator promotes an  
189 increase in the surface area, which reduces the equilibration time between gaseous and aquatic phases. A closed  
190 air circulation flows from the bottom to the top of the equilibrator at a rate of ~ 1 L min<sup>-1</sup>. The air passes through  
191 a desiccant, and then the *p*CO<sub>2</sub> in the dry air is measured by a non-dispersive infrared gas analyzer (NDIR;  
192 LICOR® 820 type). Before each field cruise, the LICOR® was calibrated using three gas mixture standards  
193 (*p*CO<sub>2</sub> of 410, 1007, and 5035 ppmv; White Martins Certified Material, RJ, Brazil). N<sub>2</sub> was used to set the zero,  
194 and the standard of 410 ppmv to set the span. The standards of 1007 and 5035 ppmv were used to check for  
195 linearity. The precision and accuracy of *p*CO<sub>2</sub> measurements were estimated at about ±3 and ±5 ppmv,  
196 respectively. The system is ideal for analyses of *p*CO<sub>2</sub> in coastal waters because the equilibration between air  
197 and water phases is promoted in about 3 minutes (Cotovicz et al. 2016). Another part of the water flow (~1L  
198 min<sup>-1</sup>) was directed to a home-made acrylic chamber where the ancillary parameters were continuously measured  
199 with probes. Water temperature, salinity and DO concentrations were measured with a calibrated YSI® 6600V2  
200 multiparameter sonde inserted in the acrylic chamber. The salinity probe (0.01 of resolution) was calibrated  
201 before the cruise with IAPSO standard seawater and deionized water; we checked the linearity of the sensor



202 along the entire 35-70 salinity range, by comparing the values observed *in situ* with the probe with those  
203 measured in the laboratory on five discrete water samples using a refractometer (slope = 1 with  $R^2 = 0.95$ ). The  
204 DO probe (optical optode) was calibrated every day of measurements through a 1-point calibration in water-  
205 saturated air. The accuracy was estimated at about  $\pm 0.2 \text{ mg L}^{-1}$  or 2% of reading. The pH was determined  
206 continuously by the potentiometric method at the NBS scale ( $\text{pH}_{\text{NBS}}$ ), with a glass electrode sentix 41 connected  
207 to a WTW® 3310 pHmeter. The calibration of the pHmeter was made prior to and after each sampling  
208 campaign, using three NBS traceable buffer solutions: pH 4.00, pH 7.01 and pH 10.00 (WTW® buffers). NBS  
209 refers to the National Bureau of Standards (now called NIST, National Institute of Standards and Technology).  
210 The reproducibility of pH measurements was typically better than 0.01. The geographical position was  
211 determined with a GPG model Garmin® 60CSx. All parameters measured continuously recorded the data at a  
212 frequency of 1 minute.

#### 213 2.2.2 Discrete sampling and laboratory analysis

214 Surface waters were sampled at a depth of approximately 0.2 m with a Van Dorn bottle (Alfakit®, 2L). Water  
215 was filtered through GF/F Whatman® filters. The filters were used for the analysis of photosynthetic pigments,  
216 and the filtrate was used for the titration of TA. The filters were frozen at  $-20^\circ\text{C}$  until chlorophyll *a* (Chl *a*) and  
217 pheopigments analysis were done few days after the cruise. In the lab, filters were inserted in assay tubes  
218 containing 90% acetone and kept for 20 hours on the dark at  $4^\circ\text{C}$ . The pigments were quantified  
219 spectrophotometrically before and after acidification of the samples, with formulations and corrections proposed  
220 by Lorenzen (1967). The total pigments content was considered as the sum between Chl *a* and pheo-pigments.  
221 The analyses of TA were carried out with an automatic titration system (Mettler Toledo® T5) using HCl 0.1N.  
222 The equivalent point was calculated by linearizing the Gran function (Gran 1952). Measurements were compared  
223 to certified reference material (CRM, provided by A. G. Dickson from Scripps Institution of Oceanography) and  
224 corrected according. The precision and accuracy of the measurements were estimated at  $\pm 3$  and  $\pm 5 \text{ } \mu\text{mol kg}^{-1}$ ,  
225 respectively.

226 The analytical procedures for  $\delta^{13}\text{C}$ -DIC are described in Gillikin and Bouillon (2007). Samples for  $\delta^{13}\text{C}$ -DIC  
227 were collected in 120 ml of serum glass bottles. 100  $\mu\text{L}$  of saturated mercuric chloride was added to the samples  
228 to inhibit microbial activity. In the laboratory, a headspace of 40 mL was created by adding helium gas. After  
229 creating the headspace, samples were acidified adding  $\text{H}_3\text{PO}_4$  to convert all inorganic carbon to  $\text{CO}_2$ . Samples  
230 were shaken and let stabilize at room temperature for 5h.  $\delta^{13}\text{C}$  of  $\text{CO}_2$  in the headspace was determined with an

231 isotopic ratio mass spectrometer (IRMS, Micromass IsoPrime), equipped with a manual gas injection port. The  
232  $\delta^{13}\text{C}$ -DIC values were corrected for the partitioning of  $\text{CO}_2$  between the gaseous (headspace) and water phases in  
233 each sample using the algorithm of Miyajima et al. (1995).  $\delta^{13}\text{C}$ -DIC measurements were calibrated against  
234 certified standard (C2, -8.25 ‰). The reproducibility of the analysis was approximately 0.2‰. The  $\delta^{13}\text{C}$ -DIC  
235 signatures are reported in ‰ relative to the standard Vienna Pee Dee Belemnite (V-PDB) scale.

## 236 2.3 Calculations

### 237 2.3.1 Carbonate System

238 DIC was calculated from the pair TA- $p\text{CO}_2$ , at *in situ* seawater temperature, and salinity, using the CO2calc  
239 1.2.9 program (Robbins et al. 2010). The dissociation constants for carbonic acid were those proposed by  
240 Mehrbach et al. (1973) refitted by Dickson and Millero (1987), the borate acidity constant from Lee et al. (2010),  
241 the dissociation constant for the  $\text{HSO}_4^-$  ion from Dickson (1990), and the solubility coefficient of  $\text{CO}_2$  from  
242 Weiss (1974). The dissociation constants of carbonic acid in natural seawater are available for limited ranges of  
243 temperature (0-50 °C), and salinities (0-50) (Chen et al. 2015). The upper values of the salinity ranges measured  
244 in Araruama Lagoon (39.0-56.5 in winter; 33.7-65.9 in summer) are above this limit. We extrapolated linearly  
245 the values of these constants as a function of salinity, in accordance with findings in other evaporative  
246 environments with similar salinity ranges where the dissociation constants were measured (Sass and Ben-Yaakov  
247 1977; Burke and Atkinson 1988).

### 248 2.3.2 Air-water $\text{CO}_2$ fluxes

249 Diffusive  $\text{CO}_2$  fluxes at air-water interface ( $F_{\text{CO}_2}$ ) were computed according to:

$$250 F_{\text{CO}_2} = k \alpha \Delta p\text{CO}_2 \quad (\text{Eq. 1})$$

251 where  $k$  is the  $\text{CO}_2$  gas transfer velocity,  $\alpha$  is the solubility of  $\text{CO}_2$  in seawater (Weiss 1974), and  $\Delta p\text{CO}_2$  is the  
252 difference between  $p\text{CO}_2$  measured in the water and in the air. Negative values represent a sink of  $\text{CO}_2$ . We used  
253 the  $k$ -wind parameterization of Jiang et al. (2008; J08) and Van Dam et al. (2019; VD09), which are coefficients  
254 specific for estuaries, and the coefficient of Wanninkhof (2014; W14), which is specific for open ocean waters.  
255 The gas transfer coefficients were normalized to a Schmidt number of 600 obtained with the three  
256 parameterizations and converted to the gas transfer velocity at *in situ* temperature and salinity, following the  
257 procedure of Jähne et al. (1987). Fluxes were computed for each sector of Araruama Lagoon (inner, central and  
258 outer sectors; Fig. 1), using water  $p\text{CO}_2$  values and wind conditions representative for each day of sampling

259 campaign. The annual budget was spatially and temporally integrated. Wind speed data were provided by the  
260 National Institute for Space Research (INPE), in a meteorological station located in the Cabo Frio city (at the  
261 mouth of the lagoon). The wind velocities in the region are strong and homogeneous due to the flat relief  
262 (Amarante et al. 2002).

### 263 2.3.3 Net Community Production (NCP)

264 The NCP can be calculated by considering the changes in DIC concentrations from the diel-moored station, and  
265 corrected for CaCO<sub>3</sub> precipitation/dissolution and air-sea CO<sub>2</sub> flux, according to the following equation:

$$266 \text{ NCP} = ((\text{DIC}_1 - \text{DIC}_2)pd)/\Delta t - ((\text{TA}_1 - \text{TA}_2)pd)/\Delta t - \text{FCO}_2 \quad (\text{Eq. 2})$$

267 Considering the fact that we did not observe significant differences of TA concentrations at the diel timescale,  
268 the CaCO<sub>3</sub> precipitation/dissolution was assumed to be negligible along this period of sampling. Thus, the NCP  
269 was calculated according:

$$270 \text{ NCP} = ((\text{DIC}_1 - \text{DIC}_2)pd)/\Delta t - \text{FCO}_2 \quad (\text{Eq. 3})$$

271 where NCP is in mmol m<sup>-2</sup> h<sup>-1</sup>, DIC<sub>1</sub> and DIC<sub>2</sub> are the salinity-normalized concentration of DIC (mmol kg<sup>-1</sup>)  
272 during two consecutive discrete sampling with one hour of interval,  $p$  is the seawater density (kg m<sup>-3</sup>),  $d$  is the  
273 average depth (m),  $\Delta t$  represents the time interval (hour) and FCO<sub>2</sub> is the carbon dioxide flux (mmol m<sup>-2</sup> h<sup>-1</sup>)  
274 across the air-water interface. The vertical density, salinity and temperature stratification were considered  
275 negligible in the lagoon (Kjerfve et al. 1996). Values of NCP were hourly-averaged for night-time period (from  
276 dusk to dawn; NCP<sub>night-time</sub>), and for daytime period (from dawn to dusk; NCP<sub>daytime</sub>).

### 277 2.3.4 Evaporation carbonate chemistry model

278 Araruama lagoon is hypersaline and the freshwater discharge is very small compared to the entire water volume  
279 of the lagoon (Kjerfve et al. 1996). In addition, the time necessary to renew 50% of the water in the lagoon with  
280 seawater is estimated at about 83 days (Kjerfve et al. 1996), favoring evaporative processes. Taking into account  
281 these characteristics, we adapted an evaporative carbonate chemistry model from a previous mixing model used  
282 by Jiang et al. (2008). The principle is that precipitation and evaporation create no salt flux across the air-water  
283 interface. Thus, in estuaries and lagoons with low or negligible freshwater inputs, the conservations of DIC and  
284 TA are written as:

$$285 \text{ DIC}_{\text{conservative}} = S_{\text{measured}}/S_{\text{ocean}} * \text{DIC}_{\text{ocean}} \quad (\text{Eq. 4})$$

286  $TA_{\text{conservative}} = S_{\text{measured}}/S_{\text{ocean}} * TA_{\text{ocean}}$  (Eq. 5)

287 Where  $S_{\text{measured}}$  is the measured salinity,  $S_{\text{ocean}}$  the salinity of the ocean end-member,  $DIC_{\text{ocean}}$  and  $TA_{\text{ocean}}$  the DIC  
288 and TA concentrations of the ocean end-member. This model adapted to estuaries assumes that  $DIC_{\text{conservative}}$  is  
289 the DIC concentration after the ocean end-member is diluted by a zero DIC freshwater. In the hypersaline  
290 lagoon, we applied this same approach for an evaporative environment, assuming that the ocean end-member is  
291 linearly concentrated by evaporation, salinity being conserved.

292 The deviation from evaporation path ( $\Delta DIC$ ) is defined as the DIC addition or loss relative to the theoretical DIC  
293 concentration during evaporation of seawater:

294  $\Delta DIC = DIC_{\text{measured}} - DIC_{\text{conservative}}$  (Eq. 6)

295 Where  $DIC_{\text{measured}}$  is the measured DIC. Deviation of TA ( $\Delta TA$ ) from the evaporation path can be calculated in  
296 the same way. As we could not measure the ocean end-member during the winter sampling, we use the value  
297 from Cotovicz et al. (2015), which measured these parameters in an adjacent coastal region with similar salinity  
298 and water temperature and during the same month.

299 According to the approach of Yang et al. (2018), the difference between the  $\delta^{13}C$ -DIC of the sample ( $\delta^{13}C$ -  
300  $DIC_{\text{measured}}$ ) and the  $\delta^{13}C$ -DIC of the marine end-member ( $\delta^{13}C$ - $DIC_{\text{ocean}}$ ) represents the stable isotopic deviation  
301 from the marine end-member ( $\Delta\delta^{13}C$ -DIC), as follows:

302  $\Delta\delta^{13}C\text{-DIC} = \delta^{13}C\text{-DIC}_{\text{measured}} - \delta^{13}C\text{-DIC}_{\text{ocean}}$  (Eq. 7)

303 If we consider only the process of seawater evaporation, the  $\delta^{13}C$ - $DIC_{\text{measured}}$  is equal do the  $\delta^{13}C$ - $DIC_{\text{ocean}}$   
304 assuming that evaporation creates no carbon stable isotope exchanges across the air-sea interface (during  
305 evaporation of seawater the  $^{12}C$  mass and  $^{13}C$  masses are conserved). In addition, the relationship between  
306  $\Delta DIC/DIC_{\text{ocean}}$  and  $\Delta\delta^{13}C$ -DIC are tightly linked in coastal waters with limited and/or absent river inputs (Yang  
307 et al. 2018; Cotovicz et al. 2019). We used this assumption for hypersaline waters, considering the ratio  
308  $\Delta DIC/DIC_{\text{ocean}}$  and the values  $\Delta\delta^{13}C$ -DIC will be null considering only the evaporation, whereas positive and/or  
309 negative deviations are attributed to  $CaCO_3$  precipitation/dissolution, photosynthesis/respiration, and/or air-water  
310  $CO_2$  exchanges (Samanta et al. 2015).

311 2.5 Statistical analysis

312 We applied the Shapiro-Wilk test to verify the normality of data distribution. As the data set showed non-  
313 parametric distributions, we used the non-paired Mann-Whitney test to verify the statistical differences between  
314 averages of two groups for spatial (differences between sectors), and temporal (seasonal, diurnal) investigations.  
315 To compare the differences between three or more groups, we applied the Kruskal-Wallis test. Linear and non-  
316 linear (second order polynomial) regressions were also calculated. All statistical analysis were based on  $\alpha=0.05$   
317 and were performed with the GraphPad Prism 7 software.

318

### 319 **3. Results**

#### 320 3.1 Spatial and Seasonal Variability

321 Air was colder during winter, with temperature averaging  $19.9 \pm 1.9^\circ\text{C}$ , while in summer temperature was  $26.1 \pm$   
322  $1.2^\circ\text{C}$ , with a maximum of  $31.2^\circ\text{C}$ . The accumulated precipitation during 7 days before sampling was higher for  
323 the summer campaign (35 mm) than winter (1.6 mm). Water parameters analyzed in the inner, central and outer  
324 lagoon sectors, in summer and winter are shown in Table 1. The inner sector represents the most confined region  
325 of the lagoon with shallow depths ( $< 3$  m), comprising the four westernmost “elliptical cells” (Fig. 1). This sector  
326 is the only one that receives some freshwater runoff from two rivulets (annual average of  $1 \text{ m}^3 \text{ s}^{-1}$ ; Knoppers et  
327 al., 1999); this sector also receives the sewage effluent discharges from the Araruama city. The central sector  
328 includes the two longer and wider “elliptical cells” with a mean depth of 3 m, a maximum depth of 17 m, and the  
329 highest water volume and surface area. Due to the high surface area, this sector experiences strong northeasterly  
330 winds year-round, producing wind-driven currents and significant waves with heights frequently exceeding 1 m  
331 (Kjerfve et al., 1996). The outer sector includes the 14-km long entrance channel where the mixing between  
332 seawater and waters from the lagoon occurs. This region includes two very shallow “lagoon cells”, and a narrow  
333 4 m deep channel close to the lagoon mouth (Kjerfve et al., 1996). This region receives direct inputs of domestic  
334 effluents from the Cabo Frio city. The wind velocities were about the double in summer (averaging  $8.0 \pm 2.5 \text{ m}$   
335  $\text{s}^{-1}$ ), compared to winter (averaging  $4.1 \pm 2.9 \text{ m s}^{-1}$ ). The water temperature followed the same seasonal tendency,  
336 with higher temperatures in summer. The highest measured water temperature was  $32.0^\circ\text{C}$ , whereas the lowest  
337 was  $21.2^\circ\text{C}$ , both in the inner lagoon. During winter, the spatial variability of water temperature was low,  
338 whereas in summer the spatial difference was pronounced, with a landward increase of  $\sim 4^\circ\text{C}$ . Salinities were  
339 also higher in summer than in winter (Mann Whitney test;  $p < 0.001$ ). In general, inner and central sectors

340 presented similar salinities, averaging 63 in summer and 54 in winter. The outer sector showed the highest  
341 spatial variability and lowest values, due to the connection with the ocean.

342 The distributions of  $p\text{CO}_2$  values in the lagoon showed marked spatial and temporal variability (Table 1; Figs. 2  
343 and 3). The outer region revealed the highest values, averaging  $225 \pm 37$  ppmv in winter and  $460 \pm 108$  ppmv in  
344 summer. Following the landward direction, the  $p\text{CO}_2$  sharply decreased with intermediate values in the central  
345 sector of the bay, averaging  $200 \pm 16$  ppmv in winter and  $385 \pm 24$  ppmv in summer. The inner region of the  
346 lagoon presented the lowest values of  $p\text{CO}_2$ , averaging  $128 \pm 31$  ppmv in winter and  $233 \pm 94$  ppmv in summer.  
347 Concerning the sector-averaged values, the winter sampling presented lower  $p\text{CO}_2$  compared to summer for all  
348 sectors (Mann Whitney test;  $p < 0.0001$ ). The plot of  $p\text{CO}_2$  versus salinity showed a significant and inverse  
349 relationship (Fig. 2). The spatial variability of DO concentrations showed opposite trend compared to  $p\text{CO}_2$   
350 during summer, but not during winter. The waters were more oxygenated in winter, exhibiting always  
351 oversaturated conditions. During summer, the levels of oxygen saturation decreased significantly (Mann  
352 Whitney;  $p < 0.0001$ ).

353 In general, the correlations between  $p\text{CO}_2$  and DO were variable and changed according to the day of sampling.  
354 In particular, we observed a drastic change in the DO versus  $p\text{CO}_2$  relationship from one day to the other, before  
355 and after a heavy storm in winter (when wind velocities exceeded  $15 \text{ m s}^{-1}$ ). For a similar  $p\text{CO}_2$  value, the DO  
356 concentration was significantly lower after the passage of the storm, with DO levels approaching the equilibrium  
357 with atmosphere whereas  $p\text{CO}_2$  levels remained well-below the atmospheric levels (Fig. 4). Temporally and  
358 spatially, water  $p\text{CO}_2$  was inversely correlated with Chl *a* concentrations ( $R^2 = 0.69$ ,  $p < 0.0001$  for winter;  $R^2 =$   
359  $0.76$ ,  $p < 0.0001$  for summer; Fig. 5); however the linear regressions showed different slopes and intercepts  
360 considering the different sampling campaigns. The highest Chl *a* concentrations were found during summer, and  
361 at the innermost region of the lagoon (up to  $151 \mu\text{g L}^{-1}$ ). Following an expected pattern, the values of pH were  
362 higher in summer and at innermost regions, showing significant and inverse correlations with  $p\text{CO}_2$ .

363 Overall, the variabilities for TA, DIC and its stable isotope composition ( $\delta^{13}\text{C-DIC}$ ) showed different spatial  
364 trends during the sampling campaigns (Table 1). During winter, TA and DIC concentrations showed lower  
365 values in the inner region ( $p < 0.001$ ), averaging  $2626 \pm 62 \mu\text{mol kg}^{-1}$  and  $1820 \pm 117 \mu\text{mol kg}^{-1}$ , and higher  
366 values in the central region, averaging  $2729 \pm 33 \mu\text{mol kg}^{-1}$  and  $2026 \pm 40 \mu\text{mol kg}^{-1}$ , respectively. The  $\delta^{13}\text{C-DIC}$   
367 did not exhibit this clear spatial tendency, with values ranging from 1.29‰ to 1.60‰. During summer, TA  
368 concentrations were almost constant in the inner and central regions, averaging  $2971 \pm 40 \mu\text{mol kg}^{-1}$  and  $2954 \pm$

369 57  $\mu\text{mol kg}^{-1}$ , respectively, while in the outer region the TA was significantly lower. For DIC concentrations and  
370  $\delta^{13}\text{C}$ -DIC signatures, spatial variability was significant, with lower values of DIC at the inner region (average of  
371  $2015 \pm 180 \mu\text{mol kg}^{-1}$ ), coincident with highest  $\delta^{13}\text{C}$ -DIC signatures (average of  $4.11 \pm 1.09\%$ ). Overall,  
372 considering the seasonal variability, TA, DIC concentrations and  $\delta^{13}\text{C}$ -DIC signatures were higher in summer  
373 compared to winter, with minimum values of  $2176 \mu\text{mol kg}^{-1}$ ,  $1678 \mu\text{mol kg}^{-1}$ , and  $1.29\%$ , and maximum of  
374  $3037 \mu\text{mol kg}^{-1}$ ,  $2269 \mu\text{mol kg}^{-1}$ , and  $5.55\%$ , respectively. TA distributions followed a positive trend with  
375 salinity ( $R^2 0.90$ ;  $p < 0.001$ ) (Fig. 2a). This trend was not verified for DIC concentrations and  $\delta^{13}\text{C}$ -DIC, which  
376 did not vary with salinity (Fig. 2b,c). TA and DIC values were well below the calculated evaporation line,  
377 indicating a net loss of inorganic carbon in the lagoon (Fig. 2). For  $\delta^{13}\text{C}$ -DIC, the values were overall above this  
378 line, with highest positive deviations during summer in the inner region of the lagoon, associated with low  $p\text{CO}_2$   
379 values, and high water temperature and Chl *a* concentrations (Fig. 6). In winter, all data points were located  
380 close to the evaporation line (within the analytical error of  $\pm 0.2\%$ ). In summer, one point in the outer region was  
381 below the line, those in the central region were on the line and those in the inner region were well above. For  
382 winter and summer, the  $\delta^{13}\text{C}$ -DIC presented lowest signatures in the outer region when the  $p\text{CO}_2$  values were at  
383 maximum.

384 Air-water  $\text{CO}_2$  flux ( $\text{FCO}_2$ ) and ancillary parameters are shown in Table 2. Data for wind velocity and  $k_{600}$  were  
385 obtained for each day of sampling, and then multiplied by the sector-averaged air-water  $p\text{CO}_2$  gradient. The air-  
386 water  $\text{CO}_2$  fluxes were integrated for the entire surface area of the lagoon for winter and summer periods. The  
387 wind velocities were higher in summer compared to winter, with averages of  $8.0 \pm 2.5 \text{ m s}^{-1}$  and  $4.1 \pm 2.9 \text{ m s}^{-1}$ ,  
388 respectively. For both sampling campaigns, peaks of wind velocity overpassed  $10 \text{ m s}^{-1}$ . Gas transfer velocities  
389 averaged  $7.7 \pm 9.0 \text{ cm h}^{-1}$  in winter and  $17.9 \pm 8.3 \text{ cm h}^{-1}$  in summer. Generally,  $k_{600}$  values calculated from the  
390 equation of Wanninkhof (2014; W14) were systematically lower than those calculated from the relationships of  
391 Van Dam et al. (2019; VD19) and Jiang et al. (2008; J08). However, at wind velocities higher than  $9 \text{ m s}^{-1}$ , the  
392 parameterization of W14 gave higher  $k_{600}$  values than that of VD19. During winter,  $\text{FCO}_2$  exhibited always  
393 negative values, indicating a permanent sink of  $\text{CO}_2$ , with fluxes ranging from  $-19.5 \pm 2.5 \text{ mmolC m}^{-2} \text{ d}^{-1}$  at the  
394 inner sector, to  $-8.2 \pm 1.9 \text{ mmolC m}^{-2} \text{ d}^{-1}$  at the outer sector. During summer, the inner and central regions  
395 remained a net sink of  $\text{CO}_2$ , with fluxes ranging between  $-19.3 \pm 9.8 \text{ mmolC m}^{-2} \text{ d}^{-1}$  to  $-1.5 \pm 1.9$ , while the outer  
396 region was a weak source of  $\text{CO}_2$ , ranging from  $6.8$  to  $7.9 \text{ mmolC m}^{-2} \text{ d}^{-1}$ . Time-integrated  $\text{CO}_2$  fluxes,  
397 accounting for seasonal variations, revealed that the lagoon behaved as a net  $\text{CO}_2$  sink during the considered  
398 period of sampling.

### 399 3.2 Diurnal Variability

400 The diurnal variations of carbonate chemistry during the summer cruise are presented in Fig. 7 and Table 3.  
401 Salinity did not present significant difference between daytime and night-time periods, suggesting moderate tidal  
402 mixing at the monitoring point (Mann Whitney Test;  $p > 0.05$ ). Daytime water samples had higher average  
403 temperature ( $30.0 \pm 0.3$  °C) than nighttime samples ( $29.5 \pm 0.3$  °C), but with no statistical significance.  $p\text{CO}_2$   
404 values averaged  $411 \pm 11$  ppmv during nighttime and decreased to  $385 \pm 25$  ppmv during daytime. The  
405 maximum  $p\text{CO}_2$  value was 432 ppmv at dawn, whereas the minimum value was 330 ppmv after midday,  
406 corresponding to a maximal diel amplitude of 102 ppmv. The highest values of  $p\text{CO}_2$  were coincident with  
407 highest concentrations of DIC, and lowest values of  $\delta^{13}\text{C-DIC}$  and pH (Table 3).  $p\text{CO}_2$  showed strong negative  
408 correlations with DO ( $R^2 = 0.90$ ;  $p < 0.0001$ ),  $\delta^{13}\text{C-DIC}$  ( $R^2 = 0.80$ ;  $p < 0.0001$ ), and Chl *a* concentrations ( $R^2 =$   
409  $0.75$ ;  $p < 0.0001$ ). During the diurnal cycle,  $\delta^{13}\text{C-DIC}$  values varied between 2.53‰ (nighttime) and 4.39‰  
410 (daytime). The air-water  $\text{CO}_2$  fluxes showed emissions during nighttime, ranging from 1.59 to 3.25  $\text{mmol C m}^{-2}$   
411  $\text{d}^{-1}$ , and from -3.99 to -2.05  $\text{mmol C m}^{-2} \text{d}^{-1}$  during daytime, considering the different gas transfer velocities. A net  
412 time-integrated flux was -1.01  $\text{mmol C m}^{-2} \text{d}^{-1}$ . The NCP was -91.4  $\text{mmol C m}^{-2} \text{d}^{-1}$  during night-time  
413 (heterotrophy), and 278.8  $\text{mmol C m}^{-2} \text{d}^{-1}$  during daytime (autotrophy), with a net time-integrated value of 93.7  
414  $\text{mmol C m}^{-2} \text{d}^{-1}$ .

415

## 416 4. Discussion

### 417 4.1 Evidence for $\text{CaCO}_3$ precipitation in the Lagoon

418 Araruama Lagoon is a hypersaline coastal lagoon, with a negative water balance along the year associated with  
419 low freshwater inputs and high atmospheric temperatures (Kjerfve et al. 1996). The historical data shows that the  
420 salinities in the lagoon are normally in the range of 52-67 (Kjerfve et al. 1996), which are quite close to our  
421 measured values. The hypersaline conditions are reflected in the higher concentrations of TA and DIC in the  
422 brines of Araruama Lagoon, compared to the initial seawater. These increases of TA and DIC in the brines  
423 illustrate the general pattern of chemical evolution of seawater during the evaporation process in hypersaline  
424 systems (Krumgalz et al. 1980; Lazar et al. 1983). Higher concentration of TA in the water increases the  
425 buffering capacity, i.e., the ability to resist changes by transferring protons (Millero 2007; Dickson 2010;  
426 Middelburg et al. 2020). This means that the changes in carbonate chemistry (like variability of pH,  $p\text{CO}_2$ )  
427 related to additions/losses of  $\text{CO}_2$  in the ecosystem will be lower in waters with higher buffering capacity



428 compared to waters with lower buffering capacity (Frankignoulle 1994; Middelburg et al. 2020). However,  
429 measured TA and DIC concentrations are still well below those predicted by the evaporation model (Fig. 2). TA  
430 and DIC do not behave conservatively and a net loss of TA and DIC occurs in the lagoon, creating negative  
431 deviations in the values of  $\Delta$ TA and  $\Delta$ DIC (Fig. 8a). Multiplying  $\Delta$ TA and  $\Delta$ DIC values by the water volume of  
432 the lagoon ( $0.618 \text{ km}^3$ ), dividing by the average water depth (7m) and considering the residence time of 167  
433 days, the estimated net losses of TA are on the order of  $0.08$  to  $0.10 \text{ gC m}^{-2} \text{ d}^{-1}$  for winter and summer,  
434 respectively, whereas for DIC these losses are  $0.11$  to  $0.12 \text{ gC m}^{-2} \text{ d}^{-1}$ . These losses of DIC are lower than the  
435 global-averaged community  $\text{CaCO}_3$  production in coral reefs ( $140$  to  $334 \text{ gC m}^{-2} \text{ yr}^{-1}$ ), similar of  $\text{CaCO}_3$   
436 production in seagrass meadows ( $30$  to  $125 \text{ gC m}^{-2} \text{ yr}^{-1}$ ) and well above the precipitation rates found in carbonate  
437 rich ( $3.8$  to  $5.3 \text{ gC m}^{-2} \text{ yr}^{-1}$ ) and poor ( $0.01$  to  $0.8 \text{ gC m}^{-2} \text{ yr}^{-1}$ ) shelves (Iglesias-Rodriguez et al. 2011; O'Mara  
438 and Dune 2019; Champenois and Borges 2021).

439 If the weather conditions remains dry and warm and evaporation continues at high rates, the solution evolves  
440 from undersaturated to oversaturated conditions and some solid phases will precipitate (Babel and Schreiber,  
441 2014; Marion et al. 2009). Carbonate minerals (aragonite, calcite, and high-magnesium calcite) are usually the  
442 salts that precipitate earliest during seawater evaporation (McCaffrey et al. 1987; Millero 2007; Morse et al.  
443 2007; Babel and Schreiber 2014). For example,  $\text{CaCO}_3$  mineral may start to precipitate at the volume reduction  
444 ratio of about 50% from the original seawater (Isaji et al. 2017), which in the Araruama lagoon is equivalent to a  
445 salinity of  $\sim 53$ . For each mole of  $\text{CaCO}_3$  formed, TA decreases by two moles and DIC by one mole (Gattuso et  
446 al. 1999), which partially explains the deficits of TA and DIC (Figs. 2 and 8a). We must also point out that the  
447 saturation state of  $\text{CaCO}_3$  ( $\Omega$ ) increases with temperature (Mucci 1983), and heating of water in the lagoon also  
448 favors the  $\text{CaCO}_3$  precipitation during summer conditions.

449 The precipitation of carbonate minerals can occurs spontaneously following the abiotic reactions of chemical  
450 thermodynamic equilibrium, or it can occurs mediated by organisms (biogenic calcification) (Morse and He  
451 1993; Morse et al. 1997; Marion et al. 2009). A theoretical study applying a chemical thermodynamic model  
452 (FREZCHEM) found that carbonate precipitation begins at salinity of about 73 under pseudo-homogeneous  
453 nucleation (Marion et al. 2009). However, an experimental study investigating the evaporation path of seawater  
454 at the Morton solar salt production (Great Inagua Island – Bahamas) revealed the occurrence of  $\text{CaCO}_3$   
455 precipitation at concentrations of about 1.8 times that of seawater, equivalent to a salinity of 63 (McCaffrey et al.  
456 1987). This was attributed to the heterogeneous nucleation in shallow waters that are probable to contain pre-  
457 existing mineral solid phases (McCaffrey et al. 1987; Marion et al. 2009). Accordingly, the presence of relevant

458 carbonate and organic solid phases including planktonic micro-organisms in the water of the Araruama lagoon  
459 may favor the occurrence  $\text{CaCO}_3$  at early stages of evaporation path. Our data confirms this process in Araruama  
460 Lagoon, which is a shallow carbonate-rich and productive environment containing suspended carbonate grains in  
461 the water column as the results of intense sediment resuspension by wind and anthropogenic activities (Kjerfve  
462 et al. 1996; Knoppers et al. 1996), creating conditions for the occurrence of high pH and spontaneous  $\text{CaCO}_3$   
463 precipitation. Indeed, in addition to carbonate precipitation, the primary productivity is also an important driver  
464 of inorganic carbon removal from the water column (see section 4.2). It is important to point out that the high  
465 rates of primary production may contribute – together with evaporation – to rise the supersaturation of  $\text{CaCO}_3$ ,  
466 thus locally counter-acting the process of ocean acidification. Indeed,  $\text{CaCO}_3$  nucleation from seawater have  
467 been associated with plankton blooms at shallow depths and hypersaline environments (Morse and He 1993).

468 Fig. 8a allows to evaluate the relative contribution of primary production and  $\text{CaCO}_3$  precipitation to the deficits  
469 of TA and DIC in the brines of Araruama Lagoon. Indeed, the slopes of  $\Delta\text{TA}$  and  $\Delta\text{DIC}$  are consistent with  
470 simultaneous photosynthesis and  $\text{CaCO}_3$  precipitation.

471 The carbonate precipitation can be written as:



473 This reaction involves consumption of TA and DIC in a ratio of 2:1. The process of primary production, can be  
474 written as:



476 This process has an almost negligible effect on TA, but a strong effect on DIC. In our calculation, we consider  
477 that TA is affected only by carbonate precipitation, whereas DIC is affected both by carbonate precipitation and  
478 primary production.

479 The effect of carbonate precipitation on DIC concentrations ( $\Delta\text{DIC}_{\text{CaCO}_3}$ ), was calculated as:

$$480 \Delta\text{DIC}_{\text{CaCO}_3} = \Delta\text{TA} / 2 \quad (\text{Eq. 10})$$

481  $\Delta\text{TA}$  is the deviation of TA concentration from the evaporation model, and was assumed to be influenced only  
482 by  $\text{CaCO}_3$  precipitation.

483 The effect of primary production on DIC concentrations ( $\Delta\text{DIC}_{\text{pp}}$ ) was calculated as follows:

$$484 \Delta\text{DIC}_{\text{pp}} = \Delta\text{DIC} - \text{DIC}_{\text{CaCO}_3} \quad (\text{Eq. 11})$$

485  $\Delta$ DIC is the deviation of DIC concentrations from the evaporation model. The effect of primary production and  
486 carbonate precipitation accounted for, respectively, 63% and 37% of the DIC deficits in the brines of Araruama  
487 during winter, and 57% and 43% during summer. This calculation reveals that even occurring  $\text{CaCO}_3$   
488 precipitation (that is a net source of  $\text{CO}_2$ ), the lagoon remains a  $\text{CO}_2$  sink because of the photosynthesis  
489 occurring simultaneously. For the calculations exposed above, we considered that photosynthesis has a  
490 negligible effect on TA concentrations. However, in fact photosynthesis slightly increase TA (in case of  
491 preferential  $\text{NO}_3^-$  assimilation) or decrease TA (in case of preferential  $\text{NH}_4^+$  assimilation) (Abril and  
492 Frankignoulle, 2001) (Fig. 8a).  $\text{NO}_3^-$  assimilation is probably more significant than  $\text{NH}_4^+$  because  $\text{NO}_3^-$   
493 concentrations are about 10-times higher than  $\text{NH}_4^+$  concentrations in the lagoon (Ramos-Régis 2020). However,  
494 during summer and under rainy conditions, the concentrations of  $\text{NH}_4^+$  increase in the outer sector of the lagoon,  
495 close to a sewage outlet (Ramos-Régis 2020), and potentially changing the TA-DIC stoichiometry in this  
496 particular region.

#### 497 4.2 $\text{CO}_2$ uptake driven by enhanced biological activities and eutrophication

498 The eutrophication of estuaries is a widespread environmental problem and particularly enhanced in densely  
499 populated regions (Nixon 1995; Cloern et al. 2014). Despite the recent efforts to implement wastewater  
500 treatment plans in developing countries (Tong et al. 2020), the delivery of nitrogen and phosphorus is continuing  
501 to grow with urbanization and population increase (Larsen et al. 2016). This situation is more critical in the  
502 tropics where are located most low-income economies. The water quality of Araruama Lagoon reflects this  
503 tropical scenario of environmental degradation, and long-term eutrophication (Knoppers et al. 1999; Souza et al.  
504 2003; Laut et al. 2020).

505 During photosynthesis, the primary producers assimilate high amounts of DIC from the water column,  
506 decreasing the levels of dissolved  $\text{CO}_2$ . The uptake of  $\text{CO}_2$  is high in warm and shallow waters, and enhanced by  
507 the high availability of light and nutrients sustaining phytoplankton blooms (Cotovicz et al. 2015; Kubo et al.  
508 2017), even in hypersaline environments (Morse and He 1993; Pages et al. 1995). High biological production  
509 enhanced by domestic nutrients was found in different estuarine types, including large river plumes (Borges and  
510 Frankignoulle 2002; Huang et al. 2015), coastal embayment's (Cotovicz et al. 2015; Kubo et al. 2017), and  
511 coastal lagoons (Koné et al. 2009; Maher et al. 2019). The lowest value of  $p\text{CO}_2$  of 70 ppmv in Araruama  
512 Lagoon occurred within a dense bloom with the highest concentration of Chl *a* of  $152 \mu\text{g L}^{-1}$  (Fig. 5). However,  
513 for the same amount of phytoplankton biomass, the values of  $p\text{CO}_2$  are higher in summer than winter. This

514 seasonality can be attributed to four main reasons: i) during summer, the water temperature was about 8°C  
515 higher, on average, than winter, meaning that temperature alone contributes to a seasonal  $p\text{CO}_2$  increase by 80  
516 ppmv due to water heating. A similar seasonal effect of heating was reported in the Paraíba do Sul River Estuary,  
517 located close to Araruama Lagoon (Cotovicz et al., 2020); ii) inner and central sectors presented salinities  
518 averaging 63 in summer and 54 in winter, which create an additional theoretical increase of about 45 ppmv of  
519  $p\text{CO}_2$  in summer compared to winter due to changes in water solubility (Millero 2007); iii) the levels of  $\text{CaCO}_3$   
520 calcification ( $\Delta\text{TA}$  values) are higher in summer, when water salinity and levels of evaporation were highest  
521 (Fig. 8), consuming DIC from the water column but releasing  $\text{CO}_2$  (Eq. 7); iv) finally, we observed the highest  
522  $p\text{CO}_2$  peak (up to 844 ppmv) in the outer sector in summer (Fig.2), when the population of the city of Cabo Frio  
523 more than doubles (Bertucci et al. 2016), discharging more domestic sewage in the lagoon (Laut et al. 2016). In  
524 summary, half of the winter to summer  $p\text{CO}_2$  increase can be attributed to changes in thermodynamics due  
525 increasing temperature and salinities (~125 ppmv). The other half is attributed to the balance between changes in  
526 DIC and TA driven mainly by autochthonous processes (primary production, respiration,  $\text{CaCO}_3$  calcification)  
527 and allochthonous sources (sewage discharge).

528 The lowest values of  $p\text{CO}_2$  (70 ppmv) found in the brines of the lagoon are comparable to those found in  
529 eutrophic coastal ecosystems; for example, 22 ppmv in Guanabara Bay, an eutrophic coastal embayment in  
530 Brazil dominated by phytoplankton blooms (Cotovicz et al. 2015); 43 ppmv in the Chesapeake Bay (USA) due  
531 to high nutrient input stimulating large phytoplankton blooms (Chen et al. 2020). The high primary productivity  
532 leads not only to low concentrations of dissolved  $\text{CO}_2$ , but also to an increase of pH, carbonate ion ( $\text{CO}_3^{2-}$ )  
533 concentration and the saturation state of  $\text{CaCO}_3$  minerals due to the thermodynamic equilibria of carbonate  
534 system in seawater (Millero 2007).

535 The high levels of primary production are also evidenced by the highly positive  $\delta^{13}\text{C}$ -DIC signatures in the most  
536 shallow and phytoplankton-rich waters (inner sector). Fig. 6 corroborates this finding, as the  $\delta^{13}\text{C}$ -DIC signature  
537 increases with increasing Chl *a* concentration (Fig. 6c), water temperature (Fig. 6b), and with decreasing  $p\text{CO}_2$   
538 (particularly during summer in shallow warm-waters; Fig. 6a). The highest phytoplankton biomass (up to 151  $\mu\text{g}$   
539  $\text{L}^{-1}$ ) occurred in the warmest waters (up to 32.7 °C), associated with the lowest  $p\text{CO}_2$  values and the most  
540 positive  $\delta^{13}\text{C}$ -DIC signatures (5.55 ‰). The positive correlations between  $\delta^{13}\text{C}$ -DIC, temperature and  
541 phytoplankton biomass reveals a control of isotopic DIC fractionation by phytoplankton blooms (Van Dam et al.  
542 2018; Cotovicz et al. 2019).  $\text{CaCO}_3$  precipitation also consumes DIC from the water but in the form of  $\text{CO}_3^{2-}$ ,  
543 which is the DIC form that has the heavier stable carbon isotope signature (compared to dissolved  $\text{CO}_2$  and

544 HCO<sub>3</sub><sup>-</sup>) (Zhang et al., 1995), turning the remaining DIC pool depleted in <sup>13</sup>C relative to the seawater (Isaji et al.  
545 2017). However, the impact of primary production on δ<sup>13</sup>C-DIC is much stronger than that of CaCO<sub>3</sub>  
546 precipitation. Indeed, the marine phytoplankton-bicarbonate enrichment factor of stable carbon isotope (typically  
547 on the order of -22.1‰ to -35.5‰; Wong and Sackett 1978) is much more pronounced than calcite-bicarbonate  
548 and aragonite-bicarbonate enrichment factors (on the order of 1.0‰ and 2.7‰, respectively; Romanek et al.  
549 1992). To our best knowledge, the highest δ<sup>13</sup>C-DIC signature measured in Araruama Lagoon (5.55‰) is the  
550 highest value reported in coastal and open waters worldwide.

551 Fig. 8b shows that the data points of Araruama Lagoon are located between the theoretical vectors representing  
552 the processes of primary production/outgassing of CO<sub>2</sub> (when DIC decrease and δ<sup>13</sup>C-DIC increase) and CaCO<sub>3</sub>  
553 precipitation (when both DIC and δ<sup>13</sup>C-DIC decrease) (Samanta et al. 2015; Cotovicz et al. 2019). As the large  
554 majority of *p*CO<sub>2</sub> values in the lagoon are below the equilibrium with the atmosphere, the effect of CO<sub>2</sub>  
555 outgassing on δ<sup>13</sup>C-DIC was considered as negligible (Fig. 2). The highest positive deviation of δ<sup>13</sup>C-DIC  
556 signatures from the evaporation conservative model (up to 4‰) was found in phytoplankton-dominated waters,  
557 during summer (Fig. 8b). The highest negative deviation of δ<sup>13</sup>C-DIC signatures from mixing (up to -0.3‰) was  
558 found in low-phytoplankton waters, during winter, meaning that photosynthesis fractionates much more than  
559 CaCO<sub>3</sub> precipitation.

560 The pattern of diurnal variability of *p*CO<sub>2</sub> values in the lagoon, with higher values during night-time and lower  
561 values during daytime, also illustrates the influence of biological activities on short-time CO<sub>2</sub> dynamics (Fig. 7).  
562 Strong diel variations of CO<sub>2</sub> concentrations have been reported in productive estuarine systems worldwide as  
563 the results of net ecosystem metabolism (Yates et al. 2007; Zhang et al. 2013; Cotovicz et al. 2015). The  
564 biological activities modify not only the daily *p*CO<sub>2</sub> variations in the water, but also the other carbonate  
565 chemistry parameters (Table 3). The diurnal variations of DIC concentrations correspond to a net community  
566 production (NCP) of 34.2 molC m<sup>-2</sup> yr<sup>-1</sup> in Araruama Lagoon in summer. This autotrophic metabolism inside the  
567 Araruama lagoon generates a diurnal variability of CO<sub>2</sub> fluxes, and the sink behavior. In the 90's (1993-1995),  
568 Knoppers et al. (1996) have investigated the metabolism in Araruama Lagoon and found higher rates of benthic  
569 net primary production (benthic chamber method, between 5.6 and 12.3 molC m<sup>-2</sup> yr<sup>-1</sup>) compared to planktonic  
570 primary production (<sup>14</sup>C-method, 0.6 molC m<sup>-2</sup> yr<sup>-1</sup>), and net heterotrophy (community respiration between 12.8  
571 and 23.9 molC m<sup>-2</sup> yr<sup>-1</sup>). Within this same period (1989-1990), but in a "low salinity year", Moreira-Turcq  
572 (2000) documented higher rates of planktonic primary production (<sup>14</sup>C method, averaging 13.5 mol C m<sup>-2</sup> yr<sup>-1</sup>)  
573 due to this atypical condition of lower salinities. Later, applying the LOICZ (Land Ocean Interaction in the

574 Coastal Zone) nutrient budget calculation, Souza et al. (2003) reported a slight net autotrophic metabolism (0.9  
575 molC m<sup>-2</sup> yr<sup>-1</sup>). These results reveal an important shift in the ecosystem metabolism along decades, from a net  
576 heterotrophic benthic-dominated metabolism in the 90's to a net autotrophic planktonic-dominated metabolism  
577 afterwards. In addition, the changes in the evaporation-precipitation balance producing lower salinity conditions  
578 during atypical years can influence the trophic state of the ecosystem and the levels of primary production  
579 (Moreira-Turcq 2000). Our result of NCP falls in the highest range of documented values, suggesting that  
580 planktonic primary production is increasing in the lagoon as the result of eutrophication. These values are higher  
581 than those documented in other highly productive hypersaline lagoons (Cohen et al. 1977; Javor 1989). The NCP  
582 of Araruama Lagoon was also higher than the mean annual phytoplankton primary production found in a  
583 compilation of 131 estuaries worldwide (21 molC m<sup>-2</sup> yr<sup>-1</sup>; Cloern et al. 2014). This NCP is close to the threshold  
584 of hypertrophic classification (500 g C m<sup>-2</sup> yr<sup>-1</sup>) considering the annual phytoplankton primary production  
585 proposed by Nixon (1995).

586 High oversaturated conditions of pCO<sub>2</sub> (maximum of 844 ppmv) were found only in the channel that connects  
587 the bay to the ocean (the most urbanized region) associated with urban wastewater discharge. A recent study  
588 found the presence of high levels of organic matter from anthropic origin in this region (Laut et al. 2020).  
589 Mineralization of organic matter in polluted areas close to sewage networks leads to heterotrophy and CO<sub>2</sub>  
590 outgassing (Cotovicz et al. 2015; 2021). The sampling in summer was carried out during a period of high  
591 rainfall, which favored CO<sub>2</sub> and organic carbon inputs from urban areas.

#### 592 4.3 Apparent decoupling between CO<sub>2</sub> and O<sub>2</sub> dynamics in hypersaline and productive waters

593 The relationship between excess of DIC (E-DIC) and apparent oxygen utilization (AOU) illustrates the specific  
594 metabolic characteristics of Araruama Lagoon (Fig. 9). E-DIC and AOU were calculated following Abril et al.  
595 (2003) and Benson and Krause (1984), respectively. In general, values of E-DIC and AOU were negative,  
596 consistent with net autotrophy in the lagoon. However, some E-DIC and AOU values were positive during  
597 nighttime. E-DIC and AOU values in the Araruama Lagoon presented strong deviations below the 1:1 line that  
598 represents the quotient between CO<sub>2</sub> and O<sub>2</sub> during primary production and community respiration (Fig. 9). The  
599 deviations were particularly important when values of pCO<sub>2</sub> are very low in the water (below 300 ppmv; Fig. 9),  
600 associate with large disequilibria of CO<sub>2</sub> concentrations between water and atmosphere. Indeed, the cycling of  
601 these gases in hypersaline and high-productive waters are not linearly coupled. It is well established that air-  
602 water exchange is faster for O<sub>2</sub> than for CO<sub>2</sub>, due to different solubility of the two gases and the buffering effect

603 of the carbonate chemistry (Garcia and Gordon 1992; Weiss 1974). The waters tend to equilibrate faster with the  
604 atmosphere for DO than for CO<sub>2</sub> to the atmosphere because the buffering effect of bicarbonate concentration  
605 affects the CO<sub>2</sub> concentrations, but not the O<sub>2</sub> concentrations.

606 This difference between air-water exchanges for O<sub>2</sub> and CO<sub>2</sub> was evident comparing samplings occurred in  
607 consecutive days with marked differences in wind speed (Fig. 5). During day 18-07-2018 the wind speed was  
608 low (< 5.5 m s<sup>-1</sup>), with high oversaturation for O<sub>2</sub> and undersaturation for pCO<sub>2</sub>. Overnight, the wind speed  
609 increased to velocities > 14 m s<sup>-1</sup>, and fast gas-exchange occurred, causing DO concentrations to decrease from  
610 oversaturation to values close to atmosphere equilibrium; however, the values of pCO<sub>2</sub> remained well below 400  
611 ppmv, evidencing the decoupling between O<sub>2</sub> and CO<sub>2</sub> in these productive and well-buffered waters.

612 Furthermore, the occurrence of CaCO<sub>3</sub> precipitation simultaneously causes additional deficits of DIC  
613 concentrations in the water, also contributing to lowering E-DIC values but not affecting AOU (Fig. 9).  
614 However, during diurnal sampling, the data distribution of E-DIC and AOU were located close to the line 1:1,  
615 suggesting that at that timescale, primary production and total respiration (autotrophic and heterotrophic) were  
616 coupled, and largely dominated diel variations, as verified in other eutrophic and phytoplankton-dominated  
617 ecosystem (Cotovicz et al. 2015).

#### 618 4.4 Atmospheric CO<sub>2</sub> fluxes and net carbon sink in the lagoon

619 Araruama Lagoon is a coastal lagoon located in a region characterized by strong winds (Barbière and Monteiro  
620 1974; Amarante et al. 2002). The k-wind speed parameterization is one of the most critical parameters to  
621 compute the air-water CO<sub>2</sub> fluxes from the gradient between pCO<sub>2</sub> in surface ocean and lower atmosphere  
622 (Borges and Abril 2011; Wanninkhof 2014). Several formulations of k-wind parameterizations are available in  
623 order to account for the main driving forces of turbulence at the air-sea interface, and applying three k<sub>600</sub>  
624 formulations allows to provide credible ranges of FCO<sub>2</sub> estimates (Jiang et al. 2008; Wanninkhof 2014; Van  
625 Dam et al. 2019).

626 Classical river-dominated estuaries are considered net sources of CO<sub>2</sub> to the atmosphere, with magnitude of  
627 emissions decreasing seaward (Borges and Abril 2011; Chen et al. 2013; Laruelle et al. 2013). The most recent  
628 global compilation of estuarine CO<sub>2</sub> emissions reports strong sources of CO<sub>2</sub> at inner regions of estuaries, on the  
629 order of 38.6 mol C m<sup>-2</sup> yr<sup>-1</sup>, and weak sources at outer regions with salinities >25, on the order of 8.4 mol C m<sup>-2</sup>  
630 yr<sup>-1</sup> (Chen et al. 2013). However, other studies in marine-dominated estuaries (coastal embayment's and lagoons)  
631 have reported pCO<sub>2</sub> undersaturation and net CO<sub>2</sub> sinks annually (Koné et al., 2009; Maher and Eyre 2012;

632 Cotovicz et al. 2015; Kubo et al. 2017), or seasonally (Koné et al., 2009; Maher et al. 2019; Yao et al. 2020). In  
633 addition, the coastal plumes of large rivers (Mississippi, Amazon) also behave as CO<sub>2</sub> sinks (Körtzinger 2003;  
634 Huang et al. 2015). The few data existing on semiarid/arid coastal ecosystems with permanent and/or  
635 intermittent hypersaline conditions suggest that these ecosystems are net sources of CO<sub>2</sub>, for example, in the  
636 semiarid subtropical region Mission-Aransas Estuary, Gulf of Mexico (12.4 mol C m<sup>-2</sup> yr<sup>-1</sup>; Yao and Hu, 2017),  
637 because heating and evaporation enhance CO<sub>2</sub> degassing (Yao et al. 2020). In the Araruama Lagoon, the high  
638 enclosure and long residence time of waters together with high availability of nutrients and light, promoted  
639 conditions for high CO<sub>2</sub> uptake, during both winter and summer conditions (Figs. 2 and 5), despite the  
640 occurrence of CaCO<sub>3</sub> precipitation (Fig. 8). The annual sink in Araruama Lagoon ranged between -2.76 and -  
641 3.80 mol C m<sup>-2</sup> yr<sup>-1</sup>, similar to those reported in other mesohaline coastal lagoons, including Australian Lagoons  
642 (-0.4 to -2.0 molC m<sup>-2</sup> yr<sup>-1</sup>, Maher and Eyre 2012) and the Aby Lagoon in Ivory Coast (-2.7 molC m<sup>-2</sup> yr<sup>-1</sup>; Koné  
643 et al. 2009). A sink of CO<sub>2</sub> has been found in other enclosed and eutrophic coastal ecosystems, particularly in  
644 embayment's, for example in Guanabara Bay (Brazil) (-9.6 to - 18.3 molC m<sup>-2</sup> yr<sup>-1</sup>, Cotovicz et al. 2015) and  
645 Tokyo Bay (Japan) (-3.2 molC m<sup>-2</sup> yr<sup>-1</sup>; Kubo et al. 2017). Even if CaCO<sub>3</sub> precipitation occurs, Araruama  
646 Lagoon is a net sink of CO<sub>2</sub> because eutrophication is enhancing the planktonic primary production, and  
647 overcoming CaCO<sub>3</sub> precipitation.

648

## 649 5. Conclusions

650 Prevalence of negative water balance along the year (evaporation higher than precipitation), associated with low  
651 freshwaters inputs and low water renewal typical of choked lagoons, create conditions of hypersalinity in the  
652 Araruama Lagoon. The residual brines of Araruama Lagoon reflect the evaporation path of seawater. The waters  
653 of Araruama have higher concentrations of TA and DIC compared to seawater as the result of salt concentration.  
654 However, the concentrations of TA and DIC are, respectively, approximately 39-44% and 20-28% lower than  
655 those expected from the evaporation model. Spontaneous CaCO<sub>3</sub> precipitation is occurring in the lagoon and  
656 contributed to about 37-43% of the DIC deficits, whereas the remaining 57-63% is attributed to uptake of DIC  
657 by primary producers.

658 The increasing human disturbances, mainly urbanization, have raised the discharges of urban effluents in the  
659 lagoon. The high availability of nutrients and the long water residence times have contributed to the development  
660 of phytoplankton blooms, particularly at the innermost-shallow region. The vast majority of *p*CO<sub>2</sub> values were



661 well-below the atmospheric values, generating a net annual sink of CO<sub>2</sub> as the result of net autotrophic  
662 metabolism and overwhelming the *p*CO<sub>2</sub> increase driven by CaCO<sub>3</sub> precipitation. Oversaturated conditions of  
663 *p*CO<sub>2</sub> were restricted to the region closest to sewage outfall (Itajuru Channel), and during night-time. The  
664 thermodynamic effects driven by water heating and increasing salinities were also significant and partially  
665 explained the higher values of *p*CO<sub>2</sub> in summer compared to winter. Overall, the brines of Araruama are  
666 dominated by phytoplankton blooms with heavier δ<sup>13</sup>C-DIC signatures (due to isotopic fractionation by primary  
667 production), higher values of pH and higher buffering capacity compared to seawater. The relationship between  
668 E-DIC and AOU presented values well-below the 1:1 line (quotient between photosynthesis and respiration),  
669 suggesting that air-water exchanges of CO<sub>2</sub> and O<sub>2</sub> are apparently decoupled due to solubility differences and  
670 high carbonate buffering capacity in these warm, hypersaline, and phytoplankton-dominated waters.

671 This study suggests that eutrophication locally amplifies the production of organic matter with important CO<sub>2</sub>  
672 uptake, counter-acting the potential effects of ocean acidification by increasing the pH. Eutrophication and  
673 negative water balance (hypersalinity) are modifying the nutrient cycling, plant productivity and carbon budgets  
674 in the lagoon. The aridity is increasing worldwide as the result of global warming, whereas at same time the  
675 inputs of anthropogenic-derived nutrients have increased in many coastal regions. Therefore, the specific results  
676 found in this semiarid coastal lagoon could reflect future conditions in other tropical coastal ecosystems.

677

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#### 683 **Conflicts of interests**

684 The authors have no conflicts of interest to declare that are relevant to the content of this article.

685

#### 686 **References**

687 Abril G, Frankignoulle M (2001) Nitrogen – alkalinity interactions in the highly polluted Scheldt Basin  
688 (Belgium). *Water Res* 35:844–850. [https://doi.org/10.1016/S0043-1354\(00\)00310-9](https://doi.org/10.1016/S0043-1354(00)00310-9)

- 689 Abril G, Etcheber H, Delille B, Frankignoulle M, Borges AV (2003) Carbonate dissolution in the turbid and  
690 eutrophic Loire estuary. *Mar Ecol-Prog Ser* 259:129-138. <https://doi.org/10.3354/meps259129>
- 691 Abril G, Libardoni B, Brandini N, Cotovicz Jr. L C, Medeiros PR, Cavalcante G, Knoppers BA (2021)  
692 Thermodynamic uptake of atmospheric CO<sub>2</sub> in the oligotrophic and semiarid São Francisco estuary (NE Brazil).  
693 *Ma Chem* 233, 103983. <https://doi.org/10.1016/j.marchem.2021.103983>.
- 694 Amarante OA, Silva FJ, Rios Filho LG (2002) Atlas Eólico, Estado do Rio de Janeiro. Secretaria de Estado da  
695 Energia, da Indústria Naval e do Petróleo, Rio de Janeiro.  
696 [http://www.cresesb.cepel.br/publicacoes/download/atlas\\_eolico/AtlasEolicoRJ.pdf](http://www.cresesb.cepel.br/publicacoes/download/atlas_eolico/AtlasEolicoRJ.pdf). Accessed 25 April 2021
- 697 Anthony A. Atwood J, August P et al. (2009) Coastal lagoons and climate change: ecological and social  
698 ramifications in U.S. Atlantic and Gulf coast ecosystems. *Ecology and Society* 14(1): 8  
699 <http://www.ecologyandsociety.org/vol14/iss1/art8/> Accessed 19 July 2021
- 700 Ávila-López MC, Hernández-Ayón JM, Camacho-Ibar VF et al. (2016) Air–Water CO<sub>2</sub> fluxes and net  
701 ecosystem production changes in a Baja California coastal lagoon during the anomalous North Pacific warm  
702 condition. *Estuaries Coast* 40:792–806. <https://doi.org/10.1007/s12237-016-0178-x>
- 703 Babel M., Schreiber C. Geochemistry of Evaporites and Evolution of Seawater. In: Mackenzie F (ed) *Treatise on*  
704 *Geochemistry*, 2nd edn. Sediments, Diagenesis, and Sedimentary Rocks. Elsevier, Amsterdam, pp 483-560
- 705 Barbière EB, Monteiro CA (1974) Ritmo climático e extração do sal em Cabo Frio. *Rev Bras Geog* 37:23-109.
- 706 Benson BB, Krause D (1984) The concentration and isotopic fractionation of oxygen dissolved in freshwater and  
707 seawater in equilibrium with the atmosphere, *Limnol Oceanogr* 29:620–632.  
708 <https://doi.org/10.4319/lo.1984.29.3.0620>
- 709 Bertucci CT, Silva EP, Marques Junior AN, Monteiro Neto C (2016) Tourism and urbanization: environmental  
710 problems of the Araruama Lagoon, state of Rio de Janeiro, Brazil. *Ambient soc* 19:59-80.  
711 <https://doi.org/10.1590/1809-4422ASOC137111V1942016>
- 712 Borges AV, Frankignoulle M (2002) Distribution and air-water exchange of carbon dioxide in the Scheldt plume  
713 off the Belgian coast. *Biogeochemistry* 59: 41–67. <https://doi.org/10.1023/A:1015517428985>
- 714 Borges AV (2005) Do we have enough pieces of the jigsaw to integrate CO<sub>2</sub> fluxes in the coastal ocean?  
715 *Estuaries* 26:3-27. <https://doi.org/10.1007/BF02732750>
- 716 Borges AV, Abril G (2011) Carbon dioxide and methane dynamics in estuaries. In: McLusky D, Wolanski E  
717 (eds) *Treatise on Estuarine and Coastal Science*. Academic Press, Amsterdam, pp 119–  
718 161. <https://doi.org/10.1016/B978-0-12-374711-2.00504-0>
- 719 Breaux N, Lebreton B, Palmer TA, Guillou G, Pollack JB (2019) Ecosystem resilience following salinity change  
720 in a hypersaline estuary. *Estuar Coast Shelf Sci* 225, 30, 106258. <http://dx.doi.org/10.1016/j.ecss.2019.106258>
- 721 Burke CM, Atkinson MJ (1988) Measurement of total alkalinity in hypersaline waters: values of  $f_H$ . *Mar Chem*  
722 25:49-55. [https://doi.org/10.1016/0304-4203\(88\)90014-X](https://doi.org/10.1016/0304-4203(88)90014-X)
- 723 Cai W-J, Pomeroy LR, Moran MA, Wang Y (1999) Oxygen and carbon dioxide mass balance for the estuarine–  
724 intertidal marsh complex of five rivers in the southeastern U.S. *Limnol Oceanogr* 44:639-649.  
725 <https://doi.org/10.4319/lo.1999.44.3.0639>
- 726 Cai W-J, Hu X, Huang W-J et al. (2011) Acidification of subsurface coastal waters enhanced by eutrophication.  
727 *Nature Geosci* 4:766–770. <https://doi.org/10.1038/ngeo1297>
- 728 Cai W-J, Huang W-J, Luther 3rd GW et al. (2017) Redox reactions and weak buffering capacity lead to  
729 acidification in the Chesapeake Bay. *Nat Commun* 8:369. <https://doi.org/10.1038/s41467-017-00417-7>
- 730 Cai W-J, Feely RA, Testa JM et al. (2020) Natural and anthropogenic drivers of acidification in large estuaries.  
731 *Annu Rev Mar Sci* 13:23-55. <https://doi.org/10.1146/annurev-marine-010419-011004>

- 732 Cao Z, Yang W, Zhao Y et al. (2020) Diagnosis of CO<sub>2</sub> dynamics and fluxes in global coastal oceans. *Nat Sci*  
733 *Rev* 7:786–797. <https://doi.org/10.1093/nsr/nwz105>
- 734 Champenois W, Borges AV (2021) Net community metabolism of a *Posidonia oceanica* meadow. *Limnol*  
735 *Oceanogr*. <https://doi.org/10.1002/lno.11724>
- 736 Chen C-TA, Huang T-H, Chen Y-C, Bai Y, He X, Kang Y (2013) Air–sea exchanges of CO<sub>2</sub> in the world’s  
737 coastal seas. *Biogeosciences* 10:6509–6544. <https://doi.org/10.5194/bg-10-6509-2013>
- 738 Chen B, Cai W-J, Chen L (2015) The marine carbonate system of the Arctic Ocean: Assessment of internal  
739 consistency and sampling considerations, summer 2010. *Mar Chem* 176:174–188.  
740 <http://dx.doi.org/10.1016/j.marchem.2015.09.007>
- 741 Chen B, Cai W-J, Brodeur JR et al. (2020) Seasonal and spatial variability in surface pCO<sub>2</sub> and air–water CO<sub>2</sub>  
742 flux in the Chesapeake Bay. *Limnol Oceanogr* 65:3046–3065. <https://doi.org/10.1002/lno.11573>
- 743 Chou C, Neelin JD, Chen C-A, Tu JY (2009) Evaluating the rich-get-richer mechanism in tropical precipitation  
744 change under global warming. *J Clim* 22:1982–2005. <https://doi.org/10.1175/2008JCLI2471.1>
- 745 Cohen Y, Krumbein WE, Shilo M (1977) Solar Lake (Sinai) 2. Distribution of photosynthetic microorganisms  
746 and primary production. *Limnol Oceanogr* 22(4): 609–620. <https://doi.org/10.4319/lno.1977.22.4.0609>
- 747 Cloern JE, Foster SQ, Kleckner AE (2014) Phytoplankton primary production in the world’s estuarine-coastal  
748 ecosystems. *Biogeosciences* 11:2477–2501. <https://doi.org/10.5194/bg-11-2477-2014>
- 749 Cotovicz LC Jr, Knoppers BA, Brandini N, Costa Santos SJ, Abril G (2015) A strong CO<sub>2</sub> sink enhanced by  
750 eutrophication in a tropical coastal embayment (Guanabara Bay, Rio de Janeiro, Brazil). *Biogeosciences*  
751 12:6125–6146. <https://doi.org/10.5194/bg-12-6125-2015>
- 752 Cotovicz LC Jr, Libardoni BG, Brandini N, Knoppers BA, Abril G (2016) Comparações entre medições em  
753 tempo real da pCO<sub>2</sub> aquática com estimativas indiretas em dois estuários tropicais contrastantes: o estuário  
754 eutrofizado da Baía de Guanabara (RJ) e o estuário oligotrófico do Rio São Francisco (AL). *Quim Nov* 39(10):  
755 1206–1214. <http://dx.doi.org/10.21577/0100-4042.20160145>
- 756 Cotovicz LC Jr, Knoppers BA, Deirmendjian L, Abril G (2019) Sources and sinks of dissolved inorganic carbon  
757 in an urban tropical coastal bay revealed by δ<sup>13</sup>C-DIC signals. *Estuar Coast Shelf Sci* 2020:185–195.  
758 <https://doi.org/10.1016/j.ecss.2019.02.048>
- 759 Cotovicz LC Jr, Vidal LO, de Rezende CE, Bernardes MC, Knoppers BA, Sobrinho RL, Cardoso RP, Muniz M,  
760 dos Anjos RM, Biehler A, Abril G (2020) Carbon dioxide sources and sinks in the delta of the Paraíba do Sul  
761 River (Southeastern Brazil) modulated by carbonate thermodynamics, gas exchange and ecosystem metabolism  
762 during estuarine mixing. *Mar Chem* 226:103869. <https://doi.org/10.1016/j.marchem.2020.103869>
- 763 Cotovicz LC Jr, Ribeiro RP, Régis CR et al. (2021) Greenhouse gas emissions (CO<sub>2</sub> and CH<sub>4</sub>) and inorganic  
764 carbon behavior in an urban highly polluted tropical coastal lagoon (SE, Brazil). *Environ Sci Pollut Res*.  
765 <https://doi.org/10.1007/s11356-021-13362-2>
- 766 Dickson AG, Millero FJ (1987) A comparison of the equilibrium constants for the dissociation of carbonic acid  
767 in seawater media. *Deep-Sea Res* 34:1733–1743. [https://doi.org/10.1016/0198-0149\(87\)90021-5](https://doi.org/10.1016/0198-0149(87)90021-5)
- 768 Dickson AG (1990) Thermodynamics of the dissociation of boric acid in synthetic seawater from 273.15 to  
769 318.15 K. *Deep-Sea Res I Oceanogr Res Pap* 37:755–766. [https://doi.org/10.1016/0198-0149\(90\)90004-F](https://doi.org/10.1016/0198-0149(90)90004-F)
- 770 Dickson AG (2010) The carbon dioxide system in seawater: equilibrium chemistry and measurements. In:  
771 Riebesell U, Fabry VJ, Hansson L, Gattuso J-P (eds) *Guide to Best Practices for Ocean Acidification Research*  
772 *and Data Reporting*. Publications Office of the European Union, Luxembourg, pp 17–40
- 773 Egleston ES, Sabine CL, Morel FMM (2010) Revelle revisited: buffer factors that quantify the response of ocean  
774 chemistry to changes in DIC and alkalinity. *Glob Biogeochem Cycles* 24:1–9.  
775 <https://doi.org/10.1029/2008GB003407>

- 776 Feng S, Fu Q (2013) Expansion of global drylands under a warming climate. *Atmos Chem Phys* 13(19):10081–  
777 10094. <https://doi.org/10.5194/acp-13-10081-2013>.
- 778 Frankignoulle, M., 1994. A complete set of buffer factors for acid/base CO<sub>2</sub> system in seawater. *J. Mar. Syst.* 5,  
779 111–118.
- 780 Frankignoulle M, Canon C, Gattuso J-P (1994) Marine calcification as a source of carbon dioxide: Positive  
781 feedback of increasing atmospheric CO<sub>2</sub>. *Limnol Oceanogr* 39(2):458–462. [https://doi.org/10.1016/0924-](https://doi.org/10.1016/0924-7963(94)90026-4)  
782 [7963\(94\)90026-4](https://doi.org/10.1016/0924-7963(94)90026-4)
- 783 Frankignoulle M, Borges AV, Biondo R (2001) A new design of equilibrator to monitor carbon dioxide in highly  
784 dynamic and turbid environments. *Water Res* 35: 1344–1347. [https://doi.org/10.1016/S0043-1354\(00\)00369-9](https://doi.org/10.1016/S0043-1354(00)00369-9)
- 785 Garcia HE, Gordon LI (1992) Oxygen solubility in seawater: better fitting equations. *Limnol Oceanogr* 37:1307–  
786 1312. <https://doi.org/10.4319/lo.1992.37.6.1307>
- 787 Gattuso J-P, Frankignoulle M, Wollast R (1998) Carbon and carbonate metabolism in coastal aquatic  
788 ecosystems. *Annu Rev Ecol Syst* 29:405–434. <https://doi.org/10.1146/annurev.ecolsys.29.1.405.1999>
- 789 Gattuso J-P, Frankignoulle M, Smith SV (1999) Measurement of community metabolism and significance in the  
790 coral reef CO<sub>2</sub> source-sink debate. *Proc Natl Acad Sci* 96:13017–13022.  
791 <https://doi.org/10.1073/pnas.96.23.13017>
- 792 Gillikin DP, Bouillon S (2007) Determination of δ<sup>18</sup>O of water and δ<sup>13</sup>C of dissolved inorganic carbon using a  
793 simple modification of an elemental analyzer-isotope ratio mass spectrometer: an evaluation. *Rapid Commun*  
794 *Mass Spectrom* 21:1475–1478. <https://doi.org/10.1002/rcm.2968>
- 795 Golan R, Gavrieli I, Ganor J, Lazar B (2016) Controls on the pH of hyper-saline lakes – A lesson from the Dead  
796 Sea. *Earth Planet Sci Lett* 434:289–297. <https://doi.org/10.1016/j.epsl.2015.11.022>
- 797 Gran G (1952) Determination of the equivalence point in potentiometric titrations-Part II. *Analyst* 77:661–671.  
798 <https://doi.org/10.1039/an9527700661>
- 799 Howarth R (2011) Coupled biogeochemical cycles: eutrophication and hypoxia in temperate estuaries and  
800 coastal marine ecosystems. *Front Ecol Environ* 9(1):18–26. . <https://doi.org/10.1890/100008>
- 801 Huang W-J, Cai W-J, Wang Y, Lohrenz SE, Murrell MC (2015) The carbon dioxide (CO<sub>2</sub>) system on the  
802 Mississippi River– dominated continental shelf in the northern Gulf of Mexico – I: Distribution and air–sea CO<sub>2</sub>  
803 flux. *J Geophys Res* (120):1429–1445. <https://doi.org/10.1002/2014JC010498>
- 804 Huang J, Li Y, Fu C et al. (2017) Dryland climate change: Recent progress and challenges. *Rev Geophys*  
805 55:719–778. <https://doi.org/10.1002/2016RG000550>
- 806 Iglesias-Rodriguez MD, Armstrong R, Feely R et al (2011) Progress made in study of oceans calcium carbonate  
807 budget. *Eos* 83(34):365–375. <https://doi.org/10.1029/2002EO000267>
- 808 Isaji Y, Kawahata H, Kuroda J et al (2017) Biological and physical modification of carbonate system parameters  
809 along the salinity gradient in shallow hypersaline solar salterns in Trapani, Italy. *Geochim Cosmochim Acta*  
810 208:354–367. <https://doi.org/10.1016/j.gca.2017.04.013>
- 811 Jähne B, Munnich KO, Bosinger R, Dutzi A, Huber W, Libner P (1987) On parameters influencing air-water  
812 exchange. *J Geophys Res* 92:1937–1949. <https://doi.org/10.1029/JC092iC02p01937>
- 813 Javor B (1989) Hypersaline environments. *Microbiology and Biogeochemistry*. Brock/Spring Series in  
814 *Contemporary Bioscience*. Springer Verlag, Berlin
- 815 Jiang LQ, Cai W-J, Wang YC (2008) A comparative study of carbon dioxide degassing in river- and marine  
816 dominated estuaries. *Limnol Oceanogr* 53:2603–2615. <https://doi.org/10.4319/lo.2008.53.6.2603>
- 817 Kjerfve B (1994) Coastal Lagoons. In: Kjerfve B (ed) *Coastal Lagoon Processes*, Oceanography Series, 1<sup>st</sup> edn.  
818 Elsevier, Amsterdam, pp 1-8

819 Kjerfve B, Schettini CAF, Knoppers B, Lessa G, Ferreira HO (1996) Hydrology and salt balance in a large  
820 hypersaline coastal lagoon: Lagoa de Araruama, Brazil. *Estuar Coast Shelf Sci* 42: 701–725.  
821 <https://doi.org/10.1006/ecss.1996.0045>

822 Knoppers BA, Kjerfve B (1999) Coastal lagoons of Southeastern Brazil: Physical and biogeochemical  
823 characteristics. In: Perillo G, Piccolo MC (eds) *Estuaries of South America. Their morphology and dynamics*.  
824 Springer-Verlag, Berlin, pp 35-66

825 Knoppers BA, Souza WF, Souza MFL, Rodriguez EG, Landim ECV, Vieira AR (1996) In situ measurements of  
826 n benthic primary production, respiration and nutrient fluxes in a hypersaline coastal lagoon of SE, Brazil. *Rev*  
827 *Bras Oceanogr* 44: 155-165. <https://doi.org/10.1590/S1413-77391996000200005>

828 Knoppers BA, Carmouze J-P, Moreira-Turcq PF (1999) Nutrient dynamics, metabolism and eutrophication of  
829 lagoons along the east Fluminense coast, state of Rio de Janeiro, Brazil, In: Knoppers BA, Bidone ED, Abrão JJ  
830 (eds) *Environmental geochemistry of coastal lagoon systems of Rio de Janeiro, Brazil*. FINEP, Rio de Janeiro,  
831 pp 123–154.

832 Koné YJM, Abril G, Kouadio KN, Dellile B., Borges AV et al (2009) Seasonal variability of carbon dioxide in  
833 the rivers and lagoons of Ivory Coast (West Africa). *Estuaries Coast* 32:246–260.  
834 <https://doi.org/10.1007/s12237-008-9121-0>

835 Körtzinger A (2003) A significant CO<sub>2</sub> sink in the tropical Atlantic Ocean associated with the Amazon River  
836 plume. *Geophys Res Let* 30:24. <https://doi.org/10.1029/2003GL018841>

837 Krumgalz S, Hoknong H, Oren OH (1980) The study of natural hypersaline lagoons in desert areas (the Bardawil  
838 Lagoon in northern Sinai). *Estuarine Coastal Mar Sci* 10:403-415. [https://doi.org/10.1016/S0302-3524\(80\)80120-4](https://doi.org/10.1016/S0302-3524(80)80120-4)

840 Kubo A, Maeda Y, Kanda J (2017) A significant net sink for CO<sub>2</sub> in Tokyo Bay. *Sci Rep* 7:44355.  
841 <https://doi.org/10.1038/srep44355>

842 Larsen TA, Hoffman S, Lüthi C, Truffer B, Maurer M (2016) Emerging solutions to the water challenges of an  
843 urbanizing world. *Science* 352:928-933. <https://doi.org/10.1126/science.aad8641>

844 Laruelle GG, Dürr HH, Lauerwald R et al (2013) Global multi-scale segmentation of continental and coastal  
845 waters from the watersheds to the continental margins. *Hydrol Earth Syst Sci* 17:2029–2051.  
846 <https://doi.org/10.5194/hess-17-2029-2013>

847 Laut L, Vilar A, Belart P et al (2020) Organic matter compounds as a tool for trophic state characterization in a  
848 hypersaline environment: Araruama Lagoon, Brazil. *J South Am Earth Sci* 97:102403.  
849 <https://doi.org/10.1016/j.jsames.2019.102403>

850 Lazar B, Starinsky A, Katz A, Sass E, Ben-Yaakov S (1983) The carbonate system in hypersaline solutions:  
851 alkalinity and CaCO<sub>3</sub> solubility of evaporated seawater. *Limnol Oceanogr* 28:978–986.  
852 <https://doi.org/10.4319/lo.1983.28.5.0978>

853 Lee K, Kim TW, Byrne RH et al (2010) The universal ratio of boron to chlorinity for the North Pacific and  
854 North Atlantic oceans. *Geochim Cosmochim Acta* 74:1801-1811. <https://doi.org/10.1016/j.gca.2009.12.027>

855 Lorenzen C (1967) Determination of chlorophyll and phaeo-pigments: spectrophotometric equations. *Limnol*  
856 *Oceanogr* 12:343-346. <https://doi.org/10.4319/lo.1967.12.2.0343>

857 Maher DT, Eyre BD (2012) Carbon budgets for three autotrophic Australian estuaries: Implications for global  
858 estimates of the coastal air-water CO<sub>2</sub> flux. *Global Biogeochem Cy* 26:GB1032.  
859 <https://doi.org/10.1029/2011GB004075>, 2012.

860 Maher DT, Call M, Macklin P, Webb JR, Santos IR (2019) Hydrological Versus Biological Drivers of Nutrient  
861 and Carbon Dioxide Dynamics in a Coastal Lagoon. *Estuaries Coast* 42:1015–1031.  
862 <https://doi.org/10.1007/s12237-019-00532-2>

863 Marion GM, Millero FJ, Feistel R (2009) Precipitation of solid phase calcium carbonates and their effect on  
864 application of seawater SA-T -P models. *Ocean Sci* 5:285–291. <https://doi.org/10.5194/os-5-285-2009>

865 McCaffrey MA, Lazar B, Holland HD (1987) The evaporation path of seawater and the coprecipitation of Br<sup>-</sup>  
866 and K<sup>+</sup> with halite. *J Sediment Petrol* 57:928–938. [https://doi.org/10.1306/212f8cab-2b24-11d7-](https://doi.org/10.1306/212f8cab-2b24-11d7-8648000102c1865d)  
867 8648000102c1865d

868 McCutcheon MR, Staryk CJ, Hu X (2019) Characteristics of the Carbonate System in a Semiarid Estuary that  
869 Experiences Summertime Hypoxia. *Estuaries Coast* 42:1509–1523. <https://doi.org/10.1007/s12237-019-00588-0>

870 Mehrbach C, Cuberson CH, Hawley JE, Pytkowicz RM (1973) Measurements of the apparent dissociation  
871 constants of carbonic acid in seawater at atmospheric pressure. *Limnol Oceanogr* 18:897–907.  
872 <https://doi.org/10.4319/lo.1973.18.6.0897>

873 Middelburg JJ, Soetaert K, Hagens M (2020) Ocean Alkalinity, Buffering and Biogeochemical Processes. *Rev*  
874 *Geophys* 58:e2019RG000681. <https://doi.org/10.1029/2019RG000681>

875 Millero FJ (2007) The Marine Inorganic Carbon Cycle. *Chem Rev* 107:308–341.  
876 <https://doi.org/10.1021/cr0503557>

877 Miyajima T, Miyajima Y, Hanba YT, Yoshii K, Koitabashi T, Wada E (1995) Determining the stable isotope  
878 ratio of total dissolved inorganic carbon in lake water by GC/C/IRMS. *Limnol Oceanogr* 40:994–1000.  
879 <https://doi.org/10.4319/lo.1995.40.5.0994>

880 Mook, W. G., 2001. *Environmental Isotopes in the Hydrological Cycle: Principles and applications*. UNESCO,  
881 Paris

882 Moreira-Turcq P (2000) Impact of a low salinity year on the metabolism of a hypersaline coastal lagoon (Brazil).  
883 *Hydrobiologia* 429:133–140. <https://doi.org/10.1023/A:1004037624787>

884 Morse JW, He S (1993) Influences of T, S and pCO<sub>2</sub> on the pseudo-homogeneous precipitation of CaCO<sub>3</sub> from  
885 seawater: implications for whiting formation. *Mar Chem* 41:291–297. [https://doi.org/10.1016/0304-](https://doi.org/10.1016/0304-4203(93)90261-L)  
886 4203(93)90261-L

887 Morse JW, Wang Q, Tsio MY (1997) Influences of temperature and Mg:Ca ratio on the mineralogy of CaCO<sub>3</sub>  
888 precipitated from seawater. *Geology* 25:85–87. [https://doi.org/10.1130/0091-](https://doi.org/10.1130/0091-7613(1997)025<0085:IOTAMC>2.3.CO;2)  
889 7613(1997)025<0085:IOTAMC>2.3.CO;2

890 Morse JW, Arvidson RS, Lüttge A (2007) Calcium carbonate formation and dissolution. *Chem Rev* 107:342–  
891 381. <http://dx.doi.org/10.1021/cr050358j>.

892 Nixon SW (1995) Coastal marine eutrophication: A definition, social causes, and future concerns. *Ophelia*  
893 41:199–219. <https://doi.org/10.1080/00785236.1995.10422044>

894 Pages J, Lemoalle J, Fritz B (1995) Distribution of carbon in a tropical hypersaline estuary, the Casamance  
895 (Senegal, West Africa). *Estuaries* 18:456–468. <https://doi.org/10.2307/1352364>

896 O'Mara NA, Dune JP (2019) Hot spots of carbon and alkalinity cycling in the coastal oceans.  
897 *Sci Rep* 9:4434. <https://doi.org/10.1038/s41598-019-41064-w>

898 Ramos-Régis C (2021) Avaliação do estado trófico da Laguna Hipersalina de Araruama e do Complexo Lagunar  
899 de Jacarepaguá (Rio de Janeiro). Master Dissertation, Federal Fluminense University

900 Regnier P, Friedlingstein P, Ciais P et al (2013) Anthropogenic perturbation of the carbon fluxes from land to  
901 ocean. *Nature Geosci* 6:597–607. <https://doi.org/10.1038/ngeo1830>

902 Ribas-Ribas M, Hernández-Ayón JM, Camacho-Ibar VF et al (2011) Effects of upwelling, tides and biological  
903 processes on the inorganic carbon system of a coastal lagoon in Baja California. *Estuar Coast Shelf Sci* 95:367-  
904 376. <https://doi.org/10.1016/j.ecss.2011.09.017>

905 Robbins LL, Hansen ME, Kleypas JA, Meylan SC (2010) CO<sub>2</sub> Calc: a user-friendly seawater carbon calculator  
906 for Windows, Mac OS X, and iOS (iPhone), U.S. Geological Survey Open-File Report, 2010–1280, 1–17.  
907 <http://pubs.usgs.gov/of/2010/1280/>. Accessed 07 December 2020

908 Romanek C, Grossman E, Morse J (1992) Carbon isotopic fractionation in synthetic aragonite and calcite:  
909 Effects of temperature and precipitation rate. *Geochim Cosmochim Acta* 56:419-430.  
910 [https://doi.org/10.1016/0016-7037\(92\)90142-6](https://doi.org/10.1016/0016-7037(92)90142-6)

911 Roobaert A, Laruelle GG, Landschützer P, Gruber N, Chou L, Regnier P (2019) The spatiotemporal dynamics of  
912 the sources and sinks of CO<sub>2</sub> in the global coastal ocean. *Global Biogeochem Cy* 33:1693-1714.  
913 <https://doi.org/10.1029/2019GB006239>

914 Safriel U, Adeel Z (2005) Dryland systems. In: Hassan R, Scholes R, Ash N (eds) *Ecosystems and Human well-*  
915 *being: Current State and Trends*. Island Press, Washington DC, pp 623–62.

916 Samanta S, Dalai TK, Pattanaik JK, Rai SK, Mazumdar A (2015) Dissolved inorganic carbon (DIC) and its  
917  $\delta^{13}\text{C}$  in the Ganga (Hooghly) River estuary, India: evidence of DIC generation via organic carbon degradation  
918 and carbonate dissolution. *Geochim Cosmochim Acta* 165:226–248. <https://doi.org/10.1016/j.gca.2015.05.040>

919 Sass E, Ben-Yaakov S (1977) The carbonate system in hypersaline solutions: Dead Sea Brines. *Mar Chem*  
920 5:183-199. [https://doi.org/10.1016/0304-4203\(77\)90006-8](https://doi.org/10.1016/0304-4203(77)90006-8)

921 Souza MF, Kjerfve B, Knoppers B, Landim de Souza W, Damasceno RN (2003) Nutrient budgets and trophic  
922 state in a hypersaline coastal lagoon: Lagoa de Araruama, Brazil. *Estuar Coast Shelf Sci* 57:843–858.  
923 [https://doi.org/10.1016/S0272-7714\(02\)00415-8](https://doi.org/10.1016/S0272-7714(02)00415-8)

924 Tong Y, Wang M, Peñuelas J et al (2020) Improvement in municipal wastewater treatment alters lake nitrogen to  
925 phosphorus ratios in populated regions *Proc Natl Acad Sci* 117(21):11566-11572.  
926 <https://doi.org/10.1073/pnas.1920759117>

927 Van Dam BR, Tobias C, Holbach A, Paerl HW, Zhu G (2018) CO<sub>2</sub> limited conditions favor cyanobacteria in a  
928 hypereutrophic lake: An empirical and theoretical stable isotope study. *Limnol Oceanogr* 63:1643–1659.  
929 <https://doi.org/10.1002/lno.10798>

930 Van Dam BR, Edson JB, Tobias C (2019) Parameterizing Air-Water Gas Exchange in the Shallow, Microtidal  
931 New River Estuary. *J Geophys Res Biogeosciences* 124:2351–2363. <https://doi.org/10.1029/2018JG004908>

932 Wanninkhof R (2014) Relationship between wind speed and gas exchange over the ocean revisited. *Limnol*  
933 *Oceanogr Methods* 12:351–362. <https://doi.org/10.4319/lom.2014.12.351>

934 Wong WW, Sackett WM (1978) Fractionation of stable carbon isotopes by marine phytoplankton. *Geochim*  
935 *Cosmochim Acta* 42:1809-1815.

936 Weiss RF (1974) Carbon dioxide in water and seawater: the solubility of a non-ideal gas. *Mar Chem* 2:203–215.  
937 [https://doi.org/10.1016/0304-4203\(74\)90015-2](https://doi.org/10.1016/0304-4203(74)90015-2)

938 Yang X, Xue L, Li Y, Han P, Liu X, Zhang L, Cai W-J (2018) Treated wastewater changes the export of  
939 dissolved inorganic carbon and its isotopic composition and leads to acidification in coastal oceans. *Environ Sci*  
940 *Technol* 52(10):5590–5599. <https://doi.org/10.1021/acs.est.8b00273>

941 Yao H, Hu X (2017) Responses of carbonate system and CO<sub>2</sub> flux to extended drought and intense flooding in a  
942 semiarid subtropical estuary. *Limnol Oceanogr* 62:S112–S130. <https://doi.org/10.1002/lno.10646>

943 Yao H, McCutcheon MR, Staryk CJ, Hu X (2020) Hydrologic controls on CO<sub>2</sub> chemistry and flux in subtropical  
944 lagoonal estuaries of the northwestern Gulf of Mexico. *Limnol Oceanogr* 65:1380-1398.  
945 <https://doi.org/10.1002/lno.11394>

946 Yates KK, Dufore C, Smiley N, Jackson C, Halley RB (2007) Diurnal variation of oxygen and carbonate system  
947 parameters in Tampa Bay and Florida Bay. *Mar Chem* 104:110–124.  
948 <https://doi.org/10.1016/j.marchem.2006.12.008>

949 Zhang J, Quay PD, Wilbur DO (1995) Carbon isotope fractionation during gas water exchange and dissolution  
950 of CO<sub>2</sub>. *Geochim Cosmochim Acta* 59(1):107–114. [https://doi.org/10.1016/0016-7037\(95\)91550-D](https://doi.org/10.1016/0016-7037(95)91550-D)

951 Zhang C, Huang H, Ye C, Huang L, Li X, Lian J, Liu S (2013) Diurnal and seasonal variations of carbonate  
952 system parameters on Luhuitou fringing reef, Sanya Bay, Hainan Island, South China Sea, Deep-Sea Res Pt II  
953 96:65–74. <https://doi.org/10.1016/j.dsr2.2013.02.013>

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985 Table 1: Mean ( $\pm$  standard deviation) and ranges of the principal parameters investigated in the brines of  
 986 Araruama Lagoon, separated by sectors and sampling campaigns.

	July-2017 (winter)			February-2018 (summer)		
	Inner Lagoon	Central Lagoon	Outer Lagoon (channel)	Inner lagoon	Central Lagoon	Outer Lagoon (channel)
<b>Salinity</b>	53.4 $\pm$ 1.5 (49.9 55.5)	55.0 $\pm$ 1.3 (39.0 56.4)	53.3 $\pm$ 2.6 (36.7 56.5)	64.3 $\pm$ 0.7 (62.4 65.9)	62.8 $\pm$ 1.8 (53.4 65.3)	43.84 $\pm$ 8.6 (33.7 64.8)
<b>Temperature (°C)</b>	21.8 $\pm$ 0.2 (21.0 22.6)	21.8 $\pm$ 0.3 (19.7 23.3)	22.5 $\pm$ 0.9 (19.0 24.0)	31.2 $\pm$ 0.7 (29.8 32.7)	29.9 $\pm$ 0.8 (27.0 32.1)	27.4 $\pm$ 1.9 (24.9 32.3)
<b>pH (NBS)</b>	8.69 $\pm$ 0.09 (8.56 8.88)	8.53 $\pm$ 0.02 (8.42 8.61)	8.51 $\pm$ 0.05 (8.38 8.71)	8.49 $\pm$ 0.16 (8.30 8.84)	8.28 $\pm$ 0.05 (7.94 8.41)	8.25 $\pm$ 0.08 (7.86 8.39)
<b>TA (<math>\mu\text{mol kg}^{-1}</math>)</b>	2626 $\pm$ 62 (2536 2686)	2729 $\pm$ 33 (2660 2772)	2642 $\pm$ 111 (2543 2770)	2971 $\pm$ 40 (2931 3037)	2954 $\pm$ 57 (2844 3003)	2483 $\pm$ 285 (2176 2925)
<b>DIC (<math>\mu\text{mol kg}^{-1}</math>)</b>	1820 $\pm$ 117 (1678 1965)	2026 $\pm$ 40 (1936 2058)	1970 $\pm$ 43 (1936 2029)	2015 $\pm$ 180 (1795 2220)	2225 $\pm$ 35 (2164 2269)	2037 $\pm$ 112 (1866 2217)
<b><math>\delta^{13}\text{C-DIC}</math> (‰)</b>	1.50 $\pm$ 0.19 (1.29 1.79)	1.58 $\pm$ 0.12 (1.41 1.78)	1.67 $\pm$ 0.20 (1.38 1.82)	4.11 $\pm$ 1.09 (2.72 5.55)	2.77 $\pm$ 0.26 (2.43 3.26)	2.69 $\pm$ 0.40 (1.94 3.11)
<b><math>p\text{CO}_2</math> (ppmv)</b>	128 $\pm$ 31 (70 182)	200 $\pm$ 16 (152 304)	225 $\pm$ 37 (136 406)	233 $\pm$ 94 (92 366)	385 $\pm$ 24 (283 435)	460 $\pm$ 108 (301 844)
<b>DO (%Sat)</b>	123 $\pm$ 4 (109 135)	114 $\pm$ 6 (90 153)	121 $\pm$ 17 (62 196)	103 $\pm$ 10 (80 143)	97 $\pm$ 7 (56 112)	92 $\pm$ 10 (61 133)
<b>Chl <i>a</i> (<math>\mu\text{g L}^{-1}</math>)</b>	31.2 $\pm$ 5.2 (25.5 37.4)	21.4 $\pm$ 3.8 (16.3 26.6)	20.9 $\pm$ 7.7 (14.0 30.5)	75.7 $\pm$ 49.2 (26.4 151.9)	33.2 $\pm$ 4.7 (23.8 38.5)	30.3 $\pm$ 24.9 (1.0 71.3)

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1005 Table 2 Summary of calculated mean values for wind speed, gas exchange coefficient ( $k_{600}$ ) and  $\text{CO}_2$  fluxes at  
 1006 the air–sea interface ( $\text{FCO}_2$ ) in each sector and the whole of Araruama Lagoon. W14 is the data calculated  
 1007 according to  $k_{600}$  of Wanninkhof (2014), VD19 is the data calculated according to  $k_{600}$  of Van-Dam et al. (2019),  
 1008 and J08 is data calculated according to  $k_{600}$  of Jiang et al. (2008).

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	Wind velocity ( $\text{m s}^{-1}$ )	$k_{600}$ ( $\text{cm h}^{-1}$ )			$\text{FCO}_2$ ( $\text{mmolC m}^{-2} \text{d}^{-1}$ )		
		(W14)	(VD19)	(J08)	(W14)	(VD19)	(J08)
<b>July-2017 (Winter)</b>							
<b>Inner (65 <math>\text{Km}^2</math>)</b>	4.1 ± 2.9	7.7 ± 9.0	10.2 ± 5.0	11.6 ± 9.9	-12.9 ± 1.7	-17.1 ± 2.6	-19.5 ± 2.5
<b>Central (123 <math>\text{Km}^2</math>)</b>	4.1 ± 2.9	7.7 ± 9.0	10.2 ± 5.0	11.6 ± 9.9	-9.2 ± 0.7	-12.2 ± 1.0	-13.9 ± 1.1
<b>Outer (32 <math>\text{Km}^2</math>)</b>	4.1 ± 2.9	7.7 ± 9.0	10.2 ± 5.0	11.6 ± 9.9	-8.2 ± 1.9	-10.8 ± 2.5	-12.3 ± 2.8
<b>All Lagoon area- weighted (220 <math>\text{Km}^2</math>)</b>					-10.15	-13.44	-15.32
<b>February-2018 (Summer)</b>							
<b>Inner (65 <math>\text{Km}^2</math>)</b>	8.0 ± 2.5	16.7 ± 10.4	15.5 ± 3.8	17.9 ± 8.3	-17.7 ± 8.9	-16.5 ± 8.4	-19.3 ± 9.8
<b>Central (123 <math>\text{Km}^2</math>)</b>	8.0 ± 2.5	16.7 ± 10.4	15.5 ± 3.8	17.9 ± 8.3	-1.5 ± 1.9	-1.4 ± 1.8	-1.7 ± 2.1
<b>Outer (32 <math>\text{Km}^2</math>)</b>	8.0 ± 2.5	16.7 ± 10.4	15.5 ± 3.8	17.9 ± 8.3	7.3 ± 9.8	6.8 ± 9.2	7.9 ± 11.0
<b>All Lagoon area- weighted (220 <math>\text{Km}^2</math>)</b>					-5.01	-4.67	-5.50

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1024 Table 3 Comparison between night-time and daytime measurements (moored station) in summer period  
1025 (February-2017) for the main parameters analyzed in this study.

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	Night-time	Daytime
Salinity	64.3 ± 0.13	64.2 ± 0.70
Temperature (°C)	29.4 ± 0.20	30.0 ± 0.38
DO (%Sat)	85 ± 6	96 ± 8
pH (NBS)	8.25 ± 0.01	8.31 ± 0.02
TA (μmol kg <sup>-1</sup> )	2971 ± 9	2990 ± 15
DIC (μmol kg <sup>-1</sup> )	2253 ± 17	2211 ± 48
δ <sup>13</sup> C-DIC	2.88 ± 0.14	3.05 ± 0.52
pCO <sub>2</sub> (ppmv)	411 ± 11	385 ± 25
Chl a (μg L <sup>-1</sup> )	32.6 ± 1.8	44.7 ± 16.5
FCO <sub>2</sub> (mmol C m <sup>-2</sup> d <sup>-1</sup> )		
W14	2.67 ± 2.59	-3.99 ± 7.01
VD19	1.59 ± 1.54	-2.05 ± 3.74
J08	3.25 ± 3.16	-4.45 ± 8.13
NCP (mmol C m <sup>-2</sup> d <sup>-1</sup> )	-91.4	278.8

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1046 Figure Captions

1047 Fig. 1 Location of the Araruama Lagoon, Brazil. The lagoon was divided into three sectors to analyse spatial  
1048 heterogeneity: IL (Inner Lagoon), CL (Central Lagoon), OL (Outer Lagoon). The blue line represents the boat  
1049 track with continuous measurements (nearly the same boat route was made in winter and summer). However,  
1050 note that the marine end-member outside the channel was sampled on in February. The red circles represent the  
1051 discrete sampling stations. The green star represents the location of the moored station. The yellow star  
1052 represents the location of meteorological station.

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1054 Fig. 2 Distributions of TA (a), DIC (b)  $\delta^{13}\text{C}$ -DIC (c), and  $p\text{CO}_2$  (d) along the salinity gradient. The blue dots  
1055 represent the winter, and the green dots represent the summer. The dashed blue and green lines represent the  
1056 theoretical evaporation path. The red line (graph d) represents the average values of atmospheric  $p\text{CO}_2$ .

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1058 Fig.3 Maps showing the boat trajectories (black lines) during sampling for winter (a) and summer (f) periods.  
1059 Below the map on the left side, it is presented the distributions of temperature (b), salinity (c),  $p\text{CO}_2$  (d) and  $\text{O}_2$   
1060 (f) vs. latitude, for winter. Below the map on the right side, it is presented the distributions of temperature (g),  
1061 salinity (h),  $p\text{CO}_2$  (i) and  $\text{O}_2$  (j) vs. latitude, for summer. The yellow, black, and red dots represent the inner,  
1062 central, and outer sectors, respectively. The black line represents the value of atmospheric  $p\text{CO}_2$  and  $\text{O}_2$ .

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1064 Fig. 4 Variation in the partial pressure of  $\text{CO}_2$  ( $p\text{CO}_2$ , ppmv) as a function of dissolved oxygen saturation level  
1065 (DO%) in the brines of Araruama Lagoon. The grey circles represent the sampling at day 18-07-2017, which  
1066 occurred before storm (under low wind speed;  $< 5.5 \text{ m s}^{-1}$ ). The light blue circles represent the sampling after  
1067 storm (during storm the wind speed overpassed  $14 \text{ m s}^{-1}$ ).

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1069 Fig. 5 Relationship between  $p\text{CO}_2$  levels and Chl *a* concentrations, separated in winter and summer periods.

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1071 Fig. 6 Scatter plots of  $\delta^{13}\text{C}$ -DIC as a function of a)  $p\text{CO}_2$ , b) water temperature, and c) Chl *a* concentration. Blue  
1072 squares represent the sampling in winter, and green circles represent the sampling in summer.

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1074 Fig. 7 Time series at the mooring station showing the diurnal variation of DO concentrations and  $p\text{CO}_2$  values.  
1075 The shaded area symbolizes the period of night-time measurement. The horizontal black line represents the  
1076 atmospheric  $p\text{CO}_2$  and  $\text{O}_2$ .

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1078 Fig. 8 The graph a) represents the deviations from evaporative model of TA ( $\Delta\text{TA}$ ) as a function of DIC ( $\Delta\text{DIC}$ )  
1079 in waters of Araruama Lagoon. The solid black lines indicate the direction and slope of the main processes  
1080 affecting TA and DIC concentrations. The graph b) is plot of  $\Delta\delta^{13}\text{C}$ -DIC vs.  $\Delta\text{DIC}/\text{DIC}_{\text{Ocean}}$  in the Araruama  
1081 Lagoon. The drawn vectors "photosynthesis" and "CO<sub>2</sub> efflux" represent the slopes of these specific processes  
1082 affecting the DIC and  $\delta^{13}\text{C}$ -DIC distributions, when DIC concentrations decrease and  $\delta^{13}\text{C}$ -DIC values increase.  
1083 The drawn vector "CaCO<sub>3</sub> precipitation" represents the slope of this specific process, when DIC concentrations  
1084 and  $\delta^{13}\text{C}$ -DIC values decrease. The drawn vector "CO<sub>2</sub> influx" represents the slope of this specific process, when  
1085 DIC concentrations increase and  $\delta^{13}\text{C}$ -DIC values decrease. Blue dots are the winter stations, and green dots are  
1086 the summer stations. The origin of these graphs (represented by the black "x") indicate no deviation from the  
1087 evaporative model (see material and methods section 2.3.4 for further explanation).

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1090 Fig. 9 Relationship between E-DIC and AOU. Blue dots are the winter stations, and green dots are the summer  
1091 stations. The 1:1 line represents the quotient between CO<sub>2</sub> and O<sub>2</sub> during the processes of photosynthesis and  
1092 respiration.

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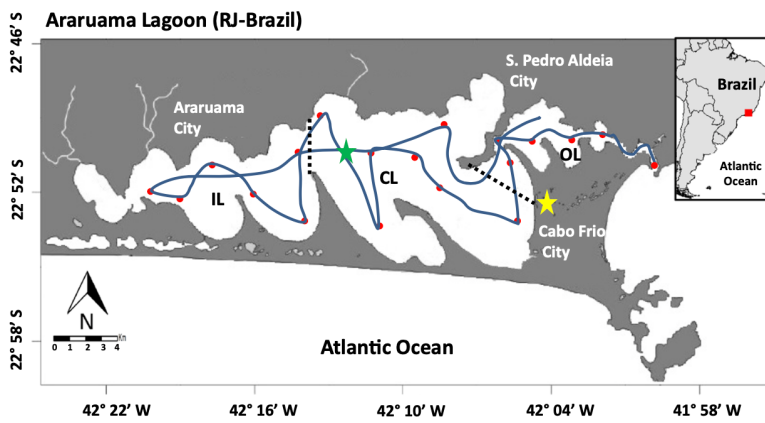
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1101 Fig. 1



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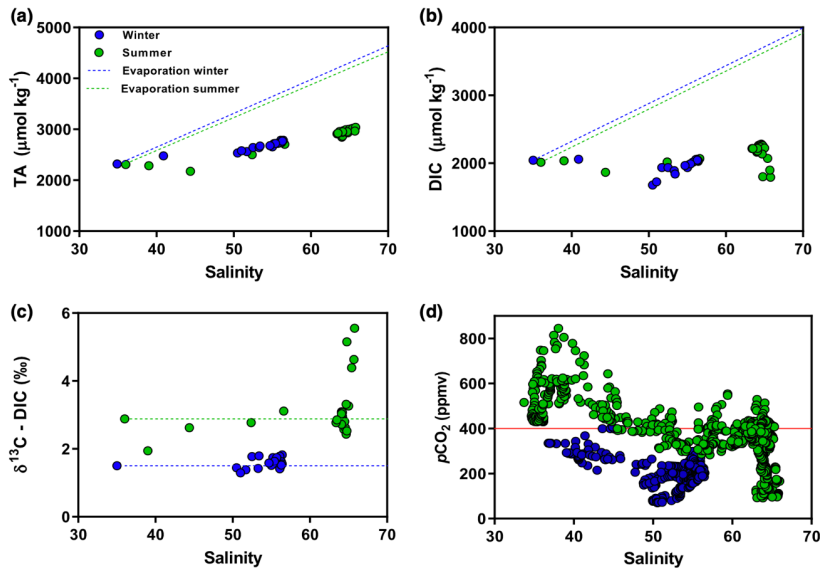
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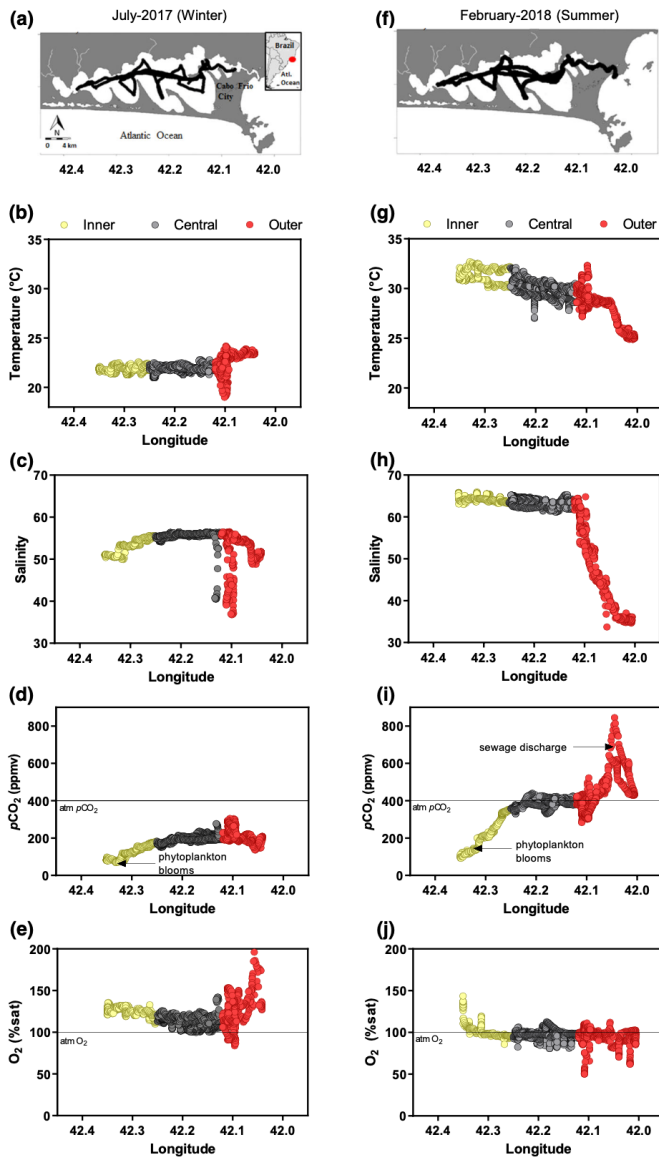
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1113 Fig. 2



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1131 Fig. 3

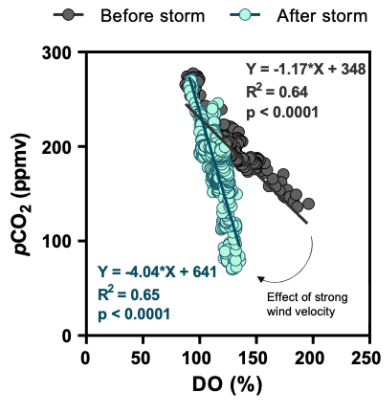


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1135 Fig. 4

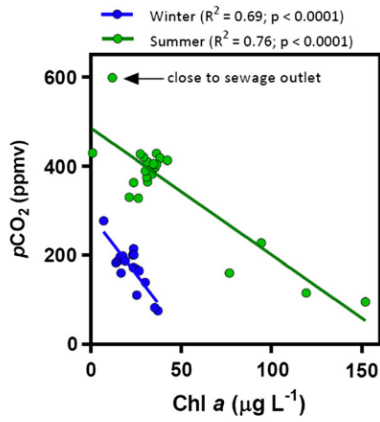


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1139 Fig. 5



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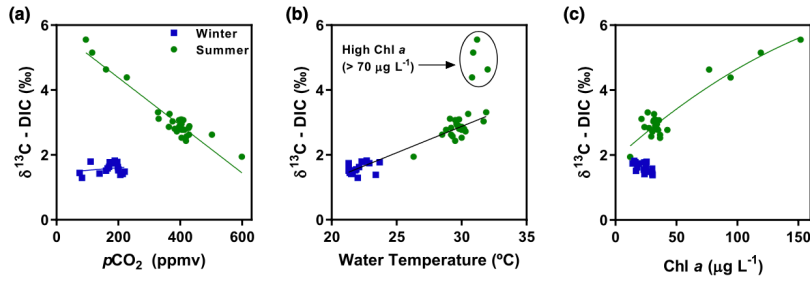
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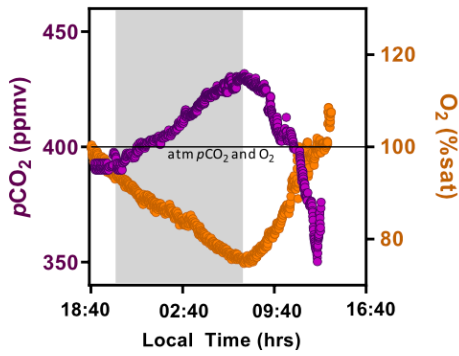
1146 Fig. 6



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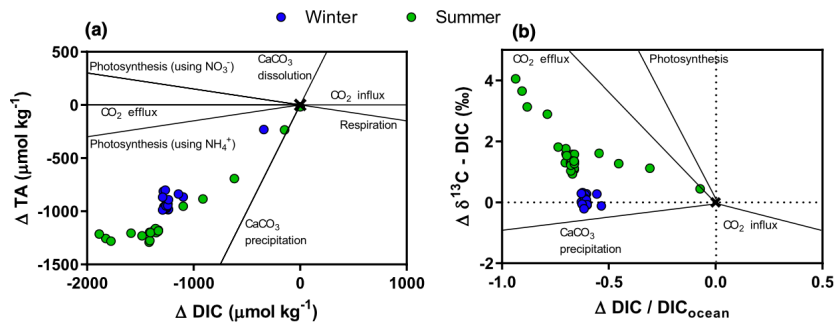
1149 Fig. 7



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1152 Fig. 8



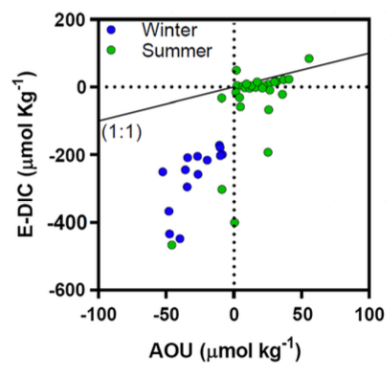
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1157 Fig. 9



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