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1 **Eutrophication overcoming carbonate precipitation in a tropical hypersaline coastal lagoon acting as a**
2 **CO₂ sink (Araruama Lagoon, SE Brazil)**

3

4 Luiz C. Cotovicz Jr.^{1,2*}; Bastiaan A. Knoppers¹; Carolina R. Régis¹; Daniel Tremmel; Suzan Costa-Santos¹;
5 Gwenaël Abril^{1,3,4}

6 ¹ Programa de Geoquímica, Universidade Federal Fluminense, Niterói, RJ, Brazil

7 ² Instituto de Ciências do Mar, Universidade Federal do Ceará, Fortaleza, Ceará, Brazil

8 ³ Biologie des Organismes et Ecosystèmes Aquatiques (BOREA), Muséum National d'Histoire Naturelle, FRE
9 2030, CNRS, MNHN, IRD, SU, UCN, UA, Paris, France.

10 ⁴ Programa de Pós-Graduação em Biologia Marinha e Ambientes Costeiros (PBMAC), Universidade Federal
11 Fluminense, Niterói, RJ, Brazil

12 * Corresponding author: Luiz C. Cotovicz Jr., lccjunior@id.uff.br (ORCID: 0000-0002-3914-8155)

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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 (CaCO₃)
36 precipitation partially explained these deficits. The negative correlation between the partial pressure of CO₂
37 (*p*CO₂) 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 CaCO₃
39 precipitation. Marked *p*CO₂ 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 CO₂ sink during winter (-15.32 to -10.15 mmolC m⁻² d⁻¹), a moderate sink during summer (-5.50 to -
43 4.67 mmolC m⁻² d⁻¹), with a net community production (NCP) of 93.7 mmolC m⁻² d⁻¹ and prevalence of net
44 autotrophic metabolism. A decoupling between CO₂ and O₂ 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 CaCO₃ precipitation and autotrophic metabolism on CO₂ 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 CO₂
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 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 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 CO_2 fluxes in coastal
76 lagoons. Findings in tropical and subtropical coastal lagoons indicate that they can act both as net 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 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, CaCO₃ precipitation, CaCO₃ dissolution, air-water CO₂ 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 CO₂ are generally autotrophic (gross primary production, GPP > community respiration, CR), and
88 ecosystems that are net sources of CO₂ are generally heterotrophic (GPP < CR) (Borges and Abril 2011).
89 However, many exceptions exist where autotrophic systems are CO₂ sources and heterotrophic systems are CO₂
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 CO₂ fluxes are significant in productive ecosystem (Cotovicz et
92 al. 2015). Estuarine systems and near-shore coastal waters are considered as significant sources of CO₂ to the
93 atmosphere due to their heterotrophic character and inputs of CO₂-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 CO₂ 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 CO₂ 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 CO₂ 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}C)
103 during photosynthesis, turning the residual DIC enriched in the heavier carbon isotope (^{13}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 CO₂.

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, CaCO₃
121 being the first salt to form (Babel and Schreiber 2014). The precipitation of CaCO₃ releases CO₂ in the water,
122 while TA and DIC are consumed in a ratio of 2:1 for every mole of CaCO₃ precipitated (Dickson 2010). To the
123 contrary, CaCO₃ dissolution can occur in areas of organic matter degradation, absorbing CO₂ from the water and
124 releasing TA and DIC (Abril et al. 2003). The CaCO₃ precipitation consumes DIC from the water in the form of
125 carbonate (CO₃²⁻), which is the DIC form that has the heavier carbon stable isotope signature, turning the
126 remaining DIC pool slightly depleted in ¹³C 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 CaCO₃ minerals (Ω), the buffering
128 capacity of the ecosystem, and the air-water CO₂ 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 CO₂) from the water, and makes the $\delta^{13}\text{C}$ -DIC signatures heavier. In
137 contrast, the CaCO₃ precipitation also consumes DIC (but releases CO₂), 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 CaCO₃ precipitation are intense and competing. We investigated the main controls on
144 the air-water CO₂ 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 km², 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 km³ (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⁻¹ (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 m³ s⁻¹
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 CO₂ in the water (*p*CO₂), 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*CO₂ 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⁻¹. 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⁻¹. The air passes through
191 a desiccant, and then the *p*CO₂ 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*CO₂ of 410, 1007, and 5035 ppmv; White Martins Certified Material, RJ, Brazil). N₂ 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*CO₂ measurements were estimated at about ±3 and ±5 ppmv,
196 respectively. The system is ideal for analyses of *p*CO₂ 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⁻¹) 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 (pH_{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°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°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 ± 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 μL 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 H_3PO_4 to convert all inorganic carbon to CO_2 . Samples
230 were shaken and let stabilize at room temperature for 5h. $\delta^{13}\text{C}$ of 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 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 HSO_4^- ion from Dickson (1990), and the solubility coefficient of 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 CO_2 fluxes

249 Diffusive CO_2 fluxes at air-water interface (F_{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 CO_2 gas transfer velocity, α is the solubility of 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 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 CaCO₃ precipitation/dissolution and air-sea CO₂ 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 CaCO₃ 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⁻² h⁻¹, DIC₁ and DIC₂ are the salinity-normalized concentration of DIC (mmol kg⁻¹)
272 during two consecutive discrete sampling with one hour of interval, p is the seawater density (kg m⁻³), d is the
273 average depth (m), Δt represents the time interval (hour) and FCO₂ is the carbon dioxide flux (mmol m⁻² h⁻¹)
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_{night-time}), and for daytime period (from dawn to dusk; NCP_{daytime}).

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_{measured} is the measured salinity, S_{ocean} the salinity of the ocean end-member, DIC_{ocean} and TA_{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 (ΔDIC) 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_{measured} is the measured DIC. Deviation of TA (ΔTA) 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_{measured}) and the $\delta^{13}C$ -DIC of the marine end-member ($\delta^{13}C$ - DIC_{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_{measured} is equal do the $\delta^{13}C$ - DIC_{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°C , with a maximum of 31.2°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 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°C , whereas the lowest
337 was 21.2°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 ± 37 ppmv in winter and 460 ± 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 ± 16 ppmv in winter and 385 ± 24 ppmv in summer. The inner region of the
346 lagoon presented the lowest values of $p\text{CO}_2$, averaging 128 ± 31 ppmv in winter and 233 ± 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 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 CO_2 flux (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 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 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 m s^{-1} , the
392 parameterization of W14 gave higher k_{600} values than that of VD19. During winter, FCO_2 exhibited always
393 negative values, indicating a permanent sink of 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 CO_2 , with fluxes ranging between $-19.3 \pm 9.8 \text{ mmolC m}^{-2} \text{ d}^{-1}$ to -1.5 ± 1.9 , while the outer
396 region was a weak source of CO_2 , ranging from 6.8 to $7.9 \text{ mmolC m}^{-2} \text{ d}^{-1}$. Time-integrated CO_2 fluxes,
397 accounting for seasonal variations, revealed that the lagoon behaved as a net 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 ± 0.3 °C) than nighttime samples (29.5 ± 0.3 °C), but with no statistical significance. $p\text{CO}_2$
404 values averaged 411 ± 11 ppmv during nighttime and decreased to 385 ± 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 CO_2 fluxes showed emissions during nighttime, ranging from 1.59 to 3.25 mmol C m^{-2}
411 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 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 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 Δ TA and Δ DIC (Fig. 8a). Multiplying Δ TA and Δ DIC values by the water volume of
432 the lagoon (0.618 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 CaCO_3 production in coral reefs (140 to $334 \text{ gC m}^{-2} \text{ yr}^{-1}$), similar of 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, 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 ~ 53 . For each mole of 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 CaCO_3 (Ω) increases with temperature (Mucci 1983), and heating of water in the lagoon also
448 favors the 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 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 CaCO₃ 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 CaCO₃
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 CaCO₃,
466 thus locally counter-acting the process of ocean acidification. Indeed, CaCO₃ 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 CaCO₃ precipitation to the deficits
469 of TA and DIC in the brines of Araruama Lagoon. Indeed, the slopes of ΔTA and ΔDIC are consistent with
470 simultaneous photosynthesis and CaCO₃ 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 (ΔDIC_{CaCO₃}), was calculated as:

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

481 ΔTA is the deviation of TA concentration from the evaporation model, and was assumed to be influenced only
482 by CaCO₃ precipitation.

483 The effect of primary production on DIC concentrations (ΔDIC_{pp}) was calculated as follows:

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

485 Δ 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 CaCO_3
488 precipitation (that is a net source of CO_2), the lagoon remains a 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 NO_3^- assimilation) or decrease TA (in case of preferential NH_4^+ assimilation) (Abril and
492 Frankignoulle, 2001) (Fig. 8a). NO_3^- assimilation is probably more significant than NH_4^+ because NO_3^-
493 concentrations are about 10-times higher than NH_4^+ concentrations in the lagoon (Ramos-Régis 2020). However,
494 during summer and under rainy conditions, the concentrations of 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 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 CO_2 . The uptake of 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 CaCO_3
520 calcification (ΔTA 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 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, 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 CO_2 , but also to an increase of pH, carbonate ion (CO_3^{2-})
533 concentration and the saturation state of 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 μg
539 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). CaCO_3 precipitation also consumes DIC from the water but in the form of CO_3^{2-} ,
543 which is the DIC form that has the heavier stable carbon isotope signature (compared to dissolved CO_2 and

544 HCO₃⁻) (Zhang et al., 1995), turning the remaining DIC pool depleted in ¹³C relative to the seawater (Isaji et al.
545 2017). However, the impact of primary production on δ¹³C-DIC is much stronger than that of CaCO₃
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 δ¹³C-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 CO₂ (when DIC decrease and δ¹³C-DIC increase) and CaCO₃
553 precipitation (when both DIC and δ¹³C-DIC decrease) (Samanta et al. 2015; Cotovicz et al. 2019). As the large
554 majority of *p*CO₂ values in the lagoon are below the equilibrium with the atmosphere, the effect of CO₂
555 outgassing on δ¹³C-DIC was considered as negligible (Fig. 2). The highest positive deviation of δ¹³C-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 δ¹³C-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 CaCO₃ precipitation.

560 The pattern of diurnal variability of *p*CO₂ 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 CO₂ dynamics (Fig. 7).
562 Strong diel variations of CO₂ 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*CO₂ 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⁻² yr⁻¹ in Araruama Lagoon in summer. This autotrophic metabolism inside the
567 Araruama lagoon generates a diurnal variability of CO₂ 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⁻² yr⁻¹) compared to planktonic
570 primary production (¹⁴C-method, 0.6 molC m⁻² yr⁻¹), and net heterotrophy (community respiration between 12.8
571 and 23.9 molC m⁻² yr⁻¹). Within this same period (1989-1990), but in a "low salinity year", Moreira-Turcq
572 (2000) documented higher rates of planktonic primary production (¹⁴C method, averaging 13.5 mol C m⁻² yr⁻¹)
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⁻² yr⁻¹). 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⁻² yr⁻¹; Cloern et al. 2014). This NCP is close to the threshold
584 of hypertrophic classification (500 g C m⁻² yr⁻¹) considering the annual phytoplankton primary production
585 proposed by Nixon (1995).

586 High oversaturated conditions of pCO₂ (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 CO₂
590 outgassing (Cotovicz et al. 2015; 2021). The sampling in summer was carried out during a period of high
591 rainfall, which favored CO₂ and organic carbon inputs from urban areas.

592 4.3 Apparent decoupling between CO₂ and O₂ 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 CO₂ and O₂ during primary production and community respiration (Fig. 9). The
599 deviations were particularly important when values of pCO₂ are very low in the water (below 300 ppmv; Fig. 9),
600 associate with large disequilibria of CO₂ 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 O₂ than for CO₂, 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 CO₂ to the atmosphere because the buffering effect of bicarbonate concentration
605 affects the CO₂ concentrations, but not the O₂ concentrations.

606 This difference between air-water exchanges for O₂ and CO₂ 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⁻¹), with high oversaturation for O₂ and undersaturation for pCO₂. Overnight, the wind speed
609 increased to velocities > 14 m s⁻¹, and fast gas-exchange occurred, causing DO concentrations to decrease from
610 oversaturation to values close to atmosphere equilibrium; however, the values of pCO₂ remained well below 400
611 ppmv, evidencing the decoupling between O₂ and CO₂ in these productive and well-buffered waters.

612 Furthermore, the occurrence of CaCO₃ 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 CO₂ 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 CO₂ fluxes from the gradient between pCO₂ 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 k₆₀₀
624 formulations allows to provide credible ranges of FCO₂ estimates (Jiang et al. 2008; Wanninkhof 2014; Van
625 Dam et al. 2019).

626 Classical river-dominated estuaries are considered net sources of CO₂ 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 CO₂ emissions reports strong sources of CO₂ at inner regions of estuaries, on the
629 order of 38.6 mol C m⁻² yr⁻¹, and weak sources at outer regions with salinities >25, on the order of 8.4 mol C m⁻²
630 yr⁻¹ (Chen et al. 2013). However, other studies in marine-dominated estuaries (coastal embayment's and lagoons)
631 have reported pCO₂ undersaturation and net CO₂ 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 CO₂ 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 CO₂, for example, in the
636 semiarid subtropical region Mission-Aransas Estuary, Gulf of Mexico (12.4 mol C m⁻² yr⁻¹; Yao and Hu, 2017),
637 because heating and evaporation enhance CO₂ 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 CO₂ uptake, during both winter and summer conditions (Figs. 2 and 5), despite the
640 occurrence of CaCO₃ precipitation (Fig. 8). The annual sink in Araruama Lagoon ranged between -2.76 and -
641 3.80 mol C m⁻² yr⁻¹, similar to those reported in other mesohaline coastal lagoons, including Australian Lagoons
642 (-0.4 to -2.0 molC m⁻² yr⁻¹, Maher and Eyre 2012) and the Aby Lagoon in Ivory Coast (-2.7 molC m⁻² yr⁻¹; Koné
643 et al. 2009). A sink of CO₂ 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⁻² yr⁻¹, Cotovicz et al. 2015) and
645 Tokyo Bay (Japan) (-3.2 molC m⁻² yr⁻¹; Kubo et al. 2017). Even if CaCO₃ precipitation occurs, Araruama
646 Lagoon is a net sink of CO₂ because eutrophication is enhancing the planktonic primary production, and
647 overcoming CaCO₃ 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 CaCO₃ 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*CO₂ values were

661 well-below the atmospheric values, generating a net annual sink of CO₂ as the result of net autotrophic
662 metabolism and overwhelming the *p*CO₂ increase driven by CaCO₃ precipitation. Oversaturated conditions of
663 *p*CO₂ 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*CO₂ in summer compared to winter. Overall, the brines of Araruama are
666 dominated by phytoplankton blooms with heavier δ¹³C-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 CO₂ and O₂ 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 CO₂
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

678 **Declarations**

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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

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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)
Salinity	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)
Temperature (°C)	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)
pH (NBS)	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)
TA ($\mu\text{mol kg}^{-1}$)	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)
DIC ($\mu\text{mol kg}^{-1}$)	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)
$\delta^{13}\text{C-DIC}$ (‰)	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)
$p\text{CO}_2$ (ppmv)	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)
DO (%Sat)	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)
Chl <i>a</i> ($\mu\text{g L}^{-1}$)	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 CO_2 fluxes at
 1006 the air–sea interface (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).

1009

	Wind velocity (m s^{-1})	k_{600} (cm h^{-1})			FCO_2 ($\text{mmolC m}^{-2} \text{d}^{-1}$)		
		(W14)	(VD19)	(J08)	(W14)	(VD19)	(J08)
July-2017 (Winter)							
Inner (65 Km^2)	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
Central (123 Km^2)	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
Outer (32 Km^2)	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
All Lagoon area- weighted (220 Km^2)					-10.15	-13.44	-15.32
February-2018 (Summer)							
Inner (65 Km^2)	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
Central (123 Km^2)	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
Outer (32 Km^2)	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
All Lagoon area- weighted (220 Km^2)					-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 ⁻¹)	2971 ± 9	2990 ± 15
DIC (μmol kg ⁻¹)	2253 ± 17	2211 ± 48
δ ¹³ C-DIC	2.88 ± 0.14	3.05 ± 0.52
pCO ₂ (ppmv)	411 ± 11	385 ± 25
Chl a (μg L ⁻¹)	32.6 ± 1.8	44.7 ± 16.5
FCO ₂ (mmol C m ⁻² d ⁻¹)		
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 ⁻² d ⁻¹)	-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 $p\text{CO}_2$.

1057

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 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 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 O_2 .

1063

1064 Fig. 4 Variation in the partial pressure of 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 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 O_2 .

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1078 Fig. 8 The graph a) represents the deviations from evaporative model of TA (ΔTA) as a function of DIC (ΔDIC)
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 "CO₂ 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 "CaCO₃ precipitation" represents the slope of this specific process, when DIC concentrations
1084 and $\delta^{13}\text{C}$ -DIC values decrease. The drawn vector "CO₂ 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 CO₂ and O₂ during the processes of photosynthesis and
1092 respiration.

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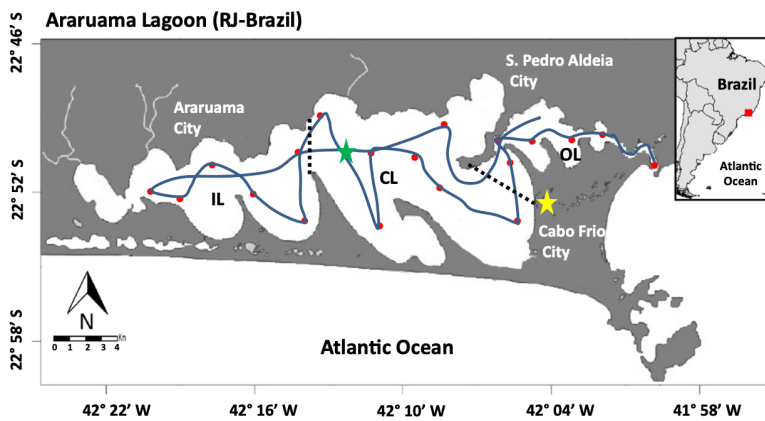
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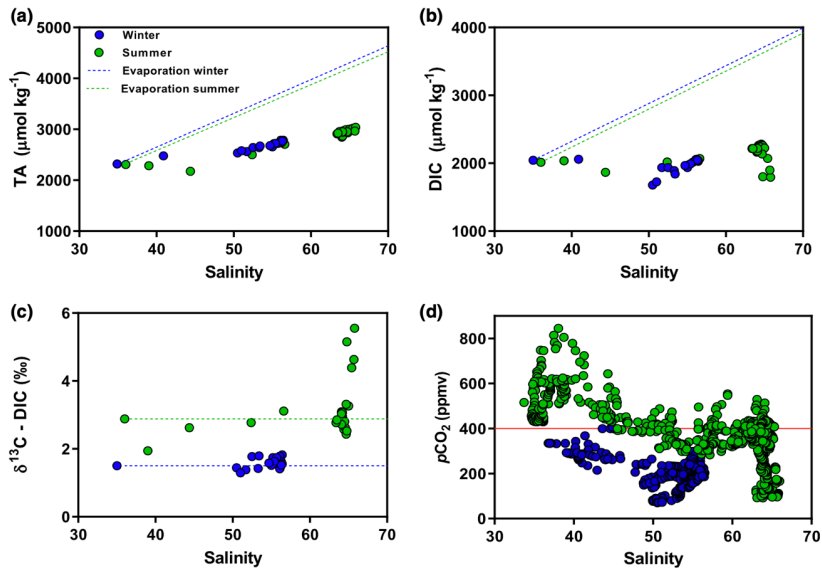
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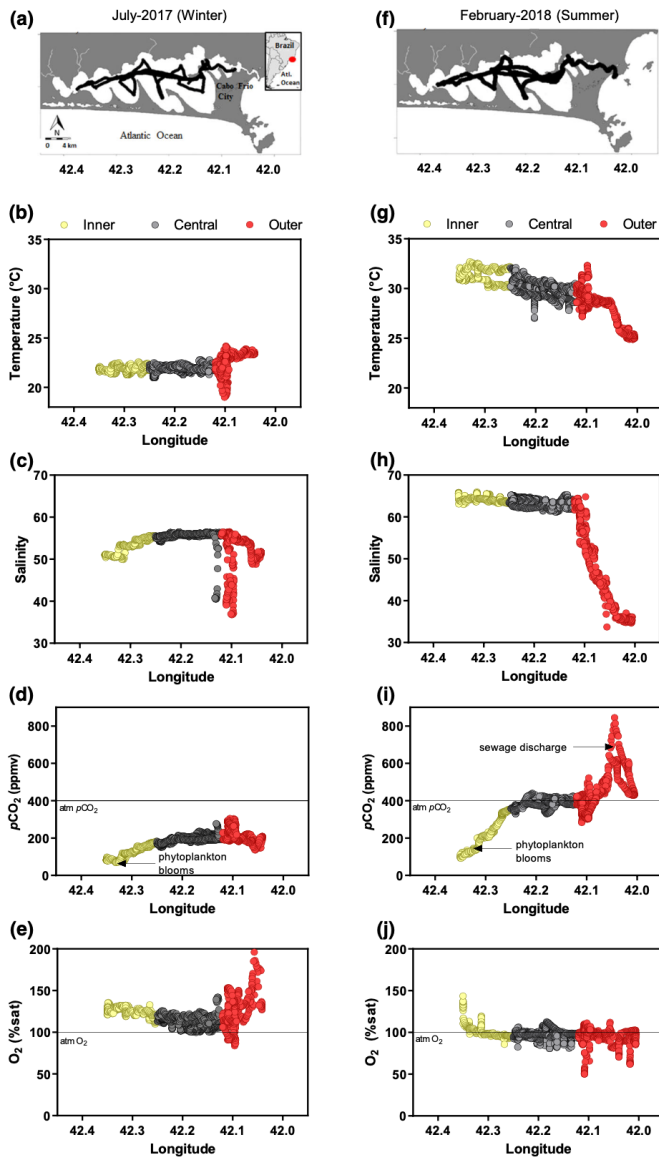
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1113 Fig. 2



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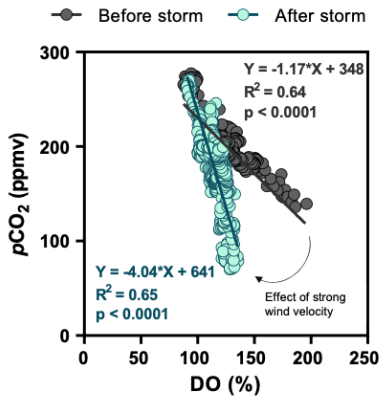


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1135 Fig. 4

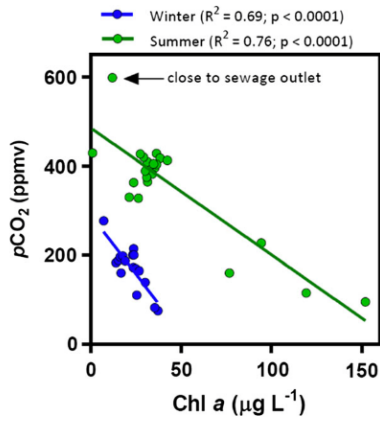


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1139 Fig. 5



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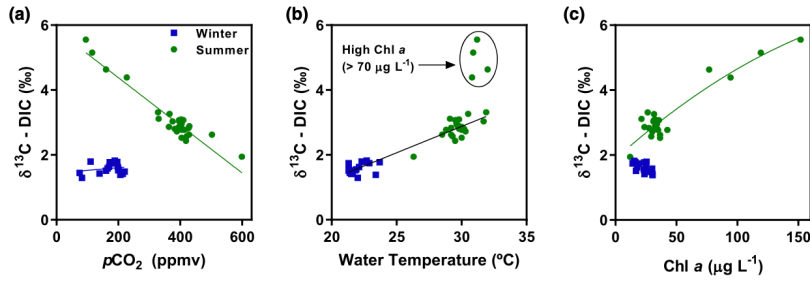
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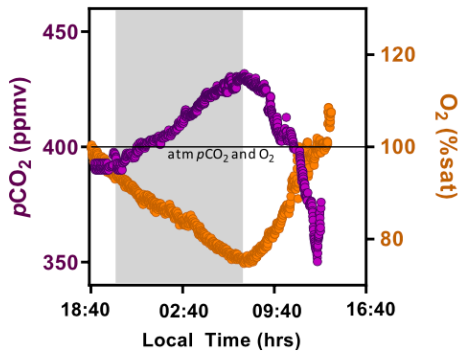
1146 Fig. 6



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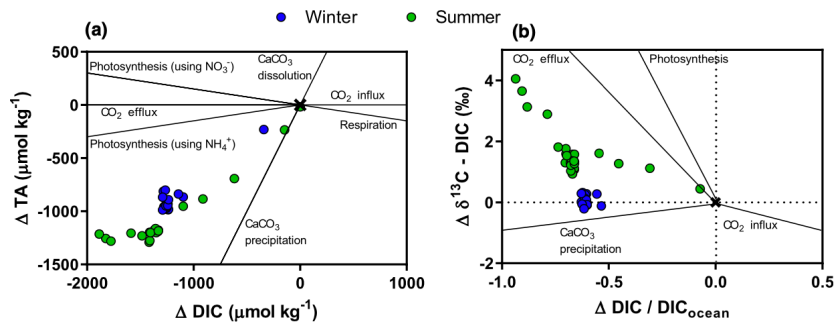
1149 Fig. 7



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1152 Fig. 8



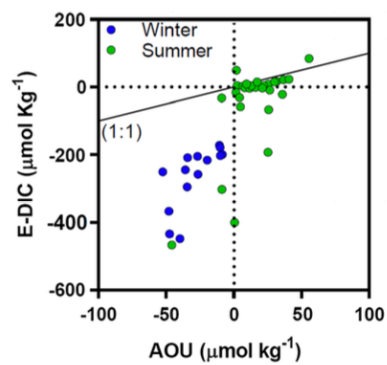
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1157 Fig. 9



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