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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)**

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Abstract

The carbonate chemistry was investigated in the semiarid eutrophic Araruama Lagoon (Brazil), one of the largest hypersaline coastal lagoons in the world. Spatial surveys during winter and summer periods were performed, in addition to a diurnal sampling in summer. The hypersaline waters have higher concentrations of total alkalinity (TA) and dissolved inorganic carbon (DIC) than the seawater that feed the lagoon, due to evaporation. However, TA and DIC concentrations were lower than those expected from evaporation. Calcium carbonate (CaCO_3) precipitation partially explained these deficits. The negative correlation between the partial pressure of CO_2 ($p\text{CO}_2$) and chlorophyll *a* (Chl *a*) indicated that DIC was also consumed by primary producers. The uptake by photosynthesis contributes to 57-63% of DIC deviation from evaporation, the remaining credited to CaCO_3 precipitation. Marked $p\text{CO}_2$ undersaturation was prevalent at the innermost region with shallow, confined, and phytoplankton-dominated waters, with a strong enrichment of heavier carbon isotope ($\delta^{13}\text{C}$ -DIC up to 5.55‰), and highest pH. Oversaturation was restricted to an urbanized region, and during night-time. The lagoon behaved as a marked CO_2 sink during winter (-15.32 to -10.15 $\text{mmolC m}^{-2} \text{d}^{-1}$), a moderate sink during summer (-5.50 to -4.67 $\text{mmolC m}^{-2} \text{d}^{-1}$), with a net community production (NCP) of 93.7 $\text{mmolC m}^{-2} \text{d}^{-1}$ and prevalence of net autotrophic metabolism. A decoupling between CO_2 and O_2 exchange rate at the air-water interface was attributed to differences in gas solubility, and high buffering capacity. The carbonate chemistry reveals simultaneous and antagonistic actions of CaCO_3 precipitation and autotrophic metabolism on CO_2 fluxes, and could reflect future conditions in populated and semiarid coastal ecosystems worldwide.

Key-words: carbonate chemistry; coastal eutrophication; hypersaline waters; climate change; atmospheric CO_2 sink

1. Introduction

Carbon is continuously displaced laterally and vertically along the land–ocean aquatic continuum comprising freshwaters, estuaries, and coastal areas (Regnier et al. 2013). Compared to the open ocean, the coastal ocean represents an important carbon sink (Cao et al. 2020) and plays a disproportionate role despite its modest surface 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 atmosphere (Chen et al. 2013; Laruelle et al., 2013), whereas continental shelf waters absorb $\sim 0.20 \text{ GtC yr}^{-1}$ (Roobaert et al. 2019); however, these fluxes are still highly uncertain owing to the complexity of processes involved in these air–sea CO_2 fluxes (Borges 2005). One of the main issues to be solved is the intrinsic spatiotemporal variability related to the heterogeneity of coastal ecosystems in different climatic domains (Borges and Abril 2011). In addition, important temporal variabilities at the tidal, diurnal, seasonal, annual and inter-annual time scales should be addressed (Borges 2005). Furthermore, anthropogenic impacts of global change and land and water uses have increased in coastal zones and have modified the biogeochemical cycles, particularly through nutrient pollution and eutrophication (Howarth et al. 2011). Coastal lagoons cover about 13% of the coastal areas (Kjerfve 1994). They are very productive ecosystems, sustaining high rates of benthic and/or planktonic primary production (Knoppers et al. 1999; Maher and Eyre 2012). Coastal lagoons present ideal conditions for human settlement, hosting $\sim 14.4\%$ of the global population (Kjerfve 1994), but suffering the increasing symptoms of demographic expansions mainly via urbanization and sewage discharge (Knoppers and Kjerfve 1999). Few studies have investigated carbonate chemistry dynamics and air–water CO_2 fluxes in coastal lagoons. Findings in tropical and subtropical coastal lagoons indicate that they can act both as net CO_2 sources or sinks depending on hydrological, chemical, and biological characteristics which are affected by natural and anthropogenic-derived disturbances, especially the inputs of nutrients and dissolved carbon from the watershed (Koné et al. 2009; Ribas-Ribas et al. 2011; Ávila-López et al. 2016; Maher et al. 2019). Furthermore, Koné et al. (2009) postulated that physical settings (mixed *versus* stratified water column) play an important role modulating air–water CO_2 fluxes.

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

production and respiration, CaCO_3 precipitation, CaCO_3 dissolution, air-water CO_2 fluxes and thermodynamic equilibration during mixing of freshwater with seawater (Cai et al. 2020; Abril et al. 2021). Ecosystems that are net sinks of CO_2 are generally autotrophic (gross primary production, $\text{GPP} > \text{community respiration, CR}$), and ecosystems that are net sources of CO_2 are generally heterotrophic ($\text{GPP} < \text{CR}$) (Borges and Abril 2011). However, many exceptions exist where autotrophic systems are CO_2 sources and heterotrophic systems are CO_2 sinks (Borges 2005; Cotovicz et al. 2020; Abril et al. 2021). In addition, the diurnal variability of carbonate chemistry parameters and associated air-water CO_2 fluxes are significant in productive ecosystem (Cotovicz et al. 2015). Estuarine systems and near-shore coastal waters are considered as significant sources of CO_2 to the atmosphere due to their heterotrophic character and inputs of CO_2 -enriched waters from rivers and intertidal vegetated areas (Cai et al. 1999; Cai et al. 2011; Borges and Abril 2011). However, net uptake of atmospheric CO_2 has been found in coastal ecosystem located in tropical (Koné et al. 2009; Cotovicz et al. 2015) and subtropical (Maher and Eyre 2012; Kubo et al. 2017) regions. The sink behavior is often associated to human-induced coastal eutrophication stimulating high levels of phytoplanktonic primary production (Cotovicz et al. 2015; Kubo et al. 2017). Capture of atmospheric CO_2 also occurs in coastal lagoons as the result of vertical haline stratification that favors phytoplankton development (Koné et al., 2009). However, the enhancement of primary production by eutrophication is associated to a concomitant enhancement of respiratory processes and emissions of CO_2 to the atmosphere (Cai et al. 2011). These processes can be tracked by analyzing the stable isotope signatures of the DIC ($\delta^{13}\text{C}$ -DIC) due to the preferential uptake of the lighter stable carbon isotope (^{12}C) during photosynthesis, turning the residual DIC enriched in the heavier carbon isotope (^{13}C) (Mook 2001). For that reason, the $\delta^{13}\text{C}$ -DIC of phytoplankton-dominated coastal waters show very positive values (Cotovicz et al., 2019; 2020). The ecosystem-level responses of carbonate chemistry in face to eutrophication are antagonists and site-specific exerting both positive and negative feedbacks on the process of coastal and ocean acidification by increasing or decreasing the aquatic levels of CO_2 .

Among tropical lagoons, hypersalinity is a common characteristic in arid and semiarid regions (Kjerfve et al. 1996). The aridity is increasing worldwide as the result of climate change (Huang et al. 2017). Observations and modelling of future scenarios suggest an increase of evaporation compared to precipitation in arid/semiarid regions; in other words, arid and semiarid regions tend to be larger and drier (Chou et al. 2009; Huang et al. 2017). Currently, semiarid regions cover ~15 % of the Earth's continental surface (Safriel and Adeel 2005). However, the area of global drylands will expand ~10 % by 2100, from inland regions to coastal zones (Feng 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_3
121 being the first salt to form (Babel and Schreiber 2014). The precipitation of CaCO_3 releases CO_2 in the water,
122 while TA and DIC are consumed in a ratio of 2:1 for every mole of CaCO_3 precipitated (Dickson 2010). To the
123 contrary, CaCO_3 dissolution can occur in areas of organic matter degradation, absorbing CO_2 from the water and
124 releasing TA and DIC (Abril et al. 2003). The CaCO_3 precipitation consumes DIC from the water in the form of
125 carbonate (CO_3^{2-}), which is the DIC form that has the heavier carbon stable isotope signature, turning the
126 remaining DIC pool slightly depleted in ^{13}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_3 minerals (Ω), the buffering
128 capacity of the ecosystem, and the air-water CO_2 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_2) from the water, and makes the $\delta^{13}\text{C}$ -DIC signatures heavier. In
137 contrast, the CaCO_3 precipitation also consumes DIC (but releases CO_2), 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_3 precipitation are intense and competing. We investigated the main controls on
144 the air-water CO_2 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 ($p\text{CO}_2$), 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 $p\text{CO}_2$ 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 $p\text{CO}_2$ 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 ($p\text{CO}_2$ 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 $p\text{CO}_2$ measurements were estimated at about ±3 and ±5 ppmv,
196 respectively. The system is ideal for analyses of $p\text{CO}_2$ 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 phaeo-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

isotopic ratio mass spectrometer (IRMS, Micromass IsoPrime), equipped with a manual gas injection port. The $\delta^{13}\text{C}$ -DIC values were corrected for the partitioning of CO_2 between the gaseous (headspace) and water phases in each sample using the algorithm of Miyajima et al. (1995). $\delta^{13}\text{C}$ -DIC measurements were calibrated against certified standard (C2, -8.25 ‰). The reproducibility of the analysis was approximately 0.2‰. The $\delta^{13}\text{C}$ -DIC signatures are reported in ‰ relative to the standard Vienna Pee Dee Belemnite (V-PDB) scale.

2.3 Calculations

2.3.1 Carbonate System

DIC was calculated from the pair $\text{TA}-p\text{CO}_2$, at *in situ* seawater temperature, and salinity, using the CO2calc 1.2.9 program (Robbins et al. 2010). The dissociation constants for carbonic acid were those proposed by Mehrbach et al. (1973) refitted by Dickson and Millero (1987), the borate acidity constant from Lee et al. (2010), the dissociation constant for the HSO_4^- ion from Dickson (1990), and the solubility coefficient of CO_2 from Weiss (1974). The dissociation constants of carbonic acid in natural seawater are available for limited ranges of temperature (0-50 °C), and salinities (0-50) (Chen et al. 2015). The upper values of the salinity ranges measured in Araruama Lagoon (39.0-56.5 in winter; 33.7-65.9 in summer) are above this limit. We extrapolated linearly the values of these constants as a function of salinity, in accordance with findings in other evaporative environments with similar salinity ranges where the dissociation constants were measured (Sass and Ben-Yaakov 1977; Burke and Atkinson 1988).

2.3.2 Air-water CO_2 fluxes

Diffusive CO_2 fluxes at air-water interface (FCO_2) were computed according to:

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

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 difference between $p\text{CO}_2$ measured in the water and in the air. Negative values represent a sink of CO_2 . We used the k -wind parameterization of Jiang et al. (2008; J08) and Van Dam et al. (2019; VD09), which are coefficients specific for estuaries, and the coefficient of Wanninkhof (2014; W14), which is specific for open ocean waters. The gas transfer coefficients were normalized to a Schmidt number of 600 obtained with the three parameterizations and converted to the gas transfer velocity at *in situ* temperature and salinity, following the procedure of Jähne et al. (1987). Fluxes were computed for each sector of Araruama Lagoon (inner, central and outer sectors; Fig. 1), using water $p\text{CO}_2$ values and wind conditions representative for each day of sampling

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

2.3.3 Net Community Production (NCP)

The NCP can be calculated by considering the changes in DIC concentrations from the diel-moored station, and corrected for CaCO_3 precipitation/dissolution and air-sea CO_2 flux, according to the following equation:

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

Considering the fact that we did not observe significant differences of TA concentrations at the diel timescale, the CaCO_3 precipitation/dissolution was assumed to be negligible along this period of sampling. Thus, the NCP was calculated according:

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

where NCP is in $\text{mmol m}^{-2} \text{h}^{-1}$, DIC_1 and DIC_2 are the salinity-normalized concentration of DIC (mmol kg^{-1}) during two consecutive discrete sampling with one hour of interval, p is the seawater density (kg m^{-3}), d is the average depth (m), Δt represents the time interval (hour) and FCO_2 is the carbon dioxide flux ($\text{mmol m}^{-2} \text{h}^{-1}$) across the air-water interface. The vertical density, salinity and temperature stratification were considered negligible in the lagoon (Kjerfve et al. 1996). Values of NCP were hourly-averaged for night-time period (from dusk to dawn; $\text{NCP}_{\text{night-time}}$), and for daytime period (from dawn to dusk; $\text{NCP}_{\text{daytime}}$).

2.3.4 Evaporation carbonate chemistry model

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

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

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

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

The deviation from evaporation path (ΔDIC) is defined as the DIC addition or loss relative to the theoretical DIC concentration during evaporation of seawater:

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

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

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

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

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

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 ($< 3\text{ m}$), 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

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

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

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

Overall, the variabilities for TA, DIC and its stable isotope composition ($\delta^{13}\text{C-DIC}$) showed different spatial trends during the sampling campaigns (Table 1). During winter, TA and DIC concentrations showed lower 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 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 $\delta^{13}\text{C-DIC}$ did not exhibit this clear spatial tendency, with values ranging from 1.29‰ to 1.60‰. During summer, TA 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 $4.11 \pm 1.09\text{‰}$). 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 $\pm 0.2\text{‰}$). 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 mmol C m⁻² d⁻¹ during daytime, considering the different gas transfer velocities. A net
412 time-integrated flux was -1.01 mmol C m⁻² d⁻¹. The NCP was -91.4 mmol C m⁻² d⁻¹ during night-time
413 (heterotrophy), and 278.8 mmol C m⁻² d⁻¹ during daytime (autotrophy), with a net time-integrated value of 93.7
414 mmol C m⁻² d⁻¹.

415

416 4. Discussion

417 4.1 Evidence for CaCO₃ 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

carbonate and organic solid phases including planktonic micro-organisms in the water of the Araruama lagoon may favor the occurrence CaCO_3 at early stages of evaporation path. Our data confirms this process in Araruama Lagoon, which is a shallow carbonate-rich and productive environment containing suspended carbonate grains in the water column as the results of intense sediment resuspension by wind and anthropogenic activities (Kjerfve et al. 1996; Knoppers et al. 1996), creating conditions for the occurrence of high pH and spontaneous CaCO_3 precipitation. Indeed, in addition to carbonate precipitation, the primary productivity is also an important driver of inorganic carbon removal from the water column (see section 4.2). It is important to point out that the high rates of primary production may contribute – together with evaporation – to rise the supersaturation of CaCO_3 , thus locally counter-acting the process of ocean acidification. Indeed, CaCO_3 nucleation from seawater have been associated with plankton blooms at shallow depths and hypersaline environments (Morse and He 1993).

Fig. 8a allows to evaluate the relative contribution of primary production and CaCO_3 precipitation to the deficits of TA and DIC in the brines of Araruama Lagoon. Indeed, the slopes of ΔTA and ΔDIC are consistent with simultaneous photosynthesis and CaCO_3 precipitation.

The carbonate precipitation can be written as:



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



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

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

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

ΔTA is the deviation of TA concentration from the evaporation model, and was assumed to be influenced only by CaCO_3 precipitation.

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

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

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

seasonality can be attributed to four main reasons: i) during summer, the water temperature was about 8°C higher, on average, than winter, meaning that temperature alone contributes to a seasonal $p\text{CO}_2$ increase by 80 ppmv due to water heating. A similar seasonal effect of heating was reported in the Paraíba do Sul River Estuary, located close to Araruama Lagoon (Cotovicz et al., 2020); ii) inner and central sectors presented salinities averaging 63 in summer and 54 in winter, which create an additional theoretical increase of about 45 ppmv of $p\text{CO}_2$ in summer compared to winter due to changes in water solubility (Millero 2007); iii) the levels of CaCO_3 calcification (ΔTA values) are higher in summer, when water salinity and levels of evaporation were highest (Fig. 8), consuming DIC from the water column but releasing CO_2 (Eq. 7); iv) finally, we observed the highest $p\text{CO}_2$ peak (up to 844 ppmv) in the outer sector in summer (Fig.2), when the population of the city of Cabo Frio more than doubles (Bertucci et al. 2016), discharging more domestic sewage in the lagoon (Laut et al. 2016). In summary, half of the winter to summer $p\text{CO}_2$ increase can be attributed to changes in thermodynamics due to increasing temperature and salinities (~125 ppmv). The other half is attributed to the balance between changes in DIC and TA driven mainly by autochthonous processes (primary production, respiration, CaCO_3 calcification) and allochthonous sources (sewage discharge).

The lowest values of $p\text{CO}_2$ (70 ppmv) found in the brines of the lagoon are comparable to those found in eutrophic coastal ecosystems; for example, 22 ppmv in Guanabara Bay, an eutrophic coastal embayment in Brazil dominated by phytoplankton blooms (Cotovicz et al. 2015); 43 ppmv in the Chesapeake Bay (USA) due to high nutrient input stimulating large phytoplankton blooms (Chen et al. 2020). The high primary productivity leads not only to low concentrations of dissolved CO_2 , but also to an increase of pH, carbonate ion (CO_3^{2-}) concentration and the saturation state of CaCO_3 minerals due to the thermodynamic equilibria of carbonate system in seawater (Millero 2007).

The high levels of primary production are also evidenced by the highly positive $\delta^{13}\text{C}$ -DIC signatures in the most shallow and phytoplankton-rich waters (inner sector). Fig. 6 corroborates this finding, as the $\delta^{13}\text{C}$ -DIC signature increases with increasing Chl *a* concentration (Fig. 6c), water temperature (Fig. 6b), and with decreasing $p\text{CO}_2$ (particularly during summer in shallow warm-waters; Fig. 6a). The highest phytoplankton biomass (up to 151 $\mu\text{g L}^{-1}$) occurred in the warmest waters (up to 32.7 °C), associated with the lowest $p\text{CO}_2$ values and the most positive $\delta^{13}\text{C}$ -DIC signatures (5.55 ‰). The positive correlations between $\delta^{13}\text{C}$ -DIC, temperature and phytoplankton biomass reveals a control of isotopic DIC fractionation by phytoplankton blooms (Van Dam et al. 2018; Cotovicz et al. 2019). CaCO_3 precipitation also consumes DIC from the water but in the form of CO_3^{2-} , which is the DIC form that has the heavier stable carbon isotope signature (compared to dissolved CO_2 and

HCO₃⁻) (Zhang et al., 1995), turning the remaining DIC pool depleted in ¹³C relative to the seawater (Isaji et al. 2017). However, the impact of primary production on δ¹³C-DIC is much stronger than that of CaCO₃ precipitation. Indeed, the marine phytoplankton-bicarbonate enrichment factor of stable carbon isotope (typically on the order of -22.1‰ to -35.5‰; Wong and Sackett 1978) is much more pronounced than calcite-bicarbonate and aragonite-bicarbonate enrichment factors (on the order of 1.0‰ and 2.7‰, respectively; Romanek et al. 1992). To our best knowledge, the highest δ¹³C-DIC signature measured in Araruama Lagoon (5.55‰) is the highest value reported in coastal and open waters worldwide.

Fig. 8b shows that the data points of Araruama Lagoon are located between the theoretical vectors representing the processes of primary production/outgassing of CO₂ (when DIC decrease and δ¹³C-DIC increase) and CaCO₃ precipitation (when both DIC and δ¹³C-DIC decrease) (Samanta et al. 2015; Cotovicz et al. 2019). As the large majority of *p*CO₂ values in the lagoon are below the equilibrium with the atmosphere, the effect of CO₂ outgassing on δ¹³C-DIC was considered as negligible (Fig. 2). The highest positive deviation of δ¹³C-DIC signatures from the evaporation conservative model (up to 4‰) was found in phytoplankton-dominated waters, during summer (Fig. 8b). The highest negative deviation of δ¹³C-DIC signatures from mixing (up to -0.3‰) was found in low-phytoplankton waters, during winter, meaning that photosynthesis fractionates much more than CaCO₃ precipitation.

The pattern of diurnal variability of *p*CO₂ values in the lagoon, with higher values during night-time and lower values during daytime, also illustrates the influence of biological activities on short-time CO₂ dynamics (Fig. 7). Strong diel variations of CO₂ concentrations have been reported in productive estuarine systems worldwide as the results of net ecosystem metabolism (Yates et al. 2007; Zhang et al. 2013; Cotovicz et al. 2015). The biological activities modify not only the daily *p*CO₂ variations in the water, but also the other carbonate chemistry parameters (Table 3). The diurnal variations of DIC concentrations correspond to a net community production (NCP) of 34.2 molC m⁻² yr⁻¹ in Araruama Lagoon in summer. This autotrophic metabolism inside the Araruama lagoon generates a diurnal variability of CO₂ fluxes, and the sink behavior. In the 90's (1993-1995), Knoppers et al. (1996) have investigated the metabolism in Araruama Lagoon and found higher rates of benthic net primary production (benthic chamber method, between 5.6 and 12.3 molC m⁻² yr⁻¹) compared to planktonic primary production (¹⁴C-method, 0.6 molC m⁻² yr⁻¹), and net heterotrophy (community respiration between 12.8 and 23.9 molC m⁻² yr⁻¹). Within this same period (1989-1990), but in a "low salinity year", Moreira-Turcq (2000) documented higher rates of planktonic primary production (¹⁴C method, averaging 13.5 mol C m⁻² yr⁻¹) due to this atypical condition of lower salinities. Later, applying the LOICZ (Land Ocean Interaction in the

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

High oversaturated conditions of $p\text{CO}_2$ (maximum of 844 ppmv) were found only in the channel that connects the bay to the ocean (the most urbanized region) associated with urban wastewater discharge. A recent study found the presence of high levels of organic matter from anthropic origin in this region (Laut et al. 2020). Mineralization of organic matter in polluted areas close to sewage networks leads to heterotrophy and CO_2 outgassing (Cotovicz et al. 2015; 2021). The sampling in summer was carried out during a period of high rainfall, which favored CO_2 and organic carbon inputs from urban areas.

4.3 Apparent decoupling between CO_2 and O_2 dynamics in hypersaline and productive waters

The relationship between excess of DIC (E-DIC) and apparent oxygen utilization (AOU) illustrates the specific metabolic characteristics of Araruama Lagoon (Fig. 9). E-DIC and AOU were calculated following Abril et al. (2003) and Benson and Krause (1984), respectively. In general, values of E-DIC and AOU were negative, consistent with net autotrophy in the lagoon. However, some E-DIC and AOU values were positive during nighttime. E-DIC and AOU values in the Araruama Lagoon presented strong deviations below the 1:1 line that represents the quotient between CO_2 and O_2 during primary production and community respiration (Fig. 9). The deviations were particularly important when values of $p\text{CO}_2$ are very low in the water (below 300 ppmv; Fig. 9), associate with large disequilibria of CO_2 concentrations between water and atmosphere. Indeed, the cycling of these gases in hypersaline and high-productive waters are not linearly coupled. It is well established that air-water exchange is faster for O_2 than for CO_2 , 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 ($< 5.5 \text{ m s}^{-1}$), with high oversaturation for O₂ and undersaturation for $p\text{CO}_2$. Overnight, the wind speed
609 increased to velocities $> 14 \text{ m s}^{-1}$, and fast gas-exchange occurred, causing DO concentrations to decrease from
610 oversaturation to values close to atmosphere equilibrium; however, the values of $p\text{CO}_2$ 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 $p\text{CO}_2$ 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_{600}
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 $38.6 \text{ mol C m}^{-2} \text{ yr}^{-1}$, 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 $p\text{CO}_2$ 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

well-below the atmospheric values, generating a net annual sink of CO₂ as the result of net autotrophic metabolism and overwhelming the *p*CO₂ increase driven by CaCO₃ precipitation. Oversaturated conditions of *p*CO₂ were restricted to the region closest to sewage outfall (Itajuru Channel), and during night-time. The thermodynamic effects driven by water heating and increasing salinities were also significant and partially explained the higher values of *p*CO₂ in summer compared to winter. Overall, the brines of Araruama are dominated by phytoplankton blooms with heavier δ¹³C-DIC signatures (due to isotopic fractionation by primary production), higher values of pH and higher buffering capacity compared to seawater. The relationship between E-DIC and AOU presented values well-below the 1:1 line (quotient between photosynthesis and respiration), suggesting that air-water exchanges of CO₂ and O₂ are apparently decoupled due to solubility differences and high carbonate buffering capacity in these warm, hypersaline, and phytoplankton-dominated waters.

This study suggests that eutrophication locally amplifies the production of organic matter with important CO₂ uptake, counter-acting the potential effects of ocean acidification by increasing the pH. Eutrophication and negative water balance (hypersalinity) are modifying the nutrient cycling, plant productivity and carbon budgets in the lagoon. The aridity is increasing worldwide as the result of global warming, whereas at same time the inputs of anthropogenic-derived nutrients have increased in many coastal regions. Therefore, the specific results 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**

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).

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	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 (mmolC 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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Figure Captions

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

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 represent the winter, and the green dots represent the summer. The dashed blue and green lines represent the theoretical evaporation path. The red line (graph d) represents the average values of atmospheric $p\text{CO}_2$.

Fig.3 Maps showing the boat trajectories (black lines) during sampling for winter (a) and summer (f) periods. 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 (f) vs. latitude, for winter. Below the map on the right side, it is presented the distributions of temperature (g), salinity (h), $p\text{CO}_2$ (i) and O_2 (j) vs. latitude, for summer. The yellow, black, and red dots represent the inner, central, and outer sectors, respectively. The black line represents the value of atmospheric $p\text{CO}_2$ and O_2 .

Fig. 4 Variation in the partial pressure of CO_2 ($p\text{CO}_2$, ppmv) as a function of dissolved oxygen saturation level (DO%) in the brines of Araruama Lagoon. The grey circles represent the sampling at day 18-07-2017, which occurred before storm (under low wind speed; $< 5.5 \text{ m s}^{-1}$). The light blue circles represent the sampling after storm (during storm the wind speed overpassed 14 m s^{-1}).

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

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 squares represent the sampling in winter, and green circles represent the sampling in summer.

Fig. 7 Time series at the mooring station showing the diurnal variation of DO concentrations and $p\text{CO}_2$ values. The shaded area symbolizes the period of night-time measurement. The horizontal black line represents the atmospheric $p\text{CO}_2$ and O_2 .

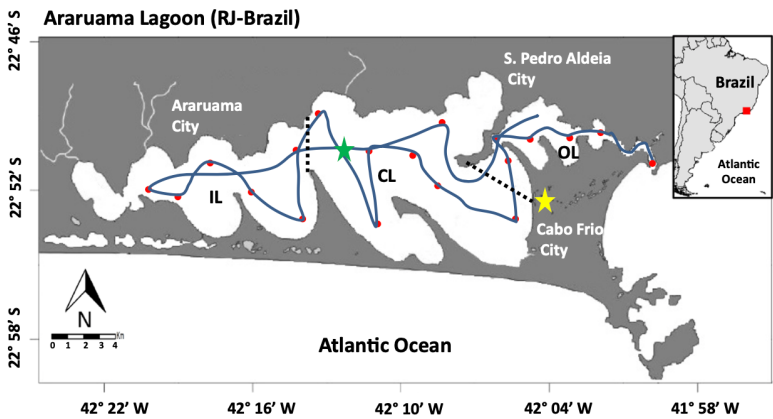
Fig. 8 The graph a) represents the deviations from evaporative model of TA (ΔTA) as a function of DIC (ΔDIC) in waters of Araruama Lagoon. The solid black lines indicate the direction and slope of the main processes affecting TA and DIC concentrations. The graph b) is plot of $\Delta\delta^{13}\text{C}$ -DIC vs. $\Delta\text{DIC}/\text{DIC}_{\text{Ocean}}$ in the Araruama Lagoon. The drawn vectors "photosynthesis" and " CO_2 efflux" represent the slopes of these specific processes affecting the DIC and $\delta^{13}\text{C}$ -DIC distributions, when DIC concentrations decrease and $\delta^{13}\text{C}$ -DIC values increase. The drawn vector " CaCO_3 precipitation" represents the slope of this specific process, when DIC concentrations and $\delta^{13}\text{C}$ -DIC values decrease. The drawn vector " CO_2 influx" represents the slope of this specific process, when DIC concentrations increase and $\delta^{13}\text{C}$ -DIC values decrease. Blue dots are the winter stations, and green dots are the summer stations. The origin of these graphs (represented by the black "x") indicate no deviation from the 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.

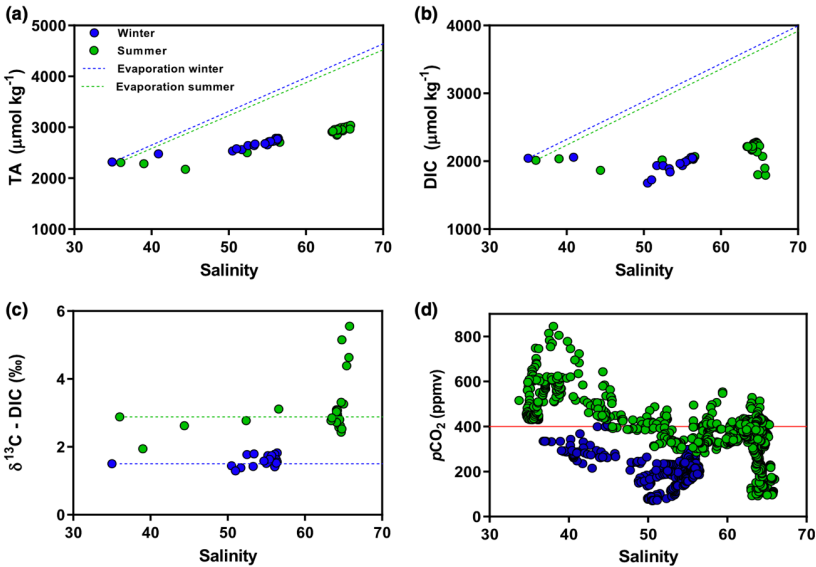
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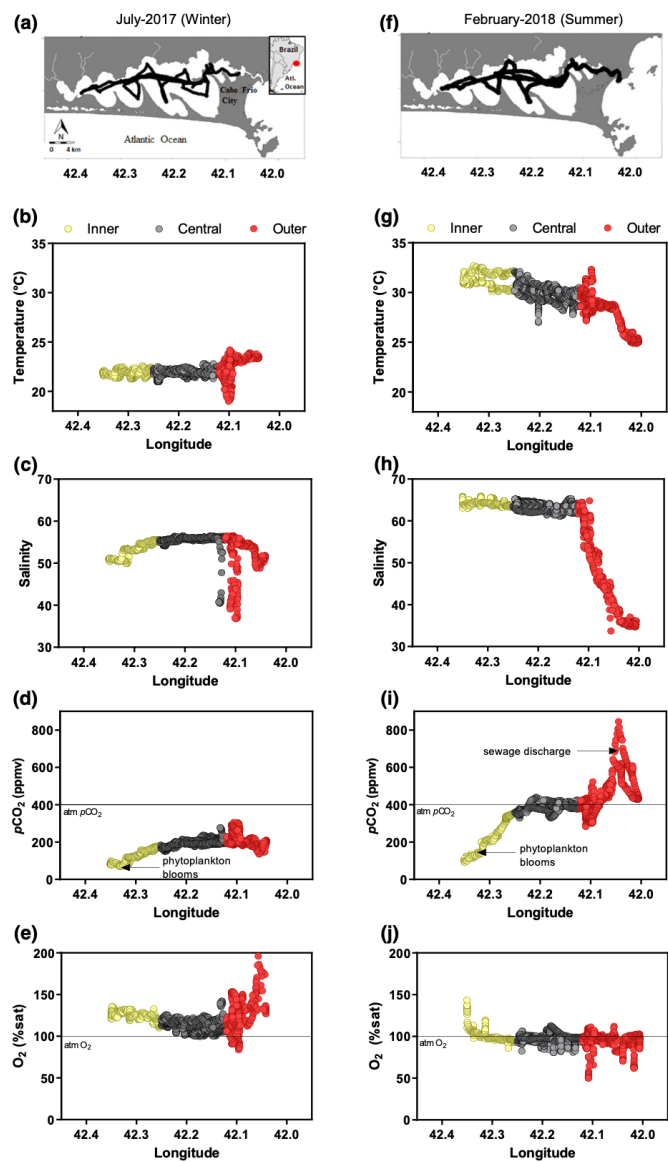
Fig. 1



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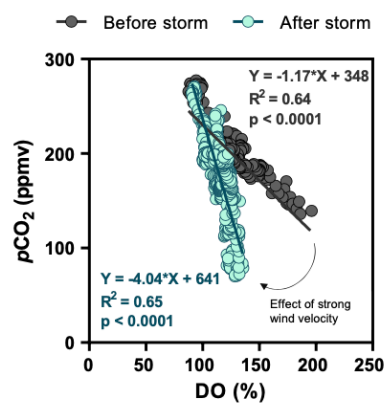


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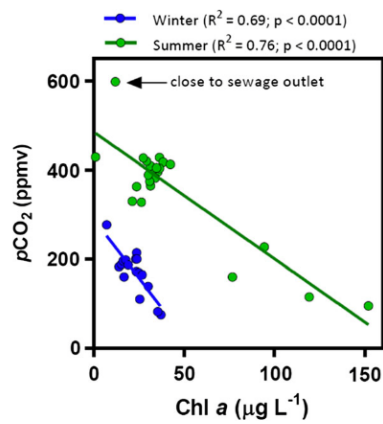
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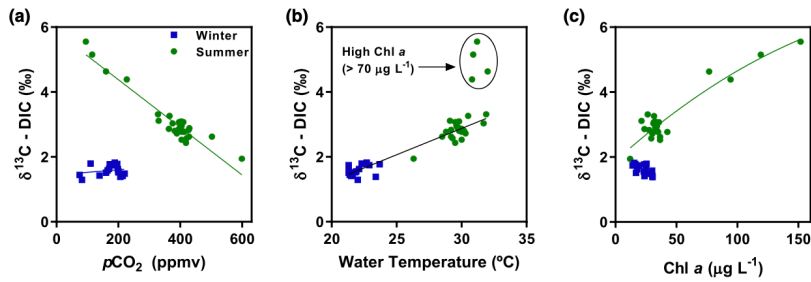
1135 Fig. 4



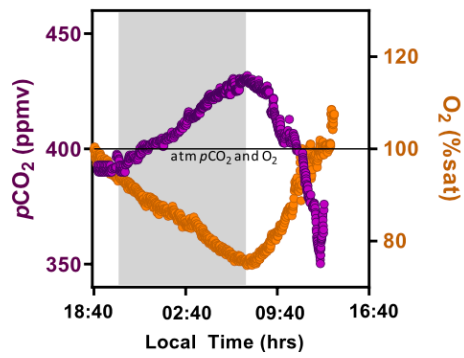
1139 Fig. 5



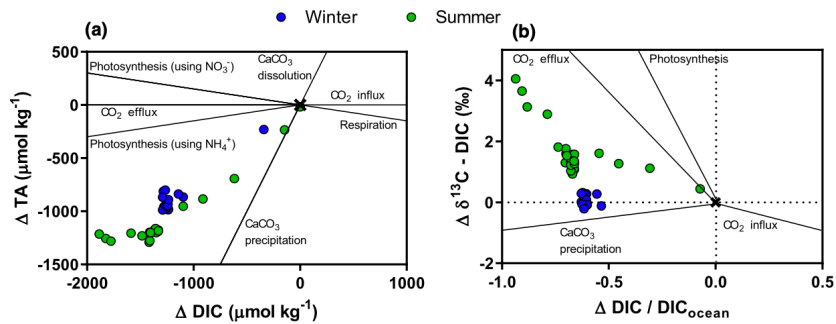
1146 Fig. 6



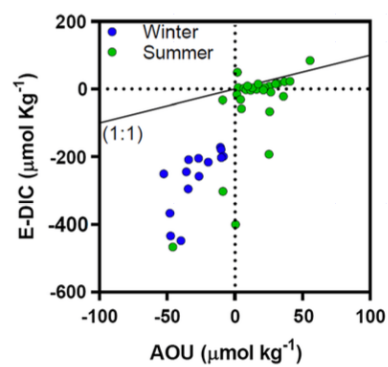
1149 Fig. 7



1152 Fig. 8



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1157 Fig. 9



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