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► **To cite this version:**

Thaís Erbas, Aguinaldo Marques, Gwenaël Abril. A CO₂ sink in a tropical coastal lagoon impacted by cultural eutrophication and upwelling. *Estuarine, Coastal and Shelf Science*, In press, 10.1016/j.ecss.2021.107633 . hal-03412147

HAL Id: hal-03412147

<https://hal.science/hal-03412147v1>

Submitted on 2 Nov 2021

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1 **A CO₂ sink in a tropical coastal lagoon impacted by cultural eutrophication and upwelling**

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11 Submitted to Estuarine Coastal and Shelf Science, revised version.

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17 **Abstract**

18 Tropical coastal lagoons are recognized as very productive ecosystems. However, very little is
19 known on the direction and magnitude of their CO₂ exchange with the atmosphere. We report on
20 air-water CO₂ fluxes and carbon concentrations in a tropical shallow lagoon impacted by cultural
21 eutrophication. During two contrasting field surveys, the first in Nov. 2019 during dry conditions
22 and the second in Feb. 2020 during wet summer condition and intrusion of coastal upwelling waters
23 inside the lagoon. At both seasons, spatial *in situ* monitoring of temperature, salinity and partial
24 pressure of CO₂ (pCO₂) reveal the presence of undersaturated pCO₂ values (between 60 and 300
25 ppmv), uptake of atmospheric CO₂ (between 0.9 and 9.2 mmol m⁻² h⁻¹) inside the lagoon, at
26 salinities between 10 and 32. Temporal monitoring data at the mouth of the lagoon throughout tidal
27 cycles revealed the entrance of cold South Atlantic Central Waters (SACW) from the Cabo Frio's
28 upwelling during flood tides in Feb. 2020 but not in Nov. 2019. The cold SACW with temperatures
29 down to 16°C were supersaturated in CO₂ (pCO₂ about 520 ppmv) and a CO₂ source to the
30 atmosphere (between 0.2 and 1.4 mmol m⁻² h⁻¹). During mixing of this SACW in the most marine
31 compartment of the lagoon, the biological CO₂ uptake and enhanced autotrophy overcame the effect
32 of degassing SACW waters by heating. For both cruises, a consistent landward trend consisted in a
33 decrease in pCO₂ and dissolved inorganic carbon (DIC) mirrored by an increase of dissolved
34 organic carbon (DOC) (between 4.6 and 19.8 mg L⁻¹), particulate organic carbon (POC) (between
35 3.3 and 12.3 mg L⁻¹), and chlorophyll *a* (Chl *a*) (between 7.6 and 217 µg L⁻¹). POC, DOC and Chl *a*
36 and the POC:Chl *a* ratio suggest that, organic carbon in the lagoon is a mixture of phytoplankton
37 biomass produced in the lagoon, domestic wastewater loaded from multiple point sources and
38 pulsed inputs from small rivers. Our study in the Saquarema lagoon confirms recent works in
39 other densely populated tropical coastal ecosystems, revealing that eutrophication enhances the
40 autotrophy of shallow tropical lagoons, making them act as efficient factories for atmospheric CO₂
41 absorption and organic carbon storage in sediments and export to the ocean.

42

43 **Keywords**

44 partial pressure of CO₂, autotrophy, carbon dynamics, tropical shallow lagoon

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49 **1 Introduction**

50 The growing concern about the impact of anthropogenic carbon dioxide (CO₂) emissions has
51 intensified research of organic and inorganic carbon fluxes through and within ecosystems. The
52 coastal environments, require particularly precise quantification as they are highly dynamic
53 components of the global carbon cycle and budget (Cai 2011; Borges and Abril 2011; Bauer et al.
54 2013). Although the global estuarine area is modest, these ecosystems have the capacity to emit a
55 quantity of CO₂ that substantially offsets the of CO₂ sink on the continental shelves (Borges 2005;
56 Borges et al. 2005; Cai et al. 2006; Chen and Borges 2009). However, owing to their strong intrinsic
57 heterogeneity, coastal ecosystems are still poorly documented in terms of CO₂ exchange, especially
58 in the tropics. Despite their modest surface area, compared to the ocean, coastal environments such
59 as estuaries, mangroves, lagoons and bays, play a fundamental role in marine primary production,
60 remineralization and sedimentation of organic carbon, and global air-sea CO₂ exchange (Wollast
61 1991; Sabine et al. 2004; Borges 2005; Cai 2011). In most estuaries, *i.e.* in semi-enclosed water bodies
62 where freshwater mixes with seawater (Pritchard 1967), total ecosystem respiration generally exceeds
63 gross primary production. As a result, estuaries are generally net heterotrophic and sources of
64 atmospheric CO₂ (Gattuso et al. 1998; Borges and Abril 2011). This conclusion was reached on the
65 basis of intensive works in estuaries with geographically well-defined salinity gradients. These
66 “funnel-type estuaries” receive significant inputs of terrestrial organic matter from the rivers that fuel
67 heterotrophic respiration, while primary production is limited by the availability of light due to the
68 high turbidity, and despite a large availability of nutrients (Borges and Abril 2011). In general, low
69 salinity regions are highly heterotrophic, oxygen depleted and strong CO₂ sources (Frankignoulle et
70 al. 1998), whereas at high salinity, estuarine and marine phytoplankton can grow, reduce CO₂
71 degassing flux and, in some cases, generate uptake of atmospheric CO₂ (Körtzinger 2003; Jiang et al.
72 2008; Borges and Abril 2011). Some recent works in tropical regions have reported different patterns
73 of CO₂ fluxes, with strong sinks of atmospheric CO₂ induced by eutrophication and/or by
74 thermodynamic mixing of poorly buffered freshwaters with seawater (Cotovicz et al. 2015; 2020;
75 2021; Abril et al. 2021). Estuaries, lagoons and tropical bays have their specific characteristics, and
76 will also present specific properties with respect of carbon cycling and CO₂ fluxes, very different
77 from those from temperate and boreal estuaries.

78

79 Tropical coastal lagoons are particularly under-sampled for CO₂ fluxes (Chen et al. 2013), and only
80 a couple of studies document the carbon cycle, carbonate chemistry and CO₂ fluxes, in these types of
81 estuaries (Koné et al. 2008; Ávila-López et al. 2016). Tropical coastal lagoons are characterized by

82 shallow depths, important intrusion of ocean water with tides, variable inputs of freshwater, and high
83 productivity, both planktonic and benthic (Knoppers and Kjerfve 1999). In the most developing
84 countries, the eutrophication is generated by anthropogenic nutrient inputs from untreated wastewater
85 from sewage and industry (Nixon 1995). An example is lagoons in the tropics that suffer from
86 anthropogenic pressure, and particularly from cultural eutrophication induced by sewage loads
87 (Knoppers et al. 1999; Cerda et al. 2013). Eutrophication can create conditions for strong CO₂ uptake,
88 as in densely populated tropical coastal embayments (Cotovicz et al. 2015; Kubo et al. 2017). In
89 addition to biological activity, drastic changes in temperature occur in tropical lagoons, induced by
90 the intrusion of cold marine waters and strong surface heating (Chen et al. 2013; Cotovicz et al. 2020).
91 These thermal variations have the potential to generate important changes in the distributions of water
92 partial pressure of CO₂ (pCO₂) and CO₂ fluxes at the air-sea interface (Ávila-López et al. 2016; Ribas
93 Ribas et al. 2011; Cotovicz et al. 2020). The aim of this paper is to present original data of air-water
94 CO₂ fluxes and inorganic and organic carbon distribution in a small shallow lagoon in the region of
95 Rio de Janeiro in Brazil, impacted by eutrophication and seasonally influenced by cold marine waters
96 coming from the upwelling of Cabo Frio (Castelão and Barth 2006). Our study includes high spatial
97 and temporal resolution data of pCO₂ and the carbonate system, as well as organic carbon and
98 chlorophyll concentrations, during two very contrasting periods with and without the intrusion of
99 upwelling cold waters in the lagoon. The objectives are, first, to describe spatially and quantitatively
100 the CO₂ exchanges between the lagoon and the atmosphere; second, to relate the air-lagoon CO₂
101 fluxes to the variations of other inorganic and organic carbon species, as well as the lateral exchanges
102 with the ocean; third, to discuss on the light our work as well as other recent studies, how
103 eutrophication is becoming a predominant driver of the carbon cycle and air-sea CO₂ exchange in
104 densely populated tropical coastlines.

105

106 **2 Materials and Methods**

107 **2.1 Study Area**

108 The Saquarema Lagoon system is located on the southeast coast of Brazil, in the city of Saquarema
109 at 73km of Rio de Janeiro city (Fig. 1), with a population estimated of 89 thousands of inhabitants
110 (IBGE 2020). The lagoon has a total surface area of 21.2 km², with four different compartments called
111 Mombaça (12.6 km²), Jardim (2 km²), Boqueirão (0.6 km²) and Fora (6 km²) and is permanently
112 connected to the sea by a sand bar (Knoppers and Kjerfve 1999). This channel has been artificially
113 opened to minimize impacts of pollution (located in Fora sub-lagoon). The mean depth of the lagoon
114 is 1.2m and the drainage basin total area is 215 km² (Oliveira 2013). Many small rivers discharge

115 freshwater in the lagoon. Among these rivers, the Mato Grosso River that ends in the Urussanga
116 Lagoon (Fig. 1) is the biggest, however the value of the total freshwater discharge by all the small
117 rivers is unknown (Alves 2003). The tides in the region are microtidal and semidiurnal, averaging 0.5
118 m and 1.5 m in amplitude during neap tide and spring conditions, respectively (Alves 2003). In spring
119 and summer, the Fora Lagoon receives cold and nutrient rich waters of the Cabo Frio coastal
120 upwelling of South Atlantic Central Water (SACW, $T < 18.0^{\circ}\text{C}$ and $S\ 34.4 - 36.0$). The region has a
121 wet tropical climate, subject to orographic rains that occur most often from October to March. The
122 prevailing winds are from the East and Northeast or winds from the south quadrant during cold fronts.
123 The residence time of water in the system is 56 to 58 days in the Mombaça compartment, 48 to 56
124 days in the Jardim compartment, 20 to 48 days in the Boqueirão compartment and from 0 to 20 days
125 in the Fora compartment, which has a connection to the sea (Alves 2003). The Saquarema lagoon
126 system is undergoing a process of cultural eutrophication, which has been intensified by the
127 accelerated urbanization that occurred since the 1970s and a lack of effective wastewater treatment
128 (Knoppers et al. 1999).

129

130 **2.2. Sampling Strategy**

131 Two sampling campaigns were carried out during two contrasted climatic situations in Nov. 2019 and
132 Feb. 2020. Both sampling corresponded to spring tide conditions (amplitudes respectively 1m and
133 1.1m). However, Nov. 2019 sampling occurred during the intrusion of a cold front coupled to an
134 extratropical cyclone that enhance humidity in the region, causing strong S-SW winds and intensives
135 rains during the preceding and sampling days. In opposite, Feb. 2020 sampling occurred during well
136 established summer conditions, with high solar radiation and the persistence of strong northeast NE
137 winds, generating intense upwelling of South Atlantic central waters (Castelão and Barth 2006;
138 Coelho-Souza et al. 2012). During the two campaigns, the sampling strategies consisted in spatial
139 surveys at daytime covering the major area of the lagoon using a small boat, with continuous
140 measurements and discrete sampling (Fig. 2). Continuous measurements included the pCO_2 , salinity,
141 temperature, and position were measured *in situ* at a frequency of 1 min. Discrete sampling was
142 performed along the continuous trails at 16 (in Nov. 2019) to 20 (in Feb. 2020) stations (Fig. 1).
143 Another sampling strategy used was the temporal sampling at a fixed point in the channel at the mouth
144 of the lagoon (Fig. 1) for 13 hours (one tidal cycle) in Nov. 2019 and for 25 hours (two tidal cycles)
145 in February 2020. During this temporal sampling we used the aforementioned continuous
146 measurements and hourly discrete sampling. Surface water samples were collected at approximately
147 20 cm depth in clean polypropylene 2 L bottles and then kept cooled in the dark for filtration within

148 the following five hours. Three rivers including the major contributor Mato Grosso River (Fig. 1)
149 were reached by car the same day as the temporal monitoring at the mouth.

150

151 **2.3. Analytical procedures**

152 **2.3.1. Continuous Measurements**

153 For continuous measurements, water was pumped from ~20cm below the water surface at a flow of
154 about 5 L min⁻¹. About 2 L min⁻¹ to an equilibrator system and the rest to a flow-through customized
155 acrylic chamber containing an YSI 6600 multiparameter probe to measure temperature and salinity.
156 The salinity probe was calibrated with IAPSO standard seawater and deionized water. The marble
157 equilibrator (Frankignoulle et al. 2001; Abril et al. 2006; Cotovicz et al. 2016) consisted in an acrylic
158 tube filled with glass marbles where water flows from the top, and a closed air circuit with a flux of
159 about (1 L min⁻¹), flowing in the opposite direction from the bottom to the top. The air is dried with
160 drierite and pumped to a non-dispersive infrared (NDIR) gas analyser (LICOR LI- 820). Before and
161 after each sampling campaigns, the NDIR was calibrated using gas standards with air pCO₂ values of
162 410, 1007 and 5035 ppmv (White Martins Certified Material, RJ, Brazil). For calibration of the gas
163 analyser, fresh soda lime was used to set the zero and the standard at 1007 ppmv to set the span. The
164 air standards at 410 and 5035 ppmv were used to verify the linearity of the response. The accuracy of
165 the pCO₂ measurements is estimated at ±5 ppmv. The partial pressure of atmospheric CO₂ was
166 measured in dry air twice a day, at the start and the end of the continuous measurements.

167

168 **2.3.2 Discrete parameters**

169 Water samples were filtrated on a glass filtration system through pre-combusted GF/F glass fiber
170 filters (porosity 0.7 µm). One filter was weighed prior to filtration and was then dried for suspended
171 particulate matter (SPM) and particulate organic carbon (POC) determination. SPM was determined
172 gravimetrically on the dried pre-weighed filters. POC content were determined after removing
173 carbonates by adding some drops of HCl 2 N on the filters (Etcheber et al. 2007). The POC analysis
174 was carried on a LECO C-S 125 total carbon analyser based on direct combustion in an induction
175 furnace and infrared absorption determination of the CO₂ produced. Another filter was frozen at -20
176 °C for further chlorophyll a (Chl *a*) analysis. After extraction in 90% acetone, the Chl *a* was quantified
177 spectrophotometrically before and after acidification of the samples, with formulations and
178 corrections proposed by Strickland and Parsons (1972). Part of the filtrated water was stored in 50
179 mL, acidified with 100 µL of ultrapure H₃PO₄ and stored in the dark until dissolved organic carbon
180 (DOC) analysis. The DOC analysis was performed with a high temperature catalytic oxidation
181 (HTCO) method using a Shimadzu TOC 500 analyser (Abril et al. 2002). Another part of the filtrate

182 was stored also in the dark in 150 mL polyethylene flasks for total alkalinity (TA) analysis. TA was
183 titrated with an automated titration system (Metler Toledo model T50) with normalized 0.1 HCl on
184 duplicate 50 mL aliquots and the equivalence point was determined using the linearization of the Gran
185 (1952) function between pH 4 and pH 3. TA measurements were compared to certified reference
186 material (CRM, provided by A. G. Dickson from Scripps Institution of Oceanography) and the
187 accuracy was of $\pm 5 \mu\text{mol kg}^{-1}$. River samples were conditioned the same way to analyse POC, DOC
188 during both cruises and also Chl *a* in Feb. 2020.

189

190 **2.4. Carbonate system and CO₂ fluxes calculations**

191 We used the CO₂sys program (Pierrot et al. 2006), version 2.1, to calculate all the chemical species
192 of the carbonate system. The DIC concentrations were calculated from the measured pCO₂ and TA,
193 using the carbonic acid constants sets proposed by Mehrbach et al. (1973) refitted by Dickson and
194 Millero (1987), the borate acidity constant from Lee et al. (2010), and the CO₂ solubility coefficient
195 of Weiss (1974). Considering the analytical accuracies for temperature (0.05°C), TA ($\pm 5 \mu\text{mol kg}^{-1}$)
196 and pCO₂ (5ppmv) we estimate the error on DIC calculation at $\pm 5 \mu\text{mol kg}^{-1}$. The water-atmosphere
197 CO₂ flux (FCO₂) was calculated using the equation, expressed in terms of partial pressure:

$$198 \quad \text{FCO}_2 = k\alpha\Delta p\text{CO}_2 \quad (1)$$

199 where *k* is the gas transfer velocity of CO₂ (m d⁻¹ or cm h⁻¹), *α* is the solubility coefficient of CO₂ (mol
200 m⁻³ atm⁻¹), and $\Delta p\text{CO}_2$ is the air–water gradient of pCO₂ (in atm).
201 The atmospheric pCO₂ data used was 410 ppmv as measured in air during the campaigns. The gas
202 transfer velocity *k* was calculated from the gas transfer velocity normalized to a Schmidt number of
203 (Jähne et al. 1987):

$$204 \quad k = k_{600} (600/\text{Sc})^n \quad (2)$$

205 where *k*₆₀₀ is the normalized gas transfer velocity, Sc is the Schmidt number of a given gas at a given
206 temperature (Wanninkhof 1992), and *n* equals 2/3 as in lakes environments (Jähne et al. 1987). To
207 calculate *k*₆₀₀, in order to account for the uncertainty on this parameter, we used three different
208 parameterizations respectively noted W92, RC01, and A09: the one of Wanninkhof (1992)
209 representative for the global ocean, and the ones of Raymond and Cole (2001) and Abril et al. (2009),
210 representative for estuarine systems. The three equations are defined as a function of wind speed at
211 10 meters (U10), and the A09 equation also considers the estuarine surface area and water current
212 velocity. To determine *k*₆₀₀ we used U10 by the Instituto Nacional de Meteorologia (INMET) at the
213 Sampaio Correia automatic weather station, located ~10 km from Saquarema lagoon (Fig. 1). In the
214 A09 model, we used an average water current set to 20 cm s⁻¹ for the Saquarema lagoon and the
215 contribution on *k*₆₀₀ was less than 8%. The fluxes were computed with the three parameterizations of

216 k_{600} . However, none of these parameterizations adapt perfectly to hydrographic and morphological
217 features of the Saquarema lagoon; the W92 equation is valid for the open ocean and probably
218 underestimates the k_{600} in the lagoon, whereas the RC01 and A09 equations are valid for funnel-
219 shaped macrotidal estuaries, and probably overestimates the k_{600} . Therefore, we present here the CO_2
220 fluxes calculated with the three different parameterizations, and the fluxes calculated as the average
221 of the three.

222

223 **2.5. Statistical analysis**

224

225 A Kolmogorov-Smirnov test was performed to check the normality of the data and the Levene's test
226 the homoscedasticity of the variances. All statistical analyses were based on $\alpha = 0.05$. When the data
227 showed a normal distribution with equal variances, we used the analysis of variance, ANOVA to
228 examine the seasonal and spatial variation in the parameters. When the data did not follow a normal
229 distribution, we used the Kruskal-Wallis test and, to examine the daytime variation in the parameters,
230 we used the Mann-Whitney test. Correlation analysis between variables was performed with the
231 Spearman rank coefficient. We used the PAST 4.0 program to perform statistical tests.

232

233 **3 Results**

234 **3.1 Spatial and temporal variations of carbon species and ancillary parameters**

235

236 The two sampling periods were quite contrasted in terms of meteorological and hydrological
237 conditions. The data were compiled according to spatial and temporal samplings and the two sampling
238 periods are presented separately. Table 1 summarizes the average concentrations, and respective
239 standard deviations and ranges, of relevant parameters for this study (T, S, pCO_2 , SPM, DOC, POC,
240 Chl *a*, TA and DIC). The most outstanding feature of the two campaigns was the presence of higher
241 salinity and colder waters entering the lagoon during the high tide in Feb. 2020 (Figs. 3 and 4).
242 Upwelling waters with temperatures down to 16 °C and salinities up to 34.47 were observed at the
243 mouth of the Saquarema lagoon in Feb. 2020 while in Nov. 2019 maximum salinity was 30.2 and
244 minimum temperature was 23.5 °C (Figs. 3 and 5; Table 1). A second important difference between
245 seasons and particularly the spatial surveys was the warmer temperature inside the lagoon in summer
246 in Feb. 2020 (29.56 ± 1.14 °C) compared to spring in Nov. 2019 (24.17 ± 0.77 °C) (Figs. 2 and 3).

247 In the Saquarema lagoon the salinity ranged from 14.3 to 34.6 and was strongly correlated with
248 carbonate chemistry parameters, including TA ($r = 0.960$; Fig. 4 I and 4 J) and DIC ($r = 0.925$; Fig.

249 4 K and 4 L). TA decreased from the mouth toward the Mombaça compartment where salinity was
250 the lowest. In salinity 14.3, the TA and DIC concentrations were, for the two cruises, 1466 and 1091
251 $\mu\text{mol kg}^{-1}$, respectively. For marine sampled in Feb. 2019 (salinity 34.6) the TA and DIC
252 concentration were respectively 2376 and 2211 $\mu\text{mol kg}^{-1}$ (Fig. 6). Furthermore, both TA and DIC
253 averages were significantly different between the two sampling periods (Mann-Whitney, $p < 0.0001$).
254 During both campaigns, pCO_2 showed undersaturated conditions inside the lagoon with a mean of
255 156 ± 82 ppmv during the spatial survey (Figs. 2 and 3). Surface water pCO_2 decreased with salinity
256 inside the lagoon (Fig. 3). However, in Feb. 2020, the cold marine waters sampled during flood tides
257 at the outlet of the lagoon presented oversaturated pCO_2 values with a mean value of 497 ± 40 ppmv
258 (salinities between 33 and 35). For both spatial and temporal surveys during the two campaigns, DOC,
259 POC and Chl *a* increased inside the lagoon, contrarily to salinity, DIC, TA and pCO_2 (Fig. 4). The
260 minimum concentration of Chl *a* was $2.7 \mu\text{g L}^{-1}$ at the mouth of the lagoon at high tide and salinity
261 35 (Fig. 4G and 4H). In the most inner part of the lagoon, in salinities below 15, the concentration of
262 the Chl *a* reached $217 \mu\text{g L}^{-1}$ (Fig. 4G and 4H). DOC concentrations showed a minimum of 1.0 mg
263 L^{-1} at high salinity (~ 35) and a maximum of the 19.8 mg L^{-1} values at salinities of ~ 17 (Fig. 4A and
264 4B). POC varied between 0.4 mg L^{-1} in seawater entering the lagoon and 12.3 mg L^{-1} in the Mombaça
265 compartment inside the lagoon (Fig. 4C and 4D).

266

267 **3.2. Spatial variation of pCO_2 in surface waters and CO_2 exchanges at the air-water interface**

268 Inside the lagoon, during both spatial sampling in Nov. 2019 and Feb. 2020, water was undersaturated
269 in CO_2 with respect to the atmosphere and strong spatial gradients occurred between the inner lagoon
270 and its mouth. The lagoon was a sink of CO_2 during the measurements at daytime. For the whole
271 lagoon, an average pCO_2 of 177 ± 73 ppmv was observed in Nov. 2019 and 126 ± 52 ppmv in Feb.
272 2020. Undersaturated pCO_2 values occurred in the interior of the lagoon with the lowest value down
273 to ~ 60 ppmv at low salinities. In Fora lagoon close to the outlet to the sea, we observed higher, but
274 still undersaturated pCO_2 values (301 ppmv in Nov. 2019 and 250 ppmv in Feb. 2020). There was
275 significant spatial differences between the measured pCO_2 in the Fora and Mombaça/Jardim
276 compartments (Kruskall-Wallis, $p < 0.001$; Table S1). However, we found no significant difference
277 between the Mombaça and Jardim compartments (Kruskall-Wallis, $p > 0.05$). The salinity was
278 significantly different between the three compartments in the lagoon (ANOVA, $p < 0.001$). In contrast,
279 temperature was not significantly different between compartments (Kruskall-Wallis, $p > 0.05$). There
280 was also significant seasonal variability in salinity and temperature (Table S2): inside the lagoon
281 water was significantly warmer in Feb. 2020 compared to Nov. 2019 (ANOVA, $p > 0.05$) at the outlet

282 of the lagoon, the seawater at high tide was cooler and more saline in Feb. 2020 compared to Nov.
283 2019 (ANOVA, $p > 0.05$).

284

285 Wind speed was in general low during the samplings, on average between $2.03 \pm 0.9 \text{ m s}^{-1}$ and 2.83
286 $\pm 0.6 \text{ m s}^{-1}$ in Nov. of 2019. In Feb. of 2020, the wind speed average was $2.8 \pm 1.0 \text{ m s}^{-1}$ in at day time
287 (Table 2). As expected, the k_{600} values calculated with the equation of Abril et al. (2009)
288 representative for macro-tidal estuaries were higher than those calculated with the relationships of
289 Raymond and Cole (2001) representative for a large variety of estuaries, and of Wanninkhof (1992)
290 representative for the open ocean. Inside the Saquarema lagoon was a sink of atmospheric CO_2 during
291 the two sampled period. Averaged calculated CO_2 fluxes with the three k_{600} parameterizations varied
292 between $-2.6 \pm 4.8 \text{ mmol m}^{-2} \text{ h}^{-1}$ in Nov. 2019 and $-5.6 \pm 2.4 \text{ mmol m}^{-2} \text{ h}^{-1}$ in Feb. 2020.

293

294 **3.3. Tidal variation of pCO_2 in surface waters and CO_2 exchanges at the air-water interface**

295 During the temporal monitoring experiments at the mouth of the lagoon significant variation of
296 salinity, temperature and pCO_2 occurred in summer (Feb. 2020) (Fig. 5; Table 1) but not in spring in
297 Nov. 2019 (Table 1). Maximum water pCO_2 of 524 ppmv was observed at high tide (Table 1, Fig. 3),
298 with corresponding temperature of $16.3 \text{ }^\circ\text{C}$ and a salinity of 34.4. At the same sampling point but at
299 low tide, water pCO_2 was 194 ppmv for temperature of $28.16 \text{ }^\circ\text{C}$ and a salinity of 28.36, showing
300 simultaneous warming and mixing with brackish waters, and biological uptake of CO_2 . The pCO_2
301 was not significantly different between day and night ($p > 0.05$ Mann–Whitney test), but it was
302 between ebb and flood tides. Calculated CO_2 fluxes were $-2.7 \pm 0.5 \text{ mmol m}^{-2} \text{ h}^{-1}$ in Nov. 2019. In
303 Feb. 2020 the CO_2 fluxes average varied between $-4.6 \pm 1.8 \text{ mmol m}^{-2} \text{ h}^{-1}$ in the ebb tide and $+0.8 \pm$
304 $2.1 \text{ mmol m}^{-2} \text{ h}^{-1}$ at the mouth of the lagoon during the intrusion of upwelling waters with flood tides.

305

306

307 **4. Discussion**

308

309 **4.1. Mixing between lagoon and ocean waters as drivers of air-sea CO_2 fluxes**

310 The contrasting climatic conditions between the two surveys were reflected by the distribution of the
311 salinity gradient in the lagoon, as well as the carbonate species, particularly pCO_2 . In Nov. 2019, we

312 could not observe an entrance of pure oceanic water during the 12h measurements. Highest salinity
313 at the mouth of the lagoon at high tide was only 30.2 (Table 1) at that season, when, in addition, the
314 Cabo Frio Upwelling is not active (Coelho-Souza et al. 2012). The monitoring in Nov. 2019 occurred
315 during particularly bad meteorological conditions, with strong S-SW winds the day before sampling.
316 Such conditions generally promote a large entrance of shelf water in the lagoon (Oliveira 2013);
317 however, this was not clear during our monitoring, even at high tide (see Table 1). Because salinity
318 remained lower than pure seawater salinity, this water contained a significant fraction of CO₂-depleted
319 water from the lagoon and pCO₂ values remained undersaturated as those inside the lagoon, at about
320 300 ppmv and salinities up to 31.9 (Fig. 3; Table 1). In contrast, in Feb. 2020, the marine end-member
321 was very marked, with colder and more saline waters, supersaturated in CO₂. At that season the Cabo
322 Frio upwelling was at maximum intensity (Coelho-Souza et al. 2012), and throughout the entire flood
323 tides, the cold SACW with a pCO₂ of 520 ppmv entered the lagoon (Fig. 5). The well-defined
324 temperature and pCO₂ gradients between the lagoon and the ocean in Feb. 2020 allow a detailed
325 quantitative analysis of carbonate thermodynamics during the mixing of two end-members: the first
326 one is located inside the lagoon at salinity 10 and the second one is the SACW sampled during flood
327 tides at the mouth of the lagoon at salinity ~ 35.

328
329 Inside the lagoon, our continuous measurements in Feb. 2020 went down to salinity 10 (Fig. 3),
330 whereas the less saline discrete sample for TA analysis had a salinity of 14.3 (Fig. 4). We could
331 extrapolate the strong linear correlation between TA and salinity (Fig. 4L) to estimate TA at salinity
332 10. In the salinity range 0 to 10 that occurs at the outlet of several small rivers, changes were too
333 abrupt to allow precise surface water sampling, in addition to being very shallow, making it
334 impossible to travel with the boat. According to previous works on the hydrology of the Saquarema
335 lagoon (Alves 2013), the mixing between lagoon and seawater during the field campaigns occurred
336 at two different timescale: the mixing between salinity 35 and 29 occurs in the Fora compartment on
337 a short timescale, related to the tide; the mixing between salinity 29 and 10 occurs all the
338 compartments until the Mombaça compartment (Fig. 1) on much a longer time scale (56-58 days;
339 Alves 2013). From the TA and pCO₂ values in these two end-members, we calculate the DIC values
340 and we established the equations of the conservative mixing lines for temperature, TA and DIC as a
341 function of salinity as follows:

342
343

344

$$TA_{cons}(S) = TA(10) + (S - 10) \cdot \frac{TA(35) - TA(10)}{35 - 10}$$

$$345 \quad DIC_{cons}(S) = DIC(10) + (S - 10) \cdot \frac{DIC(35) - DIC(10)}{35 - 10}$$

$$346 \quad T_{cons}(S) = T(10) + (S - 10) \cdot \frac{T(35) - T(10)}{35 - 10}$$

347

348 Where $TA_{cons}(S)$, $DIC_{conc}(S)$ and $T_{cons}(T)$ are respectively the TA, DIC and T at salinity S resulting
 349 from the conservative mixing of the two end-members. Then, from these three parameters, we
 350 calculated the theoretical $pCO_2(S)$ resulting from conservative mixing of the two end-members by
 351 solving the carbonate system for each 0.5 salinity increments between 10 and 35, (Jiang et al. 2008;
 352 Joesoef et al. 2015; Cotovicz et al. 2020; Abril et al. 2021). This led to a first theoretical conservative
 353 pCO_2 mixing curve (Fig. 6). We also evaluate the theoretical impact of water heating on pCO_2 . To do
 354 this, we performed the same pCO_2 calculation for each 0.5 salinity interval, using, this time, the *in*
 355 *situ* measured temperature, $TA_{cons}(S)$ and $DIC_{cons}(S)$. Finally, we have binned our measured data for
 356 0.5 salinity intervals between 10 and 35 to allow a quantitative comparison between the observed
 357 pCO_2 and the two modelled pCO_2 .

358

359 Results of this analysis are shown in Fig. 6 and reveal that in Feb. 2020, when the cold SACW
 360 supersaturated in CO_2 starts mixing with the lagoon waters at the tidal time scale in the Fora
 361 compartment, it simultaneously undergoes important heating that should potentially increase the
 362 pCO_2 until a maximum value of 580ppmv at salinity 29. At salinities lower than 29, the mixing with
 363 undersaturated lagoon water would make the pCO_2 decrease until salinity 10. The pCO_2 field
 364 measurements do not follow the trend predicted by the mixing model, revealing the occurrence of
 365 strong biological uptake of CO_2 within the lagoon. At the tidal timescale, from salinity 35 to 29,
 366 although heating should in theory increase pCO_2 by about 60ppmv, the observed pCO_2 rapidly drops
 367 from 520 to 190 ppmv. Between salinities 29 and 10, on a timescale longer than a month, the pCO_2
 368 continues to decrease remaining below the theoretical conservative mixing line (Fig. 6), within the
 369 range 80-200ppmv, and similar to the situation in Nov. 2019 (Fig. 3C). The mixing model in Feb.
 370 2020 indicates that in the Fora compartment, the biological uptake of CO_2 by the planktonic
 371 autotrophic community was efficient enough to absorb the excess CO_2 carried by upwelling waters,
 372 plus the one resulting from the heating of the oceanic cold waters, making the lagoon to act as a net
 373 CO_2 sink. This situation in Saquarema lagoon during the intrusion of upwelling waters, contrasts with
 374 the one in a Baja California coastal lagoon in Mexico, where CO_2 outgassing prevails particularly
 375 during the periods of upwelling (Ribas-Ribas et al. 2011; Ávila-López et al. 2016). In the Aby and
 376 Tendo lagoons in Ivory Coast, a CO_2 sink has also been reported, although it was related to a

377 thermohaline stratification of the water column (Koné et al. 2008). Despite its specific hydrological
378 settings, the Saquarema Lagoon acts as a CO₂ sink similarly to the neighbouring Guanabara Bay and
379 Araruama hypersaline lagoon (Cotovicz et al. 2016; 2021), with phytoplankton productivity acting as
380 the major driver on CO₂ air-sea fluxes.

381
382 Another interesting fact revealed by our study is the relative stability between the two surveys of the
383 low pCO₂ values in the most confined waters of the lagoon, in the Jardim and Mombaça compartments
384 where water residence time is longer (Table 1; Fig. 2). Seasonally, the average daytime pCO₂ inside
385 the lagoon was significantly lower (Mann-Whitney, $p > 0,001$; Table S2) in Feb. 2020 (126 ± 52 ppmv)
386 than in Nov. 2019 (177 ± 73 ppmv) (Fig. 2; Table 1). During the spatial surveys, waters were about
387 5°C cooler in Nov. 2019 compared to Feb. 2020, which corresponds to a theoretical thermal pCO₂
388 increase of about 7 ppmv, instead of the observed decrease of about 51 ppmv. In Feb. 2020 the Chl *a*
389 concentrations were significantly (Mann-Whitney, $p < 0,001$) higher than in Nov. 2019 (Fig. 4),
390 revealing that the modest seasonal pCO₂ changes inside the lagoon was associated to enhanced
391 phytoplankton production in Feb. 2020. Feb. 2020 was characterized by denser phytoplankton
392 blooms, apparently adapted to rapidly absorb large quantities of CO₂ diffusing from the atmosphere
393 as well as all the dissolved CO₂ brought with the SACW at that season. In contrast to the average
394 values, the lowest pCO₂ values were identical at both seasons at 60ppmv (Fig. 3; Table 1). These
395 pCO₂ minima were observed in the 15-25 salinity range around midday, before thermal winds start
396 to blow. This apparent constant threshold value for CO₂ consumption in the lagoon waters may be
397 due to a combination of various factors including surface heating and transient stratification, nutrient
398 and/or CO₂ limitation in the photic layer, photo-inhibition of phytoplankton species, including
399 eukaryotes and cyanobacteria (Caraco and Miller 1998; Philips et al. 2002), as well as higher re-
400 aeration rates at very low pCO₂.

401

402 **4.2. Links between inorganic and organic carbon**

403

404 In addition to the clear spatial and temporal negative correlations between pCO₂ and phytoplanktonic
405 biomass (Fig. 7), the links between inorganic and organic carbon is a crucial point in order to explain
406 the drivers of the CO₂ sinks in the Saquarema lagoon. During the 25h cycle at the mouth of the lagoon
407 in Feb. 2020, the POC and DOC expressed as mg L⁻¹, the POC% and the SPM concentrations varied
408 all together (Fig. 5). Lagoon waters flowing to the ocean during the ebb tides had much greater
409 concentrations of DOC, POC and SPM and their SPM were enriched in POC, compared to the SACW
410 entering during the flood tides. Consequently, the lagoon behaved as a source of POC and DOC for

411 the offshore marine waters. When considering the entire dataset (spatial and temporal monitoring), a
412 negative correlation is observed between DIC and Total Organic Carbon (TOC) (Fig. 9). The SACW
413 have the highest pCO₂, highest DIC and lower TOC concentrations, whereas the less saline samples
414 inside the Monbaça and Jardim compartments have lower pCO₂ and DIC and higher TOC. However,
415 the slope -2.3 ± 0.1 of the correlation in fig. 9 reveals that the landward DIC decrease is only about
416 half of the landward TOC increase. At the outlet of the lagoon in Feb. 2020, the TOC concentrations
417 during ebb tides were 11.8 ± 4.6 mgC L⁻¹ higher than those during flood tides, whereas the DIC
418 concentrations during ebb tide were only 5.1 ± 2.7 mgC L⁻¹ lower than those during flood tide. The
419 exchanges between the lagoon and the ocean can be estimated thanks to the average tidal prism in the
420 lagoon, estimated from a modelling work to $1.4 \cdot 10^6$ m³ on average (Oliveira 2013). Using this tidal
421 prism and the differences in carbon concentration between ebb and flood in Feb. 2020 (Fig. 5), we
422 calculate exports from the lagoon of 21 tC d⁻¹ of DOC and 14 tC d⁻¹ of POC and an import of only 15
423 tC d⁻¹ of DIC. The penetration of atmospheric CO₂ through the air-lagoon interface (Table 2) provided
424 an additional 1.4 tC d⁻¹ of DIC in Feb. 2020 (0.8 tC d⁻¹ of DIC in Nov. 2019). Although they are very
425 rough estimates, these fluxes suggest first, that the carbon flux at the air-lagoon interface is one order
426 of magnitude lower than the tidal exchange of DIC with the ocean, and second, that the lagoon exports
427 more than twice as much TOC than it imports DIC. Consequently, if phytoplankton converts DIC to
428 TOC with a 1:1 ratio, an additional source of TOC would be necessary to balance the carbon budget
429 of the lagoon.

430

431 Several processes can potentially contribute to this disequilibrium between inorganic and organic
432 carbon along the salinity gradient: (1) dilution of DIC and import of TOC with freshwater; (2)
433 phytoplankton production that consumes DIC and produces POC and eventually DOC; (3) gas
434 exchange and invasion of atmospheric CO₂ that will contribute to DIC; (4) other sources of POC and
435 DOC occurring in the most confined waters of the lagoon, where waters are CO₂-depleted. Estuarine
436 DOC and POC can have three origins: terrestrial, marine and estuarine primary production (Abril et
437 al. 2002; Bauer et al. 2013). In the case of the Saquarema lagoon, wastewater carried by small rivers
438 and flowing from multiple point sources all around the lagoon, is also an additional potential source
439 of POC and DOC (Carmouze et al. 1991).

440

441 The impact of mixing of the lagoon waters with freshwater is more difficult to evaluate quantitatively
442 because our river data are partial due to logistical constraints, because sampling in many more small
443 rivers as well as hydrological data would be necessary, and because the distribution of the carbon
444 species in the 0-10 salinity range was inaccessible. The significant seasonal increase in POC and DOC

445 concentrations in the rivers and inside the lagoon (Fig. 4) as well as the lower salinity in the lagoon
446 (Table 1) in Feb. 2020, suggest that rivers could deliver more POC and DOC during the rainy summer.
447 However, this season is also warmer and more productive for phytoplankton as attested by the higher
448 Chl *a* concentration and the lower pCO₂. At the river stations, DOC and POC concentrations were
449 higher than in seawater, but lower than in the Mombaça inner compartment of the lagoon at salinity
450 between 15 and 20 where Chl *a* concentrations are maximal at both seasons (Fig. 4), suggesting also
451 the presence of phytoplankton-derived POC and DOC. POC:Chl *a* ratios indicate very different
452 contributions of phytoplankton biomass to the POC in the three sampled rivers, in the inner lagoon
453 and at the mouth, and in the SACW (Fig. 8). In all the Feb. 2020 samples, and half of the Nov. 2019
454 samples in the Mombaça and Jardim compartments, as well as in the SACW samples, this ratio was
455 within the range of 15 and 140 which corresponds to a predominant contribution of living
456 phytoplankton to the POC (Cloern 1996; Abril et al. 2002; Sathyendranath et al. 2009; Cloern et al.
457 2014). In river samples, the ratio was much higher (Fig 8), which confirms a terrestrial and/or
458 domestic origin of POC (Abril et al. 2002).

459

460 Concerning DOC, the facts that concentrations inside the lagoon were highest in summer and were
461 higher than in the river and ocean end-members at both seasons (Fig. 4) indicate an internal source
462 that can be multiple sewage point sources and phytoplankton exudation or lysis. On one occasion,
463 high DOC was also observed in the most polluted river with a maximum value in February, when
464 runoff was apparently higher than in November. The distributions of DOC along the salinity gradient
465 indicate a net production inside or input into the lagoon at both seasons, as well as a close to
466 conservative dilution in the 15-35 salinity range during the mixing of lagoon waters with seawater
467 (Fig. 4). One interesting observation comes from the positive correlation between DOC and Chl *a* and
468 the negative correlation between DOC and pCO₂ (Fig. 7). The same observation was made in the most
469 eutrophic waters of the Guanabara Bay (Cotovicz et al. 2018) suggests that part of DOC comes from
470 the exudation or lysis of microalgae, a common process in coastal waters (Myklestad 2000; Augusti
471 and Duarte 2013). It is interesting to note that both in the Guanabara Bay and in the Saquarema lagoon,
472 DOC concentrations consistently increased to values above 10 mg L⁻¹, when pCO₂ was below 200
473 ppmv (Fig. 7; Cotovicz et al. 2018), thus, when CO₂ limitation of phytoplankton can occur, together
474 with a strong depletion of inorganic nutrients in the surface water (Lui et al. 2017). This could be due
475 to changes in the composition and physiological state of the planktonic microbial community induced
476 by a combination between physicochemical, biological, climatic and hydrographic factors, in these
477 two urbanized coastal environments.

478

479 **4.3. Impact of eutrophication on the carbon cycle of the Saquarema Lagoon**

480

481 Cultural eutrophication of coastal ecosystems is a secular trend in many developing countries, and
482 particularly in the densely populated state of Rio de Janeiro in Brazil (Knoppers and Kjerfve 1999).
483 Eutrophication is due to massive anthropogenic inputs of organic (mainly domestic) and, to a lesser
484 extent, inorganic (agricultural or industrial) nutrients that enrich estuarine waters and sediments with
485 bioavailable nitrogen and phosphorus (Rabalais et al. 2009). In addition, in the case of shallow
486 lagoons, the frequent resuspension of sediments caused by tidal exchange and winds, becomes an
487 important internal source of recycled nutrients, making the lagoons and bays in the region extremely
488 productive (Carmouze et al. 1991). Because of the transparency of their waters, tropical lagoons are
489 recognized as naturally autotrophic ecosystems and eutrophication will enhance this ecosystem
490 property, making them more productive (Carmouze et al. 1991; Knoppers and Kjerfve 1999). Nutrient
491 accumulation in coastal bays and lagoons leads to massive algal blooms, to a general increase of water
492 turbidity, a reduction of light at the bottom, and the progressive loss of native submerged aquatic
493 vegetation and biofilms (Carmouze and Vasconcelos 1992). Our study reveals a CO₂ sink that can be
494 in part explained by eutrophication that enhances autotrophy more than heterotrophy, as reported in
495 diverse coastal ecosystems (*e.g.* Gypens et al. 2009), and as attested by the very high Chl *a*
496 concentrations (Fig. 4GH; Table 1).

497

498 In the Saquarema lagoon, inorganic nutrients concentrations remain relatively stable since the 90's
499 with dissolved inorganic nitrogen (DIN) around 5-20 $\mu\text{mol L}^{-1}$ and dissolved inorganic phosphorus
500 around 0,5-1 $\mu\text{mol L}^{-1}$ (Carmouze and Vasconcelos 1992; Carloni et al. 2010). However, inorganic
501 nutrients concentrations are not relevant indices of eutrophication because most of the nitrogen and
502 phosphorus are present in the organic form, which is rarely analysed. Indeed, if the POC concentration
503 is 8 mg L^{-1} (Table 1), and if we assume a C/N Redfield ratio of 10, then the particulate organic nitrogen
504 concentration would be 70 mg L^{-1} , that is 2.5-10 times the DIN concentration. Some previous works
505 in Saquarema have documented Chl *a*, POC and DOC concentrations in the 80's and 90's in the
506 Jardim and Fora compartments (Pereira 1991; Table 3). Although these data are occasional and not
507 fully representative of spatial and seasonal variations in the lagoon, they suggest a decadal increase
508 of these three parameters, as well as a decrease of the POC:Chl *a* ratio, and thus, an increase of the
509 stock of phytoplankton-derived organic carbon with time, particularly in the Jardim compartment
510 (Table 3). Indeed, the most inner compartments of the lagoon have longer water residence times,
511 shallower depths, making them more adapted to the long-term accumulation of nutrients in waters
512 and sediments and enhanced planktonic primary production. In present days, the conditions that create

513 the CO₂ sink in the inner compartments of the Saquarema lagoon appear relatively stable between the
514 two campaigns (see 4.1).

515

516 If we compare with other densely populated tropical and sub-tropical regions, the inner part of the
517 Saquarema lagoon was a sink of atmospheric CO₂ ranging from -5.6 to -2.6 mmol C m⁻² h⁻¹ (Table
518 2), similar to those reported the Guanabara Bay (-7.7 to -3.53 mmol C m⁻² h⁻¹; Cotovicz et al. 2015)
519 and higher than those reported in the Araruama hypersaline lagoon (-0.2 to -0.6 mmol C m⁻² h⁻¹;
520 Cotovicz et al. 2021), in the Aby Lagoon in Ivory Coast (-0.3 mmol C m⁻² h⁻¹; Koné et al. 2009) and
521 in Tokyo Bay (-0.4 mmol C m⁻² h⁻¹; Kubo et al. 2017). The mechanism of carbon cycling in coastal
522 environments impacted by urban pollution has been discussed by Kubo et al. (2017) as the balance
523 between the more active respiration due to the presence of sewage derived organic matter and the
524 more active photosynthesis driven by nutrient accumulation. This leads to a border between nearshore
525 waters close to the sewage outlet that act as CO₂ sources because degradation of organic matter locally
526 predominates and offshore waters that act as CO₂ sink because phytoplankton production overwhelms
527 the CO₂ budget. Cultural eutrophication apparently tends to shift this border toward the landside
528 (Kubo et al. 2017). In Tokyo Bay, implementation of sewage treatments since the 70's have reduced
529 the loads of biodegradable organic carbon but not the loads of nutrients; as a result, the respiration
530 was reduced but the phytoplanktonic production was favoured, and the Tokyo Bay acts as a strong
531 CO₂ sink (Kubo and Kanda 2020). In Guanabara and Tokyo bays, and in Araruama lagoon, the
532 sewage loads are concentrated to well identified regions that emit CO₂ to the atmosphere but represent
533 a limited surface area (Cotovicz et al. 2015; 2021; Kubo et al. 2017). In the Saquarema lagoon, the
534 CO₂ supersaturation of water was linked to the intrusion of SACW in Feb. 2020 that acted as a weak
535 source of CO₂, of 0.2 ± 0.3 mmol C m⁻² h⁻¹, for kW92, well within the range reported in the continental
536 shelf of the subtropical Atlantic Ocean (ranging from 0.01 to 0.4 mmol C m⁻² h⁻¹, Ito et al. 2016).
537 CO₂ supersaturation did not occur in the inner compartments where domestic carbon and nutrient are
538 carried by rivers but also from multiple point sources all around the lagoon (Carloni et al. 2010). This
539 suggests that, even if degradation of organic matter derived from sewage is probably occurring, in the
540 environmental conditions of the lagoon, it cannot outcompete with the high phytoplanktonic
541 productivity that creates the CO₂ sink. In addition, the TOC export to the ocean was larger than the
542 DIC import (see 4.2) which suggests that this flux included organic carbon originating from sewage.

543

544 Despite the large differences in water depth and residence time, eutrophication has turned the
545 Saquarema lagoon to a CO₂ sink, similarly to the Guanabara Bay (Cotovicz et al. 2015), the Tokyo
546 Bay (Kubo et al. 2017), and the hypersaline Araruama Lagoon. If the CO₂ fluxes were very similar

547 in all these systems, the fluxes of POC and DOC are probably very different. One important issue to
548 be investigated in the next future is the fate of the organic C present in these environments: the POC
549 and DOC that is not remineralized is partially exported to the ocean, and partially stored in the
550 sediments. In Guanabara Bay, Cotovicz et al (2015) have emphasized that the air-water CO₂ flux was
551 quantitatively similar to the recent organic C burial in the sediments (Carreira et al. 2002). No carbon
552 burial data are available in the Saquarema lagoon. However, recent works in the neighbouring Itaipu
553 lagoon indicate an important increase of organic matter storage in the sediment linked to
554 eutrophication (Cerdeira et al. 2016). More hydrological and sedimentological data would be necessary
555 in order to quantitatively compare the CO₂ sink with carbon burial and export. In the sea, this organic
556 material may undergo partial degradation and only more refractory compounds would persist longer
557 times in oceanic water masses.

558

559 **5. Conclusions**

560

561 The Saquarema lagoon behaved as CO₂ sink during the two sampling surveys. Although the sampling
562 periods are probably not fully representative of the temporal variation, the similar values of pCO₂,
563 POC, DOC and Chl *a* reveal a relative stability of the autotrophic character of the inner compartments
564 of the lagoon. Important contrasts were observed at the mouth of the lagoon between seasons, with
565 the entrance of SACW in Feb. 2020. The response of the lagoon carbonate system to the intrusion of
566 the cold SACW supersaturated in CO₂ was dominated by biological uptake, pCO₂ showing a strong
567 non-conservative behaviour during the mixing of seawater with lagoon waters. The negative
568 correlation for both surveys between Chl *a*, POC, DOC on the one hand and pCO₂ and DIC on the
569 other hand reveal that phytoplankton inside the lagoon was very efficient at converting inorganic
570 carbon to both particulate and dissolved organic carbon. Our analysis also suggests the TOC exported
571 to the ocean apparently come partly from sewage sources and partly from phytoplankton production
572 inside the lagoon. Our study confirms that intense eutrophication of tropical semi-enclosed littoral
573 ecosystems, including bays and lagoons, turns these surface waters to act as CO₂ sinks and
574 accumulators and exporters of organic carbon.

575

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579

580 **Acknowledgments**

581 This research was funded by the Fundo Brasileiro para a Biodiversidade (FUNBIO) project:
582 “*Mecanismos Reguladores da Produção Pesqueira nos Sistemas Lagunares do Leste Fluminense:*
583 *estado atual e cenários futuros*” and the France-Brazil International Research Project VELITROP
584 (*Vulnérabilité des Ecosystèmes Littoraux Tropicaux face à l’Eutrophisation*) funded by the French
585 National Centre for Scientific Research (CNRS-INEE). We thank Leandro Alves, Mauricio Lorenzo
586 Cerda Lema, Francisco Fernando Lamego Simões Filho, and Tailan Moretti Mattos from the
587 Aquatic Biogeochemistry Lab. at the Universidade Federal Fluminense for their valuable help in the
588 field.

589

590 **References**

591

- 592 Abril, G., Libardoni, B.G., Brandini, N., Cotovicz, L.C.Jr, Medeiros, P.R.P., Cavalcante, G.H.,
593 Knoppers, B.A., 2021. Thermodynamic uptake of atmospheric CO₂ in the oligotrophic and
594 semiarid São Francisco estuary (NE Brazil). *Marine Chemistry* 233: 103983.
- 595 Abril, G., Nogueira, E., Etcheber, H., Cabeçadas, G., Lemaire, E., Brogueira, M., 2002. Behaviour of
596 organic carbon in nine contrasting European estuaries. *Estuar Coast Shelf Sci* 54:241–262.
- 597 Abril G., Commarieu M.V., Sottolichio, A., Bretel, P., Guérin, F., 2009. Turbidity limits gas exchange
598 in a large macrotidal estuary. *Estuar. Coast. Shelf Sci.* 83, 342–348.
- 599 Abril, G., Richard, S., Guérin, F., 2006. In-situ measurements of dissolved gases (CH₄ and CO₂) in a
600 wide range of concentrations in a tropical reservoir using an equilibrator, *Sci. Total Environ*,
601 354, 246–251.
- 602 Augusti, S. and Duarte, C.M., 2013. Phytoplankton lysis predicts dissolved organic carbon release in
603 marine plankton communities. *Biogeosciences* 10:1259–1264. [https://doi.org/ 10.5194/bg-10-](https://doi.org/10.5194/bg-10-1259-2013)
604 [1259-2013](https://doi.org/10.5194/bg-10-1259-2013)
- 605 Ávila-López, M.C., Hernández-Ayón, J.M., Camacho-Ibar, V.F., Bermúdez, A.F., Mejía-Trejo, A.
606 Pacheco-Ruiz, I., 2016. Air–Water CO₂ Fluxes and Net Ecosystem Production Changes in a
607 Baja California Coastal Lagoon During the Anomalous North Pacific Warm Condition.
608 *Estuaries and Coasts* doi.10.1007/s12237-016-0178-x
- 609 Alves, A.R., 2003. Modelagem numérica como ferramenta de gestão ambiental. Aplicação ao sistema
610 lagunar de Saquarema, RJ. Dissertação de Mestrado, Universidade Federal Fluminense, 97 p.

611 Bauer, J.E., Cai, W.-J., Raymond, P., Bianchi, T.S., Hopkinson, C.S., Regnier, P.G., 2013. The
612 changing carbon cycle of the coastal ocean. *Nature* 504, 61–70.
613 <https://doi.org/10.1038/nature12857>.

614 Borges, A.V. and Abril, G., 2011. Carbon dioxide and methane dynamics in estuaries, in: *Treatise on*
615 *Estuarine and Coastal Science*, edited by: Eric, W. and Donald, M., Academic Press,
616 Amsterdam, 119–161

617 Borges, A.V., 2005. Do We Have Enough Pieces of the Jigsaw to Integrate CO₂ Fluxes in the Coastal
618 Ocean? *Estuaries*, v. 28, n. 1, p. 3–27.

619 Borges, A.V., Delille, B., Frankignoulle, M., 2005. Budgeting sinks and sources of CO₂ in the coastal
620 ocean: Diversity of ecosystems counts. *Geophysical Research Letters*, v. 32, n. 14, GL023053.

621 Cai, W.-J., Dai, M., Wang, Y., 2006. Air-sea exchange of carbon dioxide in ocean margins: a province-
622 based synthesis. *Geophys. Res. Lett.* 33:L12603.

623 Cai, W.J., 2011. Estuarine and coastal ocean carbon paradox: CO₂ sinks or sites of terrestrial carbon
624 incineration? *Ann. Rev. Mar. Sci.* 3, 123–145.

625 Caraco, N., and Miller, R., 1998. Direct and indirect effects of CO₂ on competition between
626 cyanobacteria and eukaryotic phytoplankton, *Canadian Journal of Fisheries and Aquatic*
627 *Sciences*, n. 55, pp. 54-62.

628 Carloni, F.B.B.A., 2010. Mudanças na qualidade da água de uma laguna do leste fluminense, geradas
629 pela abertura permanente de conexão com o mar. *Geochimica Brasiliensis*. V. 24, n.
630 *Geochimica Brasiliensis* 1, p. 29 – 40.

631 Carmouze, J.P. and Vasconcelos, P., 1992. The eutrophication of the Lagoon of Saquarema, Brazil.
632 *Science of Total Environment*, v.Supplement, p.851-859.

633 Carmouze, J., Knoppers, B.A., Vasconcelos, P.A., 1991. Metabolism of Saquarema Lagoon, Brazil.
634 *Biogeochemistry*, v. 2.

635 Carreira, R.S., Wagener, A.L.R., Readman, J.W., Fileman, T.W., Macko, S.A., Veiga, Á., 2002.
636 Changes in the sedimentary organic carbon pool of a fertilized tropical estuary, Guanabara Bay,
637 Brazil: an elemental, isotopic and molecular marker approach, *Mar. Chem.*, 79(3-4), 207–227,
638 [doi:10.1016/S0304-4203\(02\)00065-8](https://doi.org/10.1016/S0304-4203(02)00065-8).

639 Castelão, R.M. and Barth, J.A., 2006. Upwelling around Cabo Frio, Brazil: The importance of wind
640 stress curl. *Geophys. Res. Lett* 33(3), doi.org/10.1029/2005GL025182.

641 Cerda, M., Barboza, C.D.N., Carvalho, C.N.S.; Jandre, K.A., Marques Jr, A.N., 2013. Nutrient
642 budgets in the Piratininga-Itaipu lagoon system (southeastern Brazil): effects of sea-exchange
643 management. *Proceedings of the 3rd Brazilian Congress of Marine Biology*. *Lat. Am. J. Aquat.*
644 *Res.*, 41(2): 226-238.

645 Cerda, M., Scali, C., Valde, J., Macario, K.D., Anjos, R.M., Vogel, V., Lamego, F., Nepomuceno, A.,
646 2016. Coupling fallout ^{210}Pb and stable isotopes ($\delta^{13}\text{C}$, $\delta^{15}\text{N}$) for catchment urbanization
647 reconstruction in southeastern coastal zone of Brazil. *J. Radioanal. Nucl. Chem.* 310, 1021–
648 1032.

649 Chen, C.T.A. and Borges, A.V., 2009. Reconciling opposing views on carbon cycling in the coastal
650 ocean: Continental shelves as sinks and near-shore ecosystems as sources of atmospheric CO_2 ,
651 *Deep-Sea Res.*, v. 56, p. 578–590.

652 Chen, C.-T.A., Huang, T.-H., Chen, Y.-C., Bai, Y., He, X., Kang, Y., 2013. Air–sea exchanges of
653 CO_2 in the world’s coastal seas. *Biogeosciences* 10, 6509–6544. [https://doi.org/10.5194/bg-10-](https://doi.org/10.5194/bg-10-6509-2013)
654 [6509-2013](https://doi.org/10.5194/bg-10-6509-2013).

655 Cloern, J.E., Foster, S.Q., Kleckner, A.E., 2014. Phytoplankton primary production in the world’s
656 estuarine-coastal ecosystems. *Biogeosciences*, v. 11, p. 2477–2501.

657 Cloern, J.E., 1996. Phytoplankton bloom dynamics in coastal ecosystems: a review with some general
658 lessons from sustained investigation of San Francisco Bay, California. *Rev. Geophys.* 2, 127–
659 168. <https://doi.org/10.1029/96RG00986>.

660 Coelho-Souza, S.A., López, M.S., Guimarães, J.R.D., Coutinho, R., Candella, R.N., 2012.
661 Biophysical interactions in the Cabo Frio upwelling system, Southeastern Brazil. *Brazilian J.*
662 *Oceanogr.* 60, 353–365. <https://doi.org/10.1590/S1679-87592012000300008>.

663 Cotovicz, Jr. L.C., Knoppers, B.A., Régis, C.R.; Tremmel, D., Costa-Santos, S., Abril, G., 2021.
664 Eutrophication overcoming carbonate precipitation in a tropical hypersaline coastal lagoon
665 acting as a CO_2 sink (Araruama Lagoon, SE Brazil). *Biogeochemistry* [doi.org/10.1007/s10533-](https://doi.org/10.1007/s10533-021-00842-3)
666 [021-00842-3](https://doi.org/10.1007/s10533-021-00842-3).

667 Cotovicz Jr, L., Vidal, L., Rezende, C., Bernardes, M., Knoppers, B., Sobrinho, R., Cardoso, R.,
668 Muniz, M., dos Anjos, R., Biehler, A., Abril, G., 2020. Sources and sinks of CO_2 in the delta of
669 the Paraíba do Sul River (Southeastern Brazil) modulated by carbonate thermodynamics, gas
670 exchange and ecosystem metabolism during estuarine mixing. *Marine Chemistry.* 103869.
671 [10.1016/j.marchem.2020.103869](https://doi.org/10.1016/j.marchem.2020.103869).

672 Cotovicz Jr, L.C., Knoppers, B.A., Brandini, N., Poirier, D., Costa Santos, S.J., Cordeiro, R.C., Abril,
673 G., 2018. Predominance of phytoplankton-derived dissolved and particulate organic carbon in
674 a highly eutrophic tropical coastal embayment (Guanabara Bay, Rio de Janeiro, Brazil).
675 *Biogeochemistry*, 137, 1–14.

676 Cotovicz Jr, L.C., Knoppers, B. A., Brandini, N., Costa Santos, S.J., Abril, G., 2015. A strong CO_2
677 sink enhanced by eutrophication in a tropical coastal embayment (Guanabara Bay, Rio de
678 Janeiro, Brazil). *Biogeosciences* 12, 6125–6146.

679 Cotovicz Jr, L.C., Libardoni, B., Brandini, N., Knoppers, B., Abril, G., 2016. Comparações entre
680 medições em tempo real da pCO₂ aquática com estimativas indiretas em dois estuários
681 tropicais contrastantes: o estuário eutrofizado da Baía de Guanabara (RJ) e o estuário
682 oligotrófico do Rio São Francisco (AL). *Quím. Nova* 39, 1206–1214.

683 Dickson, A.G. and Millero, F.J., 1987. A comparison of the equilibrium constants for the dissociation
684 of carbonic acid in seawater media, *Deep-Sea Res.*, 34, 1733–1743.

685 Etcheber, H., Taillez, A., Abril, G., Garnier, J., Servais, P., Moatar, F., Commarieu M.-V., 2007.
686 Particulate organic carbon in the estuarine turbidity maxima of the Gironde, Loire and Seine
687 estuaries: origin and lability. *Hydrobiologia* 588:245–259.

688 Frankignoulle, M., Abril, G., Borges, A., Bourge, I., Canon, C., Delille, B., Libert, E., Theate, J.M.,
689 1998. Carbon dioxide emission from European estuaries. *Science* 282, 434–436.
690 <https://doi.org/10.1126/science.282.5388.434>.

691 Frankignoulle, M., Borges, A., Biondo, R., 2001. A new design of equilibrator to monitor carbon
692 dioxide in highly dynamic and turbid environments, *Water Res.*, 35, 344 – 7.

693 Gattuso, J.-P., Frankignoulle, M., Wollast, R., 1998. Carbon and Carbonate Metabolism in Coastal
694 Aquatic Ecosystems. *Annual Review of Ecology and Systematics*, v. 29, n. 1, p. 405–434.

695 Gran, G., 1952. Determination of the equivalence point in potentiometric titrations. Part II. *The*
696 *Analyst*, v. 77, n. 920, p. 661.

697 Gypens, N., Borges, A.V., Lancelot, C., 2009. Effect of eutrophication on air-sea CO₂ fluxes in the
698 coastal Southern North Sea: a model study of the past 50 years. *Global Change Biology* 15 (4):
699 1040-1056. [10.1111/j.1365-2486.2008.01773.x](https://doi.org/10.1111/j.1365-2486.2008.01773.x).

700 IBGE, 2020. Pesquisa nacional de saneamento básico 2017: abastecimento de água e esgotamento
701 sanitário / IBGE, Coordenação de População e Indicadores Sociais. – Rio de Janeiro: Instituto
702 Brasileiro de Geografia e Estatística.

703 Ito, R.G., Garcia, C.A.E., Virginia, M., 2016. Net sea-air CO₂ fluxes and modelled pCO₂ in the
704 southwestern subtropical Atlantic continental shelf during spring 2010 and summer 2011.
705 *Continental Shelf Research* 119, 68-84. doi: [10.1016/j.csr.2016.03.013](https://doi.org/10.1016/j.csr.2016.03.013).

706 Jähne, B., Munnich, K.O., Bosinger, R., Dutzi, A., Huber, W., Libner, P., 1987. On parameters
707 influencing air-water exchange. *J. Geophys. Res.* 92, 1937–1949.
708 <https://doi.org/10.1029/JC092iC02p01937>.

709 Jiang, L.-Q., Cai, W.-J., Wang, Y., 2008. A comparative study of carbon dioxide degassing in river-
710 and marine-dominated estuaries. *Limnol. Oceanogr.* 53, 2603–2615.
711 doi.org/10.4319/lo.2008.53.6.2603.

712 Joesoef, A., Huang, W.-J., Gao, Y., Cai, W.-J., 2015. Air–water fluxes and sources of carbon dioxide
713 in the Delaware estuary: spatial and seasonal variability. *Biogeosciences* 12, 6085–6101.
714 <https://doi.org/10.5194/bg-12-6085-2015>.

715 Knoppers, B.A., Carmouze, J.P., Moreira-Turcqo, P.F., 1999. Nutrient dynamics, metabolism and
716 eutrophication of lagoons along the east Fluminense coast, state of Rio de Janeiro, Brazil. In:
717 Knoppers, B.A., Bidone, E.D., Abrão, J.J. (Eds.). *Environmental geochemistry of coastal*
718 *lagoon systems of Rio de Janeiro, Brazil*. Rio de Janeiro: FINEP. p. 123–154.

719 Knoppers, B. and Kjerfve, B., 1999. Coastal lagoons of southeastern Brazil: physical and
720 biogeochemical characteristics. In *Estuaries of South America*. Springer Berlin Heidelberg. 35–
721 66.

722 Koné, Y.J.M., Abril, G., Kouadio, K.N., Delille, B., Borges, A.V., 2008. Seasonal variability of
723 carbon dioxide in the Rivers and lagoons of Ivory Coast (West Africa). *Estuar. Coasts* 32, 246–
724 260. <https://doi.org/10.1007/s12237-008-9121-0>.

725 Körtzinger, A., 2003. A significant CO₂ sink in the tropical Atlantic Ocean associated with the
726 Amazon river plume. *Geophys. Res. Lett.* 30, 2287, doi:10.1029/2003GL018841.

727 Kubo, A., Maeda, Y., Kanda, J., 2017. A significant net sink for CO₂ in Tokyo Bay. *Sci Rep* 7:44355.
728 <https://doi.org/10.1038/srep44355>.

729 Kubo, A. and Kanda, J., 2020. Coastal urbanization alters carbon cycling in Tokyo Bay. *Sci Rep* 10,
730 20413. <https://doi.org/10.1038/s41598-020-77385-4>.

731 Lee, K., Kim, T.W., Byrne, R.H., Millero, F.J., Feely, R.A., Liu, Y.M., 2010. The universal ratio of
732 boron to chlorinity for the North Pacific and North Atlantic oceans, *Geochim. Cosmochim. Ac.*,
733 74, 1801–1811, doi:10.1016/j.gca.2009.12.027.

734 Liu, X., Li, Y., Wu, Y., Huang, B., Dai, M., Fu, F., Hutchins, D.A., Gao, K., 2017. Effects of elevated
735 CO₂ on phytoplankton during a mesocosm experiment in the southern eutrophicated coastal
736 water of China. *Scientific reports*, 7(1), 6868. <https://doi.org/10.1038/s41598-017-07195-8>

737 Mehrbach, C., Cuberson, C.H., Hawley, J.E., Pytkowicz, R.M., 1973. Measurements of the apparent
738 dissociation constants of carbonic acid in seawater at atmospheric pressure. *Limnol. Oceanogr.*
739 18, 897–907.

740 Myklestad, S.M., 2000. Dissolved organic carbon from phytoplankton. *Mar Chem* 5:112–144.
741 <https://doi.org/10.1016/j.marchem.2009.01.001>.

742 Nixon, S.W., 1995. Coastal marine eutrophication: a definition, social causes, and future concerns,
743 *Ophelia*. v. 41, p. 199–219.

744 Oliveira, M.L.P., 2013. Análise da hidrodinâmica do sistema lagunar de Saquarema frente às
745 projeções de aumento do nível médio do mar. Programa de Pós-graduação e Pesquisa de
746 Engenharia. Universidade Federal do Rio de Janeiro. Dissertação de mestrado. 102p.

747 Pereira, E.R.C., 1991. Estudo Experimental da Influência do Sedimento sobre as Atividades
748 Metabólicas na Laguna de Saquarema - RJ. Dissertação de Mestrado. Niterói: Programa de
749 Geoquímica, UFF.

750 Pierrot, D., Lewis, D.E., Wallace, D.W.R., 2006. MS Excel Program Developed for CO₂ System
751 Calculations. ORNL/CDIAC-105a. Carbon Dioxide Information Analysis Center, Oak Ridge
752 National Laboratory, U.S. Department of Energy, Oak Ridge, Tennessee. Doi:
753 10.3334/CDIAC/otg.CO2SYS_XLS_CDIAC105a.

754 Philips, E.J., Badylak, S., Grosskopf, T., 2002. Factors Affecting the Abundance of Phytoplankton in
755 a Restricted Subtropical Lagoon, the Indian River Lagoon, Florida, USA. *Estuarine, Coastal
756 and Shelf Science* 55 (3), 385-402 doi:10.1006/ecss.2001.0912.

757 Pritchard, D.W., 1967. Observation of circulation in coastal plain estuaries. In: Lauff GH, editor.
758 *Estuaries*, Washington, DC: American Association for the Advancement of Science, pp.3-5.

759 Rabalais, N. N., Turner, R. E., Díaz, R.J., Justic, D., 2009. Global change and eutrophication of coastal
760 waters. *ICES Journal of Marine Science*, 66 (7) 1528–1537,
761 <https://doi.org/10.1093/icesjms/fsp047>.

762 Raymond, P.A. and Cole, J.J., 2001. Gas Exchange in Rivers and Estuaries: Choosing a Gas Transfer
763 Velocity. *Estuaries*, v. 24, n. 2, p. 312.

764 Ribas-Ribas, M., Hernández-Ayón, J.M., Camacho-Ibar, V.F., Cabello-Pasini, A., Mejia-Trejo, A.,
765 Durazo, R., Galindo-Bect, S., Souza, A.J., Forja, J.M., Siqueiros-Valencia, A., 2011. Effects of
766 upwelling, tides and biological processes on the inorganic carbon system of a coastal lagoon in
767 Baja California. *Estuarine, Coastal and Shelf Sci* 95(4): 367–376.

768 Sabine, C.L., Feely, R.A., Gruber, N., Key, R.M., Lee, K., Bullister, J.L., Wanninkhof, R., Wong,
769 C.S., Wallace, D.W.R., Tilbrook, B., Millero, F.J., Hung Peng, T., Kozyr, A., Ono, T., Rios,
770 A.F., 2004. The Oceanic Sink for Anthropogenic CO₂. *Science* 305(5682):367–71.

771 Sathyendranath, S., Stuart, V., Nair, A., Oka, K., Nakane, T., Bouman, H., Forget, M.H., Maass, H.,
772 Platt, T., 2009. Carbon to chlorophyll ratio and growth rate of phytoplankton in the sea. *Mar
773 Ecol Prog Ser* 383:73–84. <https://doi.org/10.3354/meps07998>.

774 Strickland, J.D.H. and Parsons, T.R., 1972. A practical handbook of seawater analysis. Fisheries
775 Research Board of Canada Bulletin, 167.

776 Wanninkhof, R., 1992. Relationship between wind speed and gas exchange. *J. Geophys. Res.* 97,
777 7373–7382. <https://doi.org/10.1029/92JC00188>.

778 Weiss, R.F., 1974. Carbon dioxide in water and seawater: the solubility of a non-ideal gas, *Mar.*
779 *Chem.*, 2, 203–215.

780 Wollast, R., 1991. The coastal organic carbon cycle: fluxes, sources and sinks. In: Montoura, R.F.C.,
781 Martin, J.M., Wollast, R. (Eds.). *Ocean margin processes in global change*. [S.l.]: Wiley
782 Intersciences Publishers. p. 365-381.

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786 **Table 1.** Mean (\pm standard deviation), minimum and maximum of the principal physicochemical
 787 parameters of the waters of Saquarema Lagoon for the sampling periods.

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	November 2019		February 2020	
	Spatial sampling	Temporal sampling (12h)	Spatial sampling	Temporal sampling (24h)
Temperature (°C)	24.17 \pm 0.77 (22.19 - 25.42)	23.01 \pm 0.27 (19.8 - 23.5)	29.56 \pm 1.14 (26.26 - 32.3)	20.74 \pm 4.62 (16.33 - 30.03)
Salinity	25.25 \pm 4.64 (16.17 - 31.92)	29.37 \pm 0.71 (27.87 - 30.2)	20.43 \pm 5.63 (14.32 - 30.85)	32.05 \pm 2.32 (28.11 - 34.47)
pCO₂ (ppmv)	177 \pm 73 (60 - 301)	253 \pm 19 (222 - 280)	126 \pm 52 (60 - 249)	357 \pm 150 (183 - 529)
SPM (mg L⁻¹)	29.9 \pm 7.6 (20.5 - 44)	25.5 \pm 23.9 (9.5 - 98.7)	43.7 \pm 24.7 (14 - 118.5)	20.2 \pm 8.3 (8.7 - 42.5)
DOC (mg L⁻¹)	9.2 \pm 3.3 (4.7 - 14.3)	5.4 \pm 0.8 (4.6 - 6.5)	15.6 \pm 4.6 (6.3 - 19.8)	5.0 \pm 3.8 (1.0 - 10.3)
POC (mg L⁻¹)	6.0 \pm 2.0 (3.4 - 9.8)	3.5 \pm 0.6 (2.5 - 4.4)	8.6 \pm 3.3 (3.3 - 12.3)	2.8 \pm 2.5 (0.4 - 6.6)
POC (%of SPM)	20.3 \pm 4.9 (12.2 - 28.4)	19.8 \pm 6.5 (5.71 - 29.6)	22.0 \pm 7.3 (8.3 - 31.2)	11.5 \pm 8.3 (2.42 - 26.3)
Chl-<i>a</i> (µg L⁻¹)	22.9 \pm 14.9 (7.6 - 77.1)	15.7 \pm 3.3 (7.3 - 31.5)	138.1 \pm 56.6 (35.8 - 217.1)	16.1 \pm 13.8 (2.7 - 36.0)
TA (µmol kg⁻¹)	2007 \pm 213 (1705 - 2319)	2229 \pm 24 (2188 - 2265)	1762 \pm 246 (1466 - 2229)	2253 \pm 105 (2098 - 2376)
DIC (µmol kg⁻¹)	1717 \pm 255 (1287 - 2071)	1897 \pm 14 (1869 - 1920)	1373 \pm 248 (1091 - 1816)	1998 \pm 203 (1748 - 2211)
Ω Calcite	6.5 \pm 1.8 (1.8 - 8.7)	6.0 \pm 0.4 (5.5 - 6.6)	6.9 \pm 0.8 (5.2 - 8.3)	5.2 \pm 1.9 (3.4 - 7.8)
Ω Aragonite	4.1 \pm 1.1 (1.1 - 5.3)	3.9 \pm 0.3 (3.6 - 4.3)	4.3 \pm 0.6 (5.3 - 3.1)	3.4 \pm 1.3 (2.2 - 5.1)

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795 **Table 2.** Mean values measured in situ of $\Delta p\text{CO}_2$ ($p\text{CO}_{2\text{water}} - p\text{CO}_{2\text{air}}$) and wind speed at 10 m height
 796 (U10). Calculated mean values for gas exchange coefficient (k_{600}) and CO_2 fluxes at the air-water
 797 interface in each sampling campaign. W92 is the data calculated according to k_{600} of Wanninkhof
 798 (1992), RC01 is the data calculated according to k_{600} of Raymond and Cole (2001), and A09 is data
 799 calculated according to k_{600} of Abril et al. (2009).

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		Nov. 2019		Feb. 2020		
		Spatial sampling	Temporal sampling	Spatial sampling	Temporal sampling (ebb tide)	Temporal sampling (flood tide)
$\Delta p\text{CO}_2$ (ppmv)		-233±73	-157±19	-283±52	-192±40	94±68
U10 (m s^{-1})		2.03±0.89	2.83±0.64	2.8±1.02	1.46±0.51	1.69±1.02
k_{600} (cm h^{-1})	W92	1.4±0.3	2.5±0.2	2.4±0.5	0.8±0.1	1.1±0.5
	RC01	3.9±2.6	5.1±2.4	5.1±2.7	3.2±2.3	3.4±2.7
	A09	7.0±4.1	9.0±3.4	9.0±4.4	5.5±3.1	6.1±4.4
FCO_2 ($\text{mmol C m}^{-2} \text{h}^{-1}$)	W92	-0.9±0.9	-1.2±0.1	-2.5±0.5	-0.4±0.2	0.2±0.3
	RC01	-2.5±2.3	-2.6±0.3	-5.2±1.1	-1.5±0.9	0.8±1.0
	A09	-4.5±4.2	-4.5±0.5	-9.2±2.1	-2.7±1.6	1.4±1.8
	Average	-2.6±4.8	-2.7±0.5	-5.6±2.4	-4.6±1.8	0.8±2.1

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805 **Table 3.** Comparison of the values of DOC, POC, Chl *a* observed during the study with values in the
 806 late 80's and 90's.

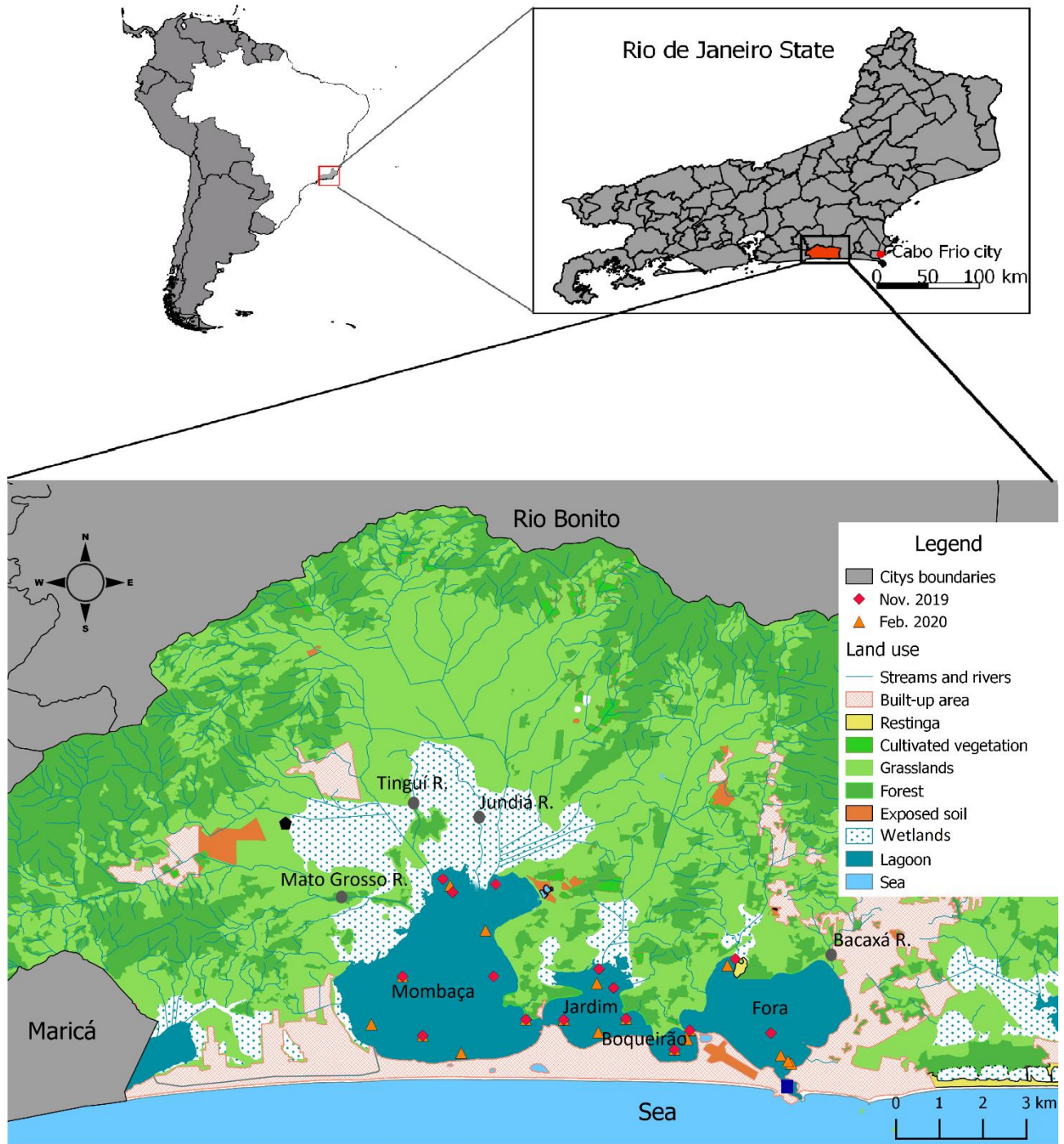
	Pereira (1991)		This study	
	Jardim*	Fora#	Jardim	Fora
DOC	12.6±3.5	8.6±2.6	13.8±5.6	7.5±2.5
POC	7.1±1.4	1.7±0.3	8.7±2.9	4.1±0.9
Chl-a	16.7±10.3	13.3±3.3	116.8±85.2	45.2±23.4

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808 *from Mar. 89 to Jul.89; # from Oct.89 to Jan.90

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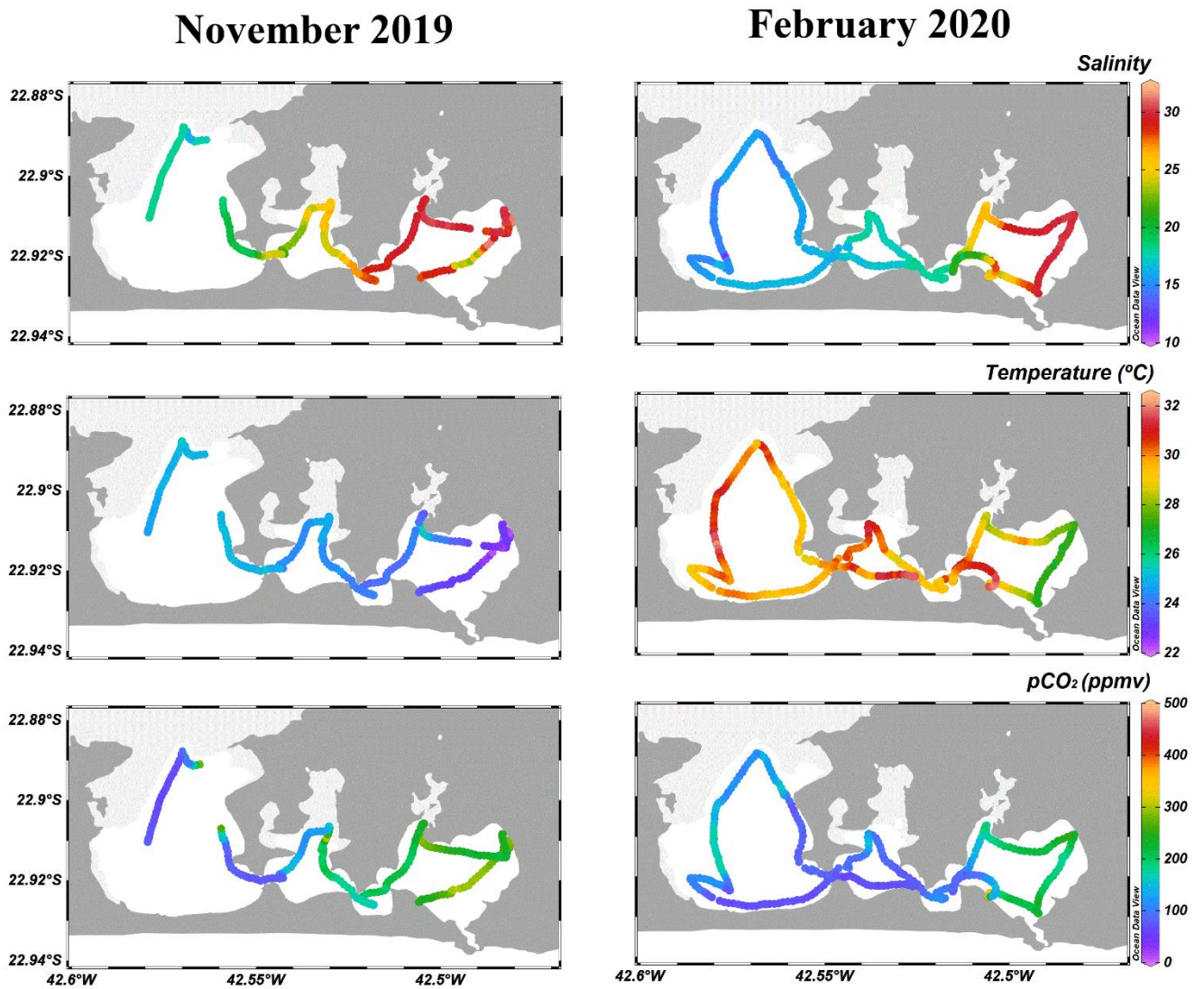
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813 **Figure 1.** Map of land use and occupation of the watershed of the Saquarema Lagoon. The red
 814 diamonds represent the sampling stations during the first campaign (Nov 2019), the orange triangles
 815 represent the sampling stations during the second campaign (Fev 2020), the blue square represent the
 816 temporal monitoring , black point represents the Sampaio Correa meteorological station (22.87° S,
 817 42.61° W) where wind speed was measured and the grey points indicate the sampled river stations.

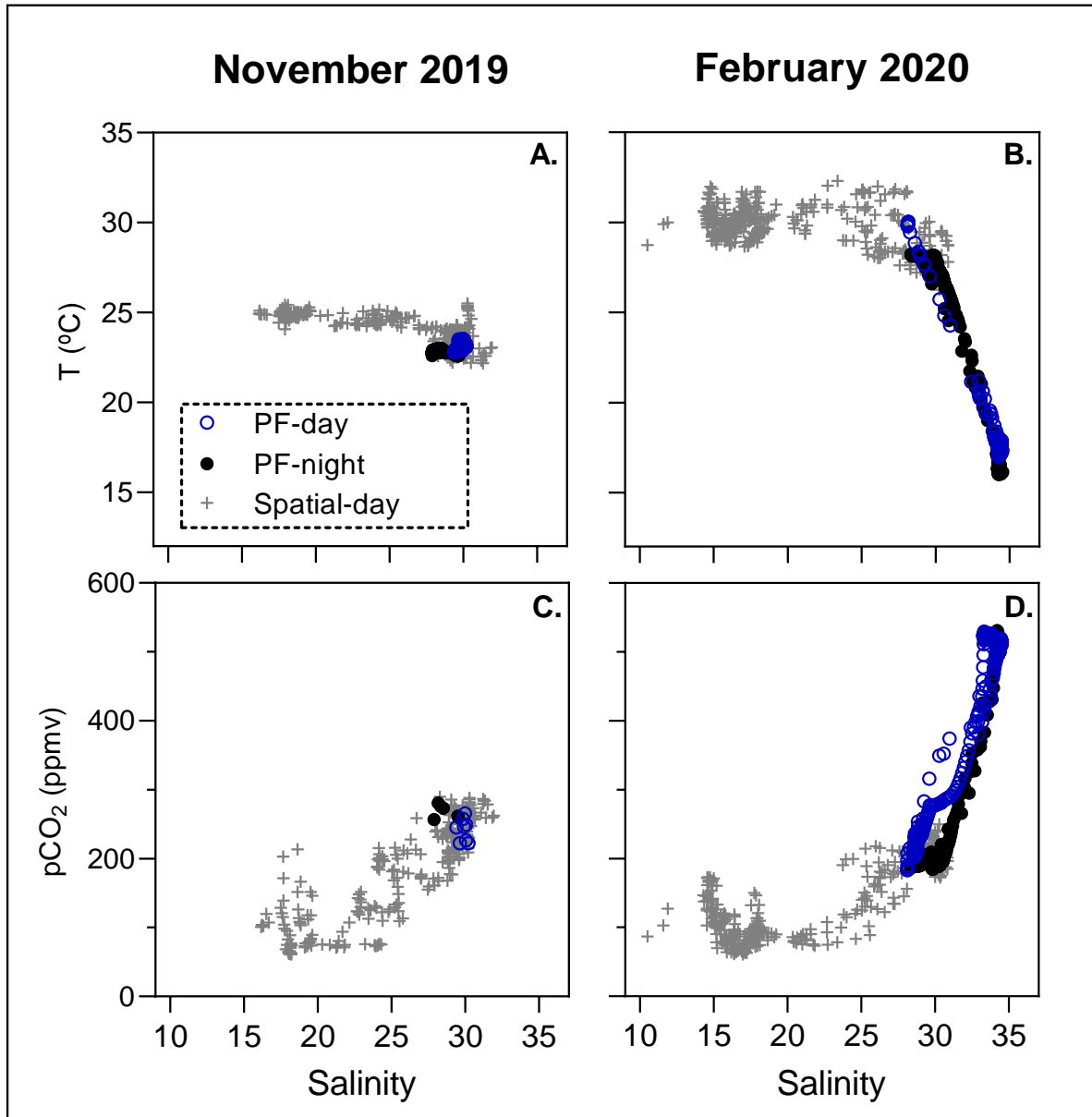
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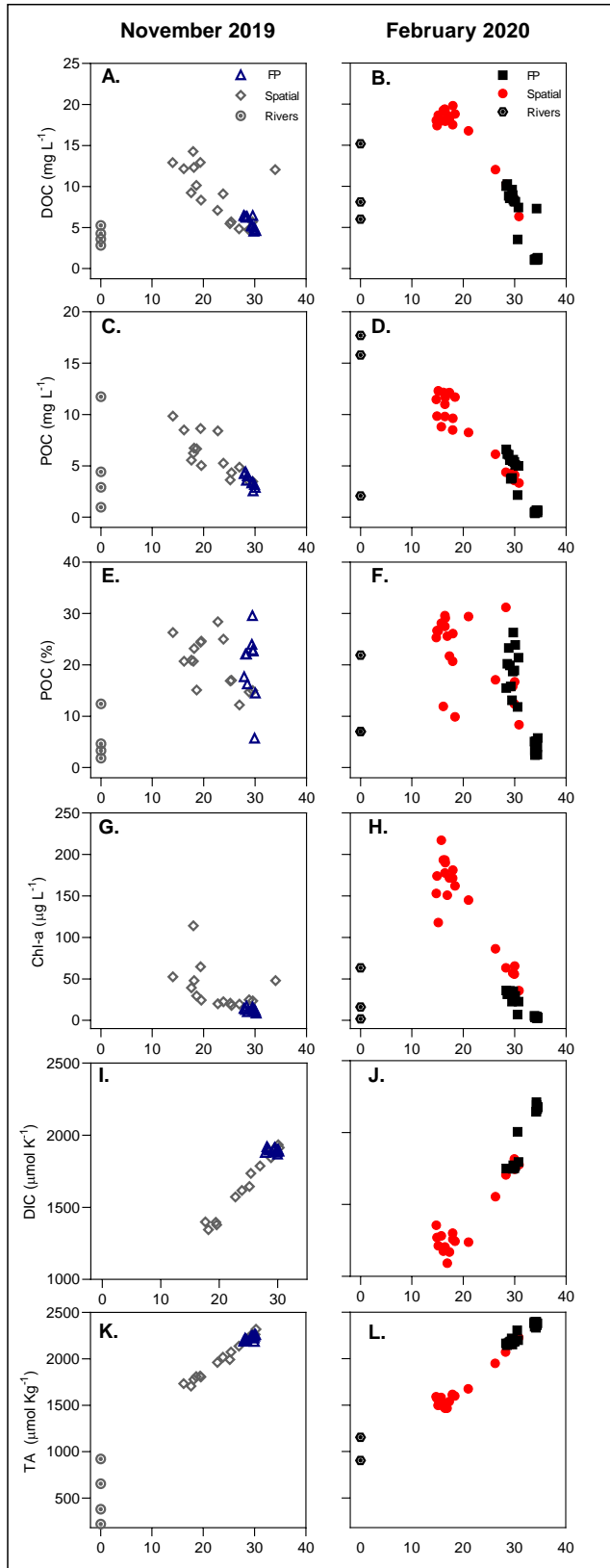
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Figure 2. Maps showing the boats tracks and the spatial continuous measurements of salinity, temperature and pCO₂ in surface waters of Saquarema lagoon for both sampling campaigns in Nov 2019 - and Feb 2020.



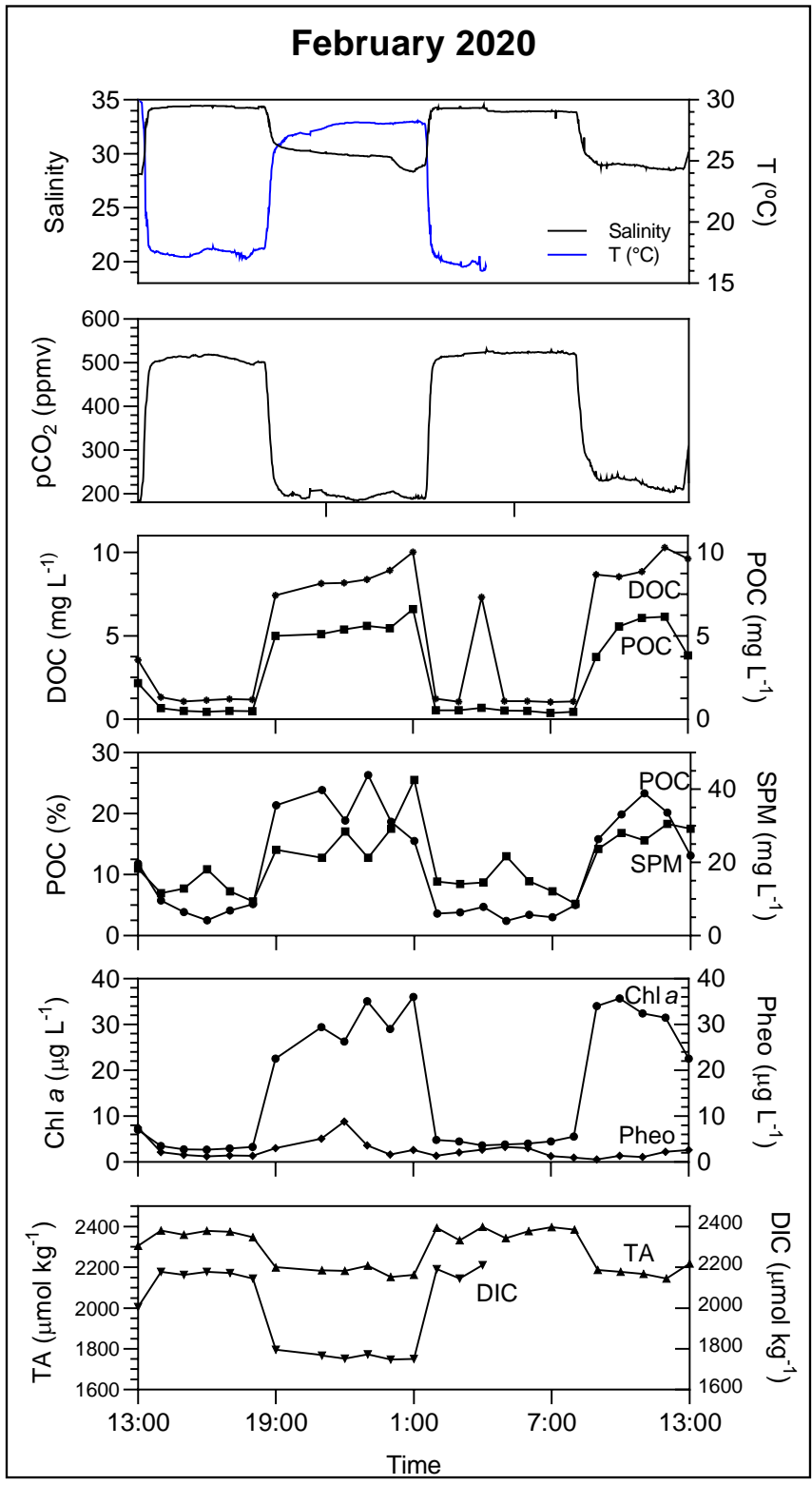
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 834 **Figure 3:** Distribution of pCO₂ and temperature as a function of salinity during the spatial and
 835 temporal monitoring for the two campaigns. “FP” refers to fixed point monitoring at the lagoon
 836 outlet, “Spatial” to spatial monitoring during the day inside the lagoon.

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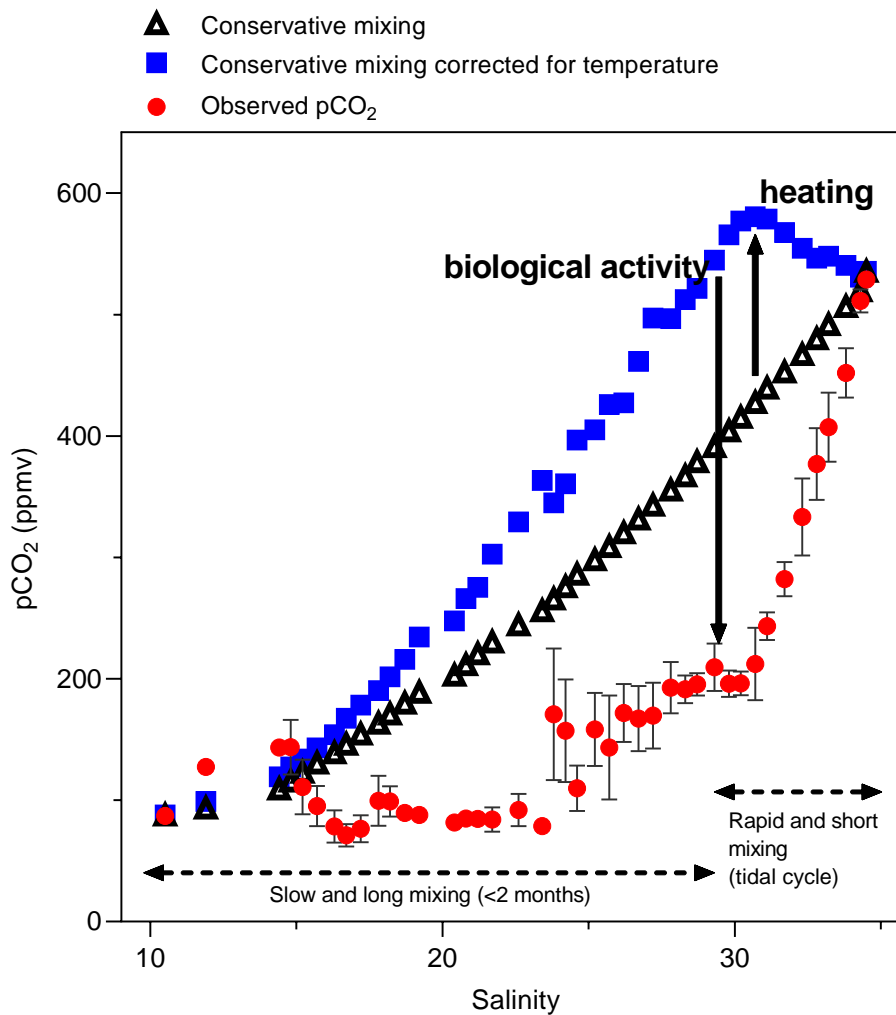
845 **Figure 4:** Distributions of DOC, POC, POC %, Chl *a*, DIC, TA as a function of salinity for the two
 846 samplings. “FP” refers to fixed point monitoring at the lagoon outlet, “Spatial” to spatial monitoring
 847 during the day inside the lagoon.



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 849 **Figure 5:** Diurnal variation of the concentrations of the main water parameters at the mouth of the
 850 lagoon during Feb. 2020. Note that a temporal monitoring of 12h was also performed in Nov. 2019,
 851 but the parameters were relatively constant, and the average values are reported in Table 1.

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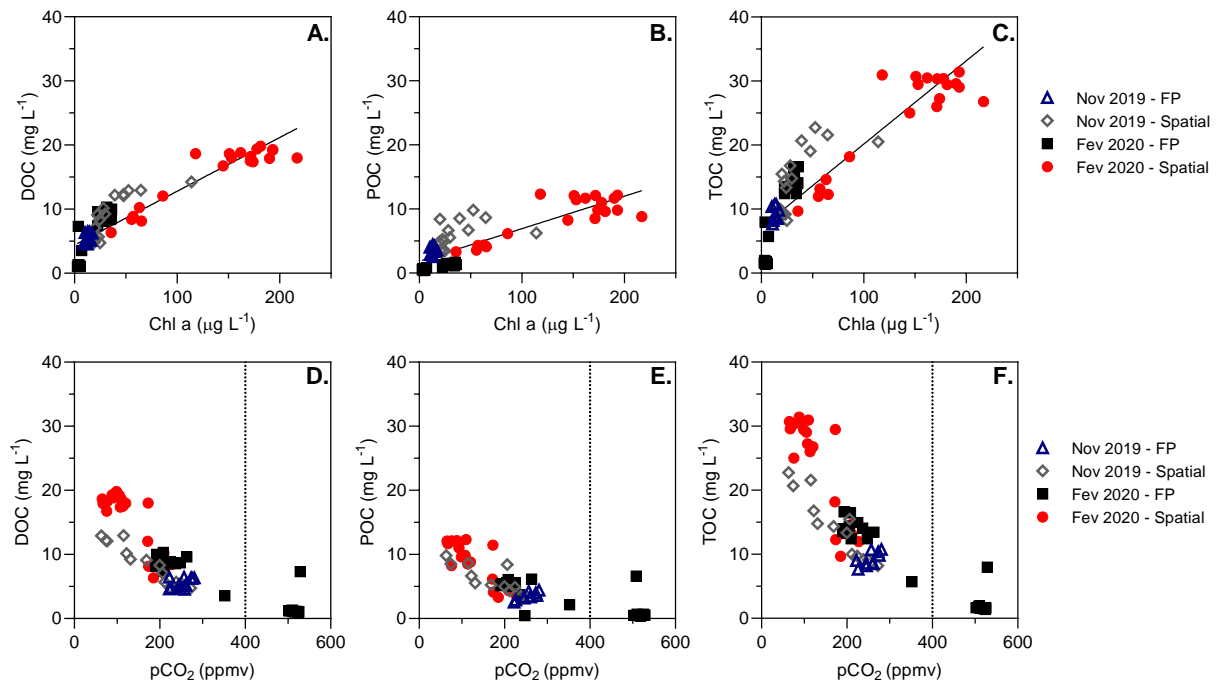
856 **Figure 6:** Comparison of observed water pCO₂ (red) with the results of the mixing model of South
857 Atlantic Central Water (Salinity 34.6) with lagoon waters (Salinity 10). The “conservative mixing”
858 curve (black) is calculated by considering TA, DIC and temperature conservativity between the two
859 end-members; The “conservative mixing corrected for temperature” curve (blue) is calculated by
860 considering TA, DIC conservativity between the two end-members and the observed temperature
861 along the salinity gradient.

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870 **Figure 7:** Relationships between: (A) DOC versus Chl *a*; (B) POC versus Chl *a*; (C) TOC versus
 871 Chl *a*; (D) DOC and pCO₂; (E) POC and pCO₂; (F) TOC and pCO₂. The dashed lines at 400 ppmv
 872 represent the global average atmospheric CO₂ concentration. “FP” refers to fixed point monitoring
 873 at the lagoon outlet, “Spatial” to spatial monitoring during the day inside the lagoon.

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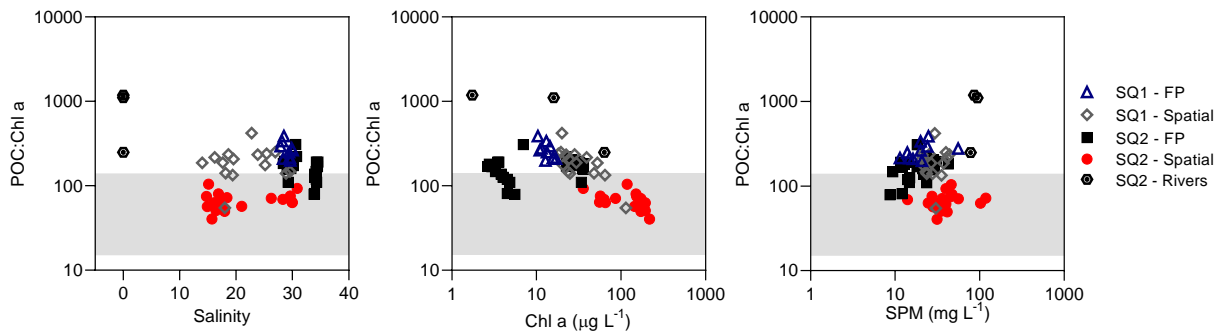
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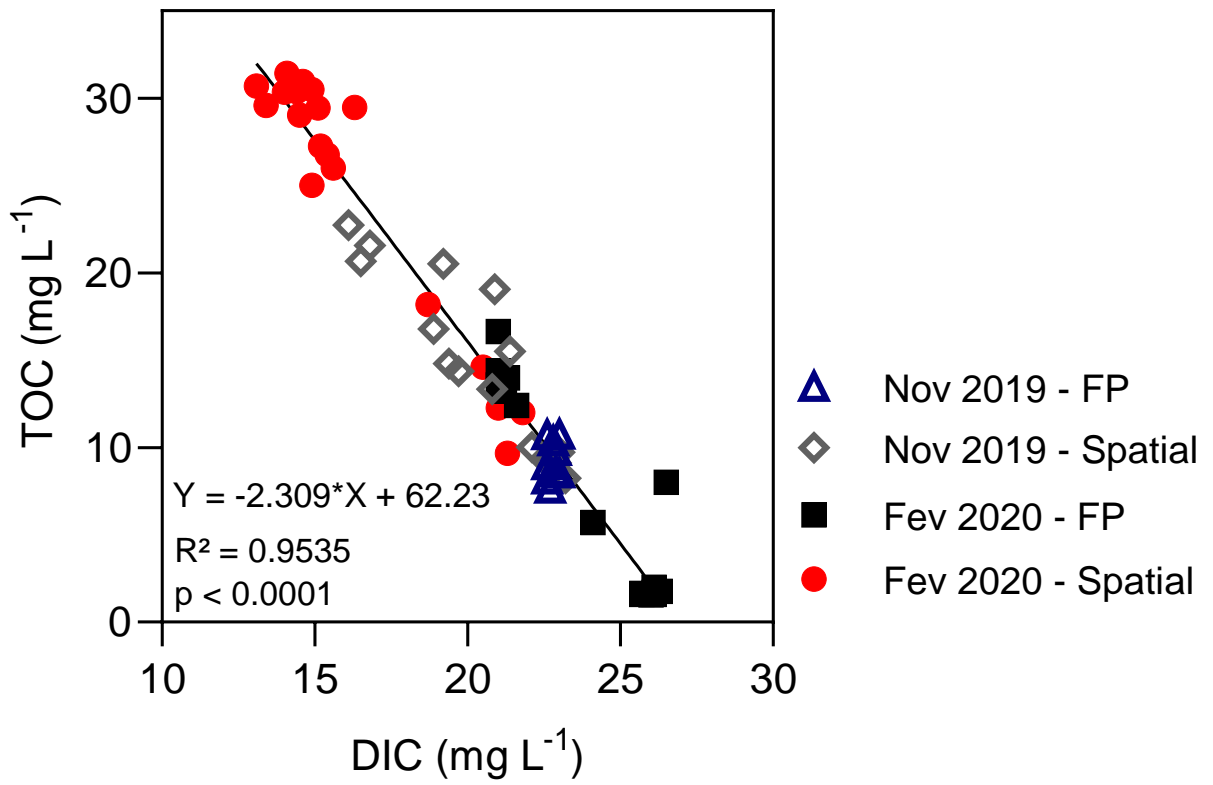
889 **Figure 8:** plots of (A) POC% (percent of SPM) versus SPM; (B) POC:Chl *a* vs Chl *a*, of the two
890 samples campaigns for the spring and summer. The shaded area represents POC:Chl *a* range for
891 living phytoplankton. “FP” refers to the monitoring at fixed point at the lagoon outlet, “Spatial” to
892 spatial monitoring during the day inside the lagoon.

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899 **Figure 9:** Linear Regression between DIC and TOC for the two sampling campaigns.

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901 **Table S1:** Statistical analysis comparing the spatial variation of parameters measured between
 902 different lagoon's compartments.

		Mombaça	Fora	Jardim			Mombaça	Fora	Jardim
	Salinity				TA				
	Mombaça	-			Mombaça	-			
	Fora	< 0.001	-		Fora	< 0.001	-		
	Jardim	< 0.001	< 0.001	-	Jardim	< 0.01	< 0.001		-
ANOVA	SPM								
	Mombaça	-							
	Fora	> 0.05	-						
	Jardim	> 0.05	> 0.05	-					
	Temperature				DOC				
	Mombaça	-			Mombaça	-			
	Fora	> 0.05	-		Fora	< 0.001	-		
	Jardim	> 0.05	> 0.05	-	Jardim	> 0.05	< 0.01		-
kruskal-Wallis	Chla				DIC				
	Mombaça	-			Mombaça	-			
	Fora	> 0.05	-		Fora	< 0.001	-		
	Jardim	> 0.05	> 0.05	-	Jardim	> 0.05	< 0.01		-
	POC				pCO₂				
	Mombaça	-			Mombaça	-			
	Fora	< 0.001	-		Fora	< 0.01	-		
	Jardim	> 0.05	< 0.001	-	Jardim	> 0.05	< 0.001		-

903 **Table S2:** Statistical analysis comparing the two sampling periods, November 2019 and February
904 2020.

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	Mann-Whitney	ANOVA
Temperature (°C)	>0.05	
Salinity		< 0.001
pCO₂ (ppmv)	<0.001	
SPM (mg L⁻¹)		>0.05
DOC (mg L⁻¹)	<0.0001	
POC (mg L⁻¹)	<0.0001	
Chl-<i>a</i> (µg L⁻¹)	<0.001	
TA(µmol kg⁻¹)		< 0.001
DIC (µmol kg⁻¹)	<0.0001	