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1 Greenhouse gas emissions (CO₂ and CH₄) and inorganic carbon in an urban tropical coastal lagoon (Jacarepagua
2 Lagoon Complex, Brazil)

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Highlights

Oxygen-depleted river waters were associated with high concentrations of TA and DIC
TA and DIC decreased in the mixing region due to re-oxidation processes
Extreme high concentrations and emissions of CO₂ and CH₄ were found in hypoxic/anoxic polluted river waters
Concentrations and emissions of GHG decreased seaward direction as results of mixing, degassing and biological uptake
The diffusive CH₄ emissions were more important than CO₂ emissions in terms of global warming potential

Abstract

Increasing eutrophication of coastal waters have been associated with disturbances in greenhouse gases (GHGs) concentrations and emissions to the atmosphere, but still overlooked globally. Here, we investigated the concentrations and diffusive fluxes of carbon dioxide (CO₂) and methane (CH₄) in the urban-dominated Jacarepagua Lagoon Complex (JLC) (Southeastern Brazil). This lagoonal complex presents high polluted and eutrophic waters, showing frequent occurrences of anoxia and hypoxia, and phytoplankton blooms. Between 2017 and 2018, four spatial surveys were performed (dry and wet conditions) in the system, with sampling in the river waters that drain the urban watershed, and in the lagoon waters. Strong oxygen depletion was found in the polluted rivers, associated with high values of partial pressure of CO₂ ($p\text{CO}_2$) and CH₄ concentrations. These rivers receive massive amounts of organic matter and nutrients from untreated domestic effluents. The high GHGs concentrations are attributed to organic matter degradation mediated by aerobic and anaerobic processes, with concomitant production of total alkalinity (TA) and dissolved inorganic carbon (DIC). In the lagoon, GHGs concentrations decreased due to dilution with seawater, degassing and phytoplankton growth. TA concentrations were minimal at salinity of ~20 suggesting processes of organic matter re-oxidation during estuarine mixing. Emissions of CO₂ ranged from 22 to 48 mmol C m⁻² d⁻¹, and those of CH₄ from 2.2 to 16.5 mmol C m⁻² d⁻¹, this later among the highest documented in coastal waters. Compared in terms of global warming potential (GWP), the diffusive emissions of CH₄ were more important than CO₂ emissions. These results highlight that high-polluted coastal ecosystems are hotspots of GHGs emissions to the atmosphere, and must be included in global budgetary assertions.

Key-words: Greenhouse Gas Emissions, Carbon Dioxide, Methane, Carbonate Chemistry, Coastal Eutrophication, Coastal Lagoons

1. Introduction

Coastal eutrophication is one of the major environmental threats to coastal ecosystems worldwide, and particularly accelerated and severe in ecosystems densely populated (Nixon 1995; Cloern 2001, Bricker et al. 2008). At advanced stages of eutrophication, the high nutrient and organic matter enrichment lead to profound changes in ecosystem metabolism and biogeochemical cycling, deteriorating the ecological health and water quality. Some

80 adverse effects include occurrence of harmful algal blooms (HABs), accelerate growth of fungal and bacterial
81 communities, oxygen depletion, and coastal acidification (Bricker et al. 2008; Cai et al. 2011). Studies have
82 suggested that coastal eutrophication has been perturbing the carbon cycling, leading to alteration in carbon
83 budgets and greenhouse gas emissions (GHGs), such as carbon dioxide (CO₂) and methane (CH₄) (Howarth et al.
84 2011). CO₂ and CH₄ are the principal well-mixed and long-lived GHGs present in the atmosphere and, together,
85 these gases answer to more than 80% of the actual increase in the global average atmospheric temperature (IPCC
86 2013). Global mean atmospheric CO₂ concentrations increase from 280 ppmv during the pre-Industrial Revolution
87 (Siegenthaler et al. 2005), to reach actual concentration overpassing 415 ppmv (NOAA 2019). For CH₄, a more
88 powerful GHG, the concentration changed from 0.72 ppmv in the pre-Industrial period (Etheridge et al. 1998) to
89 the current level of about 1.80 ppmv (NOAA 2019). Despite of this well-documented atmospheric rise, the sources
90 and sinks of these GHGs in the diverse compartments of the Earth global system are not yet properly understood
91 and quantified, particularly in disturbed coastal ecosystems at subtropical and tropical latitudes.

92 The low levels of oxygen concentrations in coastal waters are associated with high levels of aquatic partial pressure
93 of CO₂ (*p*CO₂), enhancing the CO₂ degassing and coastal acidification (Cai et al. 2011). In this way, coastal
94 eutrophication can act amplifying the CO₂ emissions by stimulating heterotrophic processes through the respiration
95 of anthropogenic-derived organic carbon (Frankignoulle et al. 1998; Zhai et al. 2007). The internal processes of
96 respiration of organic matter in eutrophic aquatic ecosystems modifies not only the CO₂ concentrations, but all the
97 parameters of the carbonate chemistry, with influences on the acid-base properties, altering the pH, and
98 concentrations of total alkalinity (TA) and dissolved inorganic carbon (DIC) (Abril and Frankignoulle 2001; Cai
99 et al. 2011; Sunda and Cai 2012; Cotovicz et al. 2018). However, eutrophication can also contributes to promote
100 CO₂ sink by stimulating the primary production with important CO₂ uptake in coastal waters that receives
101 important amounts of nutrients (Borges and Gypens 2010; Cotovicz et al. 2015, 2020; Kubo et al. 2017). In this
102 regard, eutrophication can both amplify CO₂ outgassing (when organic matter is intensely degraded by microbial
103 activities) or CO₂ ingassing (when organic matter is intensely produced by primary producers). These interplays
104 between sources and sinks of CO₂ and alteration in carbonate chemistry depends on local/regional characteristics,
105 and are not well-understood.

106 For CH₄, the eutrophication is related to increasing concentrations in aquatic compartments. Pristine rivers are
107 usually organic matter poor-environments and weak sources of CH₄ compared to impacted ecosystems (Richey et
108 al. 1988; Purvaja and Ramesh 2000; Brigham et al. 2019). The production of CH₄ increases with hypoxic and
109 anoxic conditions associated to the increased inputs of organic matter to water and sediments. In coastal waters,
110 the CH₄ production is most important in low salinity regions, where methanogenesis is promoted by the low
111 availability of electron acceptors (Chanton et al. 1989; Kelley et al. 1990); in high salinity regions sulphate
112 reduction outcompetes with methanogenesis as the main pathway of sedimentary anaerobic organic matter
113 degradation (Martens and Klump 1980; Martens et al. 1998). In coastal marine sediments with high salinity, large
114 inputs of organic matter are necessary for methanogenesis to occur and generate CH₄ rich gassy-sediments
115 (Martens and Klump 1980; Martens et al. 1998). It is particularly relevant the contributions from wastewater
116 treatment plants and direct inputs from untreated domestic effluents that are rich in CO₂ and CH₄ in disturbed
117 coastal ecosystems (Nirmal-Rajkumar et al. 2008; Burgos et al. 2015; Cotovicz et al. 2016; Brigham et al. 2019).
118 This means that regions under influence and/or close to sewage discharge present higher CO₂ and CH₄
119 concentrations and emissions. In addition, it is important to point that anaerobic respiration processes (such as
120 denitrification, manganese reduction, iron reduction and sulfate reduction), produce TA, and in some cases also
121 involve alteration in DIC concentrations (Abril and Frankignoulle 2001; Rassmann et al. 2020).

122 Coastal lagoons represent an estuarine typology highly sensitive to develop eutrophication due to the long
123 residence times and due to host large human settlements (Knoppers et al. 1999). These near-shore coastal
124 environments occurs in 13% of the World's coastline (Kjerfve 1985), normally exhibiting high levels of primary
125 production (Knoppers et al. 1999). There have been very few studies conducted in coastal lagoons regarding the
126 assessment of concentrations and quantification of emissions of GHGs, particularly in tropical regions (Borges
127 and Abril 2011, Koné et al. 2009, 2010), creating large uncurtains in global GHG budgets. In the present study,
128 we analyze and quantify the concentrations and fluxes of CO₂ and CH₄ in a high-polluted and urban-dominated
129 coastal lagoon, the Jacarepagua Lagoon Complex (JLC), located at the Rio de Janeiro coast (Southeastern, Brazil).
130 The system hosts a population near of 1 million of inhabitants along the watershed (Santos Neves et al. 2017). We
131 hypothesized that the strong pollution and eutrophication will contribute with high emissions of GHG in this
132 system, especially in the riverine waters that receive high loads of organic matter and nutrients from untreated
133 urban effluents (Fig. 1). For this, we constructed a sampling design turned to contrast riverine and lagoonal

134 conditions, by choosing 05 stations in river waters, and 05 stations in lagoon waters. Our results showed extremely
135 high concentrations and emissions of CO₂ and CH₄ in anoxic/hypoxic freshwaters. The concentrations and
136 emissions of CO₂ and CH₄ in the freshwaters are among the highest documented in coastal waters worldwide, and
137 are hotspots of GHGs emissions.

138 **2. Material and Methods**

139 **2.1. Study Area**

140 The JLC (Lat. 22°55'S and 23°03'S; Long. 43°30'O and 43°18'O) is located in the west region of the Rio de
141 Janeiro City (Southeastern Brazil). The system is composed by four coastal lagoons: Jacarepaguá (Area = 4.07
142 km²), Camorim (A = 0.80 km²), Tijuca (A=4.34 km²) and Marapendi (A = 3.33 km²) (Fig. 1). The total surface
143 area covers about 12.8 km², and the drainage basin extends over approximately 280 km² (Salloto et al. 2012). The
144 water volume in the lagoon is estimated at about 2.38 x10⁷ m³ (Sampaio 2008). The annual freshwater inputs to
145 the system are weak, about 3.00 m³ s⁻¹ (Sampaio 2008). However, under strong levels of precipitation, the
146 freshwater inflow can be significantly higher. These lagoons present microtidal amplitude, are enclosed and
147 connected to the sea by only one channel, the Joa Channel (Gomes et al. 2009). The climate in the region is
148 classified as tropical humid, with a wet warm summer and a dry winter (Sampaio 2008). This lagoon complex has
149 been suffering with intense anthropogenic activities developed in its surroundings and along the watershed, mainly
150 urbanization and industrialization (Gomes et al. 2009). Actually, the human population surrounding the JLC is
151 about 1 million of inhabitants, reflecting in high loads of domestic and industrial effluents discharged directly into
152 the water body and its rivers. The wastewater services collection are still very precarious and inefficient, covering
153 only about 60% of the total produced (ANA 2019). Taking account the population of the watershed and the
154 estimates of emissions of effluents per capita (Wallace 2005), the amount of effluents discharges are on the same
155 order of the freshwater inputs to the system (~ 3.4 m³ s⁻¹), i.e., the mean wastewater volume loaded to the lagoon
156 is almost equivalent to the freshwater river loads. This results in a heavily eutrophication process in this system,
157 with perennial presence of cyanobacterial blooms and frequent episodes of hypoxia/anoxia (Gomes et al. 2009;
158 De-Magalhães et al. 2017).

159 **2.2. Sampling Strategy**

160 Four sampling campaigns were conducted in the months of March-2017, June-2017, November-2017 and May-
161 2018. In each sampling campaign, five stations were sampled on the rivers that compose the drainage basin of the
162 lagoon complex, and five stations were sampled in the lagoons of Tijuca and Marapendi (Fig. 1). The sampling
163 stations in the rivers were accessed by car. The sampling stations in the lagoons were accessed using a small boat.
164 The depths of the sampling stations were always lower than 2.5 m. A Niskin bottle model Alfakit 3L was used to
165 collect water samples in sub-surface (~0.5 m depth). The samples were conditioned (fixed and or/ maintained in
166 ice in the dark) for further analysis in the laboratory. A calibrated multiparametric Sonde (YSI Professional Plus)
167 measured *in situ* the salinity, temperature, and levels of dissolved oxygen (DO). The samplings were always
168 conducted during the ebb tide, to assess the major contribution from land runoff. Important to point that we were
169 not allowed to access the lagoons of Camorim and Jacarepagua due to the presence of an “ecological barrier”,
170 which prevented the boat navigation inside these water bodies (Fig. 1).

171 **2.3. Laboratory analysis**

172 Whatman GF/F filters were used for chlorophyll *a* (Chl *a*) analysis, and the filtrate for nutrients and total alkalinity
173 (TA) analysis. All the filters were pre-combusted (at 500° C for 6 h). Chl *a* concentrations were extracted in 90%
174 acetone and quantified spectrophotometrically before and after acidification of the samples, with formulations and
175 corrections proposed by Lorenzen (1967). Dissolved inorganic nitrogen, including ammonium (NH₄⁺), nitrite
176 (NO₂⁻), and nitrate (NO₃⁻) were quantified by the colorimetric method as in Grasshoff et al. (1999). TA was
177 determined on 60 mL of filtrate using the Gran (1952) electro-titration method with an automated titration system
178 (Metler Toledo model T50). The reproducibility of TA was about 3 μmol kg⁻¹ (n = 7). Measurements were
179 compared to certified reference material (CRM, provided by A. G. Dickson from Scripps Institution of
180 Oceanography) and consistent at a maximum accuracy level of 5 μmol kg⁻¹. pH was measured with a WTW 3310
181 pH meter equipped with a Sentix 41 electrode, calibrated in the National Institute of Standards and Technology
182 (NIST) scale, using a three point standard (pH 4.01, pH 7.00 and pH 10.01), always before and after each sampling
183 campaign. The precision of the pH measurements was about 0.01 (after seven verifications against standards).

184 Samples for dissolved CH₄ were collected in 30 ml, of pre-weighted serum glass bottles, completely filled with
185 water using a homemade sampler that prevents gas exchanges and bubble formation. After sealed, 0.2 ml of
186 saturated mercuric chloride were added in all bottles to prevent microbial activities. In the laboratory, a headspace
187 of 10 mL of N₂ were created in the samples, followed by a vigorous agitation to obtain a complete equilibrium
188 between the air and water phases inside the bottles. CH₄ concentrations were determined by gas chromatography
189 (GC) with flame ionization (FI methanizer detector) (Abril et al. 2007). In situ CH₄ concentrations were calculated
190 taking account the volume of water and headspace in the vial and solubility coefficient of methane of Yamamoto
191 et al. (1976), as function of temperature and salinity. Reproducibility of the CH₄ analysis was better than 5%.

192 **2.4. Calculations**

193 **2.4.1. Carbonate System**

194 The pCO₂ values and DIC concentrations were calculated using the concentrations of TA, pH, nutrients, seawater
195 temperature, and salinity by the CO₂calc 1.2.9 program (Robbins et al. 2010). The dissociation constants for
196 carbonic acid were those proposed by Mehrbach et al. (1973) refitted by Dickson and Millero (1987), the borate
197 acidity constant from Lee et al. (2010), the dissociation constant for the HSO₄⁻ ion from Dickson (1990) and the
198 CO₂ solubility coefficient of Weiss (1974). For the anoxic/hypoxic waters we calculated the pCO₂ and DIC using
199 the update version of the program CO₂SYS that include acid-base system of NH₄⁺ to TA (Xu et al. 2017).

200 **2.4.2. The excess of DIC (E-DIC) and Apparent Utilization of Oxygen (AOU)**

201 The excess of DIC (E-DIC, μmol kg⁻¹) was calculated according to Abril et al. (2003):

$$202 \text{E-DIC} = \text{DIC}_{\text{sample}} - \text{DIC}_{\text{equilibrium}},$$

203 Where DIC_{sample} represents the measured concentration of DIC (μmol kg⁻¹) and DIC_{equilibrium} is the theoretical DIC
204 at atmospheric equilibrium (μmol kg⁻¹). DIC_{equilibrium} was calculated from observed TA and the atmospheric pCO₂
205 measured in the estuary.

206 The apparent oxygen utilization (AOU, μmol kg⁻¹) was calculated as proposed by Benson and Krause (1984):

$$207 \text{AOU} = \text{DO}_{\text{equilibrium}} - \text{DO}_{\text{sample}}$$

208 Where DO_{sample} is the measured DO, and DO_{equilibrium} is the DO saturation.

209 **2.4.3. End-Member Mixing Models**

210 We applied mixing models to investigate the gains and losses of TA, DIC and δ¹³C-DIC along the estuary. The
211 model assumes conservative mixing for a solute (E) according to (Samanta et al. 2015):

$$212 E_{\text{mix}} = E_{\text{freshwater}}F_{\text{freshwater}} + E_{\text{marine}}(1 - F_{\text{freshwater}})$$

213 Where E_{mix} is the concentration of a given solute during conservative mixing (in our case TA and DIC), and the
214 subscripts freshwater and marine indicate the endmember concentrations in the river and the ocean, respectively.
215 The freshwater fraction (F_{freshwater}) is calculated as:

$$216 F_{\text{freshwater}} = 1 - \text{Sal}_{\text{sample}}/\text{Sal}_{\text{marine}}$$

217 Where Sal is the salinity, the subscript sample refers to the *in situ* values for each station.

218 **2.4.4. Calculations of air-water GHG fluxes**

219 Diffusive fluxes of CO₂ and CH₄ at the air-water interface were computed according to the following equation:

$$220 F(\text{GHG}) = \text{kg}, T \Delta \text{GHG}$$

221 Where F(GHG) represents the diffusive fluxes of CO₂ and CH₄, kg, T represents the gas transfer velocity of a given
222 gas (g) at a given temperature (T), and the ΔGHG represents the concentration gradient between the water and the
223 water at equilibrium with the overlying atmosphere. The considered atmospheric partial pressure of CO₂ and CH₄
224 were considered, respectively, 410 ppmv and 1.80 ppmv, which corresponds to global averages of atmospheric
225 GHG concentrations. These values are consistent with previous direct measurements of CO₂ and CH₄ atmospheric
226 concentrations realized near to the study area (Cotovicz et al. 2015, 2016).

227 For calculate the gas transfer velocity, we first normalized by a Schmidt number, applying the following equation
228 (Jähne et al. 1987):

$$229 K_{g,T} = k_{600} (600/Sc_{g,T})^n$$

230 Where k_{600} is the gas transfer velocity normalized to a Schmidt number of 600 ($Sc = 600$, for CO_2 at a temperature
231 of $20^\circ C$), $Sc_{g,T}$ is the Schmidt number of a gas at a given temperature (Wanninkhof, 1992), and n is related to wind
232 velocity, being equal to $2/3$ for wind speed $< 3.7 \text{ m s}^{-1}$, and equal to $1/2$ for higher wind velocities (Jähne et al.
233 1987; Guérin et al. 2007).

234 We used three empirical equations to derive k_{600} values: the parameterization as a function of wind speed applied
235 for oceanic waters by Wanninkhof (1992, W92), the parameterization as a function of wind speed estimated for
236 estuarine ecosystems by Raymond and Cole (2001, RC01), and the parameterization as a function of wind speed
237 produced by regressing the literature data in coastal environments by Jiang et al. (2008; J08). The three
238 parameterizations cover an important variability of values, with the value of W92 providing the lowest estimations,
239 and that of J08 providing the highest values of k_{600} .

240 The W92, RC01 and J08 parameterizations can be calculated applying the following equations:

$$241 k_{600}(W92) = 0.31(U_{10}^2)$$

$$242 k_{600}(RC01) = 1.91 \exp(0.35U_{10})$$

$$243 k_{600}(J08) = 0.314(U_{10}^2) - 0.436U_{10} + 3.99 \text{ (J08)}$$

244 Where k_{600} is the gas transfer velocity normalized to a Schmidt number of 600 (cm h^{-1}), U_{10} is the wind speed at
245 10 m height (m s^{-1}), v is the water current velocity in m s^{-1} , and S is the surface area of the estuary in km^2 . Water-
246 to-air CO_2 fluxes were calculated using the GHG concentrations for each sampled station. After, these fluxes per
247 station were daily-averaged considering the “polluted rivers” stations (1 to 5) and the “lagoons” stations (5 to 10)
248 using the averaged gas transfer velocities calculated for each day of sampling. Gas transfer velocities were
249 calculated from wind speed data, which were logged every hour and averaged at 12 h intervals throughout the
250 sampling days. The fluxes calculated for each domain, i.e., “polluted rivers” and “lagoons” were separated in
251 nighttime (measurements conducted before 09:30 a.m.) and daytime (measurements conducted after 09:30 a.m.)
252 periods to account for the diel wind patterns and then integrated over the entire sampled period and the entire
253 sampled area. We divided the gas transfer velocities in these periods because the region receive important
254 influences from marine brises, where the winds are stronger during midday/afternoon than during the night/early
255 morning (Amarante et al. 2002; Cotovicz et al. 2015). The meteorological data were kindly provided by the
256 National Institute of Meteorology (INMET). To compare the air-water fluxes of CH_4 with those of CO_2 we used
257 the concepts of global warming potential (GWP) and CO_2 equivalent emissions ($CO_2\text{-eq}$), by considering that 1g
258 of CH_4 has a GWP equivalent to 28g of CO_2 on a time horizon of 100 years (IPCC 2013).

259 2.5. Statistical Analysis

260 To verify if the data followed parametric or non-parametric distributions we applied the Shapiro-Wilk test. As the
261 data set was not normally distributed, we used the non-parametric and non-paired Man-Whitney test to compare
262 the average differences between the river and lagoons stations for each sampling campaign (spatial variability). The
263 non-parametric and paired Friedman Test was applied to compare the averages of sampled stations considering
264 the different sampling campaigns (temporal variability). Linear and non-linear regressions were calculated to
265 compare the distributions and correlations between variables. All statistical analysis were based on $\alpha = 0.05$. We
266 used the GraphPad Prism 6 program (GraphPad Software, Inc., La Jolla, California) to perform the statistical tests.

267 3. Results

268 3.1. Ancillary parameters

269 The main parameters analyzed in this study are provided in Table 1, with averages, standard deviations, and ranges.
270 The data were separated by sampling campaigns, and by sampled stations (rivers and lagoon). Box plots of the
271 main parameters, separated by sampling stations, with maximum, minimum, and medians are presented in the
272 supplemental file (Online Resource Fig. S1). Water temperature was related to the period of the year. The highest
273 temperatures were measured in summer, reaching a maximum of $29.0^\circ C$ in Mar-17, whereas the lowest
274 temperatures were measured in winter/autumn, with a minimum of $20.4^\circ C$ in Nov-17. The water temperature did

275 not present significant spatial differences when comparing rivers and lagoon (Mann-Whitney test, $p > 0.05$), except
276 in the campaign of Nov-17, when the lagoon stations presented lower temperature than the freshwaters (Mann-
277 Whitney test, $p < 0.01$). The salinity at river stations was always closest to 0, excepting at stations 4 and 5, which
278 present occasional saline intrusion reaching a maximum value of 5 (Tab. 1, Fig. 2). The salinity in the lagoon
279 stations ranged between 6.6 and 34. As expected, the highest salinities were observed in the stations located closest
280 to the mouth of the lagoon complex (stations 6 and 8).

281 DO concentrations exhibited strong depletion in the river stations, reaching values very close to 0 in almost all
282 stations and sampling campaigns (Tab. 01; Fig. 2f). Exceptions were verified in the station 4, which exhibited
283 occasional occurrence of high DO concentrations. In the lagoons, the concentrations of DO were variable, usually
284 exhibiting undersaturated conditions, with very little occasions of oversaturation with respect to the atmosphere
285 equilibrium (Fig. 2f). This pattern of DO distributions was inverse of that verified for the concentrations of NH_4^+
286 (Fig. 2g). The highest values of NH_4^+ were found in the hypoxic/anoxic freshwaters, reaching an extreme
287 maximum concentration of $5,660 \mu\text{mol L}^{-1}$. The concentrations of NH_4^+ decreased exponentially with the increase
288 of salinity and with the increase of DO concentrations (Fig. 3a), reaching a minimum of $3.5 \mu\text{mol L}^{-1}$. As expected,
289 DO distributions were positively related to the concentrations of NO_3^- (Fig. 3b). NO_3^- exhibited low concentrations
290 in the polluted rivers, with increasing tendency with the increase of salinity and DO concentrations (Fig. 3b). The
291 concentrations of Chl *a* were significantly lower in the freshwaters compared to the lagoon stations (Mann-
292 Whitney test, $p < 0.01$) (Fig. 2h). In general, the anoxic/hypoxic freshwaters presented low concentrations of Chl
293 *a*, excepting at station 4, which presented occasional occurrence of high Chl *a* concentrations, with an extreme
294 highest value of $347 \mu\text{g L}^{-1}$, and coincident with a peak in DO concentration (Fig. 2f,h). In the lagoon stations,
295 the distributions of Chl *a* were high variable (“patch distributions”), exhibiting the highest concentrations at
296 intermediate salinities (10-20). The results of Chl *a* for the sampling in May-2018 are not presented due to
297 problems during sampling.

298 3.2. Carbonate Chemistry

299 The distributions of TA and DIC were very different considering the river and lagoon stations (Fig. 2a,b). TA
300 and DIC concentrations were significantly higher in freshwaters compared to the lagoon waters (Mann-Whitney
301 test, $p < 0.001$), except in the campaign in Nov-17, when the river TA and DIC concentrations were lower than
302 the lagoons (Fig 2a,b). The ranges of concentrations of freshwater TA were between 572 and $3,680 \mu\text{mol kg}^{-1}$,
303 and for DIC these ranges varied between 652 and $4,026 \mu\text{mol kg}^{-1}$. Considering the lagoon stations, these ranges
304 varied between 1,431 and 2,567 for TA, and between 1,205 and 2,319 for DIC. DIC and TA distributions did not
305 exhibit a clear pattern with salinity. In the camping in Nov-17, the tendency between TA and DIC versus salinity
306 was positive, whereas for the other three sampling campaigns this relationship was negative. However, in all
307 sampling campaigns the distributions of TA and DIC showed large deviations from the conservative mixing
308 considering the end-member mixing models (Fig. 4). In general, the lagoon stations presented negative values of
309 ΔTA and ΔDIC (Δ representing the differences between measured DIC and/or TA concentrations and the
310 expected value for the conservative mixing), indicating important consumption of DIC and TA in the mixing
311 regions. The highest values of TA were found in hypoxic/anoxic waters, presenting positive relationship with
312 NH_4^+ concentrations and negative relationship with NO_3^- (Fig. 3c,d). A TA minimum was observed in the
313 middle salinity region, corresponding to lowest NH_4^+ , highest NO_3^- , DO and Chl *a* concentrations.

314 As expected, the river waters presented low values of pH, with a minimum value of 6.93, and average of $7.22 \pm$
315 0.20 (Tab. 1; Fig. 2d). The pH increased inside the lagoons, presenting the highest concentrations in the
316 intermediate salinities (10-20), and coincident with the highest values of Chl *a*, despite of the absent significant
317 correlation between these parameters. The values of pH were strongly correlated to the distributions of DO
318 concentrations (Fig. 5a).

319 3.3. Dissolved GHG concentrations and air-water fluxes

320 As showed for the most parameters analyzed in this study, the averaged values of $p\text{CO}_2$ were highly different
321 considering the “polluted rivers” and “lagoons” for all the sampling campaigns (Tab. 1, Fig. 2c). High
322 supersaturated conditions were observed in the anoxic/hypoxic river waters. The highest $p\text{CO}_2$ value was 20,417
323 ppmv. Freshwater $p\text{CO}_2$ exceeding 12,000 ppmv were verified in all sampling campaigns. In the lagoons, the
324 values decreased substantially, lowering about one order of magnitude. The average value was 764 ± 320 ppmv
325 in the lagoon stations. Values of $p\text{CO}_2$ below the equilibrium with the atmosphere were verified only in four
326 occasions, being three in the lagoons and one in the river domain, all related to high concentrations of Chl *a* and

327 oversaturation of DO (Fig. 2c,d,f). Considering all data (river and lagoon stations), the averaged values of $p\text{CO}_2$
328 were significantly different considering the sampling campaigns ($p < 0.05$; Friedman Test). We used the
329 relationship between the apparent utilization of oxygen (AOU) and the excess of dissolved inorganic carbon (E-
330 DIC) to investigate the influence of biological processes on the concentrations of DIC and DO (Fig. 5b). The
331 scatter plot of E-DIC versus AOU shows that the data of the lagoon stations were close to the 1:1 line. This line
332 represents the theoretical quotient of photosynthesis and respiration. The river stations presented a marked
333 deviation above the 1:1 line, corresponding to hypoxic/anoxic conditions.

334 For the distributions of CH_4 , the behavior was similar to that of $p\text{CO}_2$, exhibiting extreme supersaturation
335 conditions in the hypoxic/anoxic river waters (Figs. 2e, 5c). The highest CH_4 concentration was 288,572 nmol L^{-1}
336 $^{-1}$, coincident with anoxic conditions (0.1 % O_2), representing one of the uppermost concentration even reported in
337 coastal waters worldwide. All the concentrations of dissolved CH_4 were higher than 25,000 nmol L^{-1} in the
338 polluted rivers, excepting in one situation in the station 4 (Nov-17), which displayed concentration of 550 nmol
339 L^{-1} , and coincident with the high concentration of Chl a and supersaturation of DO. In the lagoons, the CH_4
340 concentrations decreased exponentially compared to the rivers, spanning between two to three orders of
341 magnitude. CH_4 concentrations in the lagoons ranged between 47 to 4,666 nmol L^{-1} . The CH_4 concentrations
342 were significantly different considering the sampling campaigns, including all data, and the river and lagoons
343 stations separately (rivers x lagoons). The highest concentrations of CH_4 in the river were observed in Nov-2017,
344 which was the sampling with the low rates of accumulated precipitation over 3 days (the precipitation rate
345 reaching the ground over the period of 3 days before sampling). The results of CH_4 in the month of May-2018
346 are not presented due to logistical problems during sampling.

347 The relationship between dissolved CH_4 concentrations and $p\text{CO}_2$ values were positive and statistically
348 significant for all sampling campaigns (Fig. 6). However, it is clear that the tendency was different considering
349 the sampled periods, with distinct slopes and intercepts. In two samplings (Mar-2017 and Nov-2017), the
350 relationship showed a linear tendency between these two parameters showing, respectively, the following
351 equations: $Y = 4.21 * X - 4179$; $R^2 = 0.97$; $p < 0.0001$ and $Y = 19.81 * X - 5119$; $R^2 = 0.91$; $p < 0.0001$. In the
352 sampling of Jun-2017, the relationship followed a non-linear trend, fitting in an exponential growth equation
353 type “one phase decay”, with the equation $Y = -6472 * 69867 * \exp(-0.00023 * X) + 69867$; $R^2 = 0.81$. This figure
354 also showed that for similar values of $p\text{CO}_2$ (~ 15,000 ppmv), the concentrations of CH_4 can span one order of
355 magnitude (from ~25,500 to 170,000 nmol L^{-1}).

356 The values of gas transfer velocities as well as fluxes of CH_4 and CO_2 are presented in Table 2. The gas transfer
357 velocities were lower for the calculated with the parametrization of W92, followed by the parameterization of
358 RC01 and J08. The k_{600} values ranged between 0.99 and 5.10 m s^{-1} for the river sampled stations, whereas for the
359 lagoon stations this range was between 1.12 and 6.13 m s^{-1} . In general, the k_{600} did not present significant
360 differences considering the sampling campaigns ($p > 0.05$; Friedman Test), except in the sampling of Nov-17 in
361 the second day of sampling, when the values of wind speed were higher. The calculated diffusive fluxes of CO_2
362 and CH_4 at the air-water interface showed marked differences considering the river and lagoons stations, with the
363 river showing very higher emissions than the lagoons (Tab. 2). The fluxes calculated for each sampling
364 campaign, including fluxes for the river and lagoon stations separately, as well as the fluxes with all data (area-
365 weighted). The emissions of CO_2 and CH_4 , with the averages and standard deviations calculated with the three
366 parameterizations are presented in supplemental file (Online Resource Fig. S2). The river stations always
367 showed high emissions of CO_2 , with averages of emissions ranging between 72.85 and 652.48 $\text{mmol C m}^{-2} \text{d}^{-1}$.
368 For the lagoons, the emissions spanned between one to two orders of magnitude lower than the rivers. The
369 emissions in the lagoons ranged between 4.27 and 17.59 $\text{mmol C m}^{-2} \text{d}^{-1}$. The samplings in Mar-17 and May-18
370 showed the higher emissions, whereas the samplings in Jun-17 and Nov-17 showed the lower. Considering all
371 the lagoon complex (area-weighted including rivers and lagoons stations), the CO_2 emissions ranged between 9.8
372 to 70.5 $\text{mmol C m}^{-2} \text{d}^{-1}$. For the diffusive emissions of CH_4 , the rivers showed extreme high values of degassing,
373 with the magnitudes of emissions being between two and three orders of magnitude higher than those verified in
374 the lagoon stations. The ranges of riverine CH_4 emissions were between 22.58 to 185.12 $\text{mmol C m}^{-2} \text{d}^{-1}$. In the
375 lagoons, the emissions ranged between 0.2 to 1.4 $\text{mmol C m}^{-2} \text{d}^{-1}$. Considering all the lagoon complex (area-
376 weighted of rivers and lagoons), the CH_4 emissions ranged between 2.2 and 16.5 $\text{mmol C m}^{-2} \text{d}^{-1}$.

377

378 4. Discussion

379 4.1. The high concentrations of TA and DIC in hypoxic/anoxic river waters

380 TA is considered a relative conservative property of natural waters (Kempe 1990; Wolf-Gladrow et al. 2007). In
381 estuaries, TA generally shows a linear distribution versus the salinity exhibiting conservative mixing. However,
382 in coastal regions enriched in organic matter where anaerobic processes are significant, the assumption of
383 conservatively TA can be abusive because the reactions of reduction and oxidation are coupled to proton
384 production and consumption, contributing to changes in TA (Abril and Frankignoulle 2001; Hu and Cai 2011).
385 Indeed, anaerobic decomposition of organic matter by denitrification, reduction of iron and manganese oxides,
386 and sulfate reduction are proton consuming processes that will produce TA and DIC with specific stoichiometric
387 ratios. Table 3 presents the stoichiometry of main chemical reactions involved in generation/consumption of TA
388 in coastal regions. In the polluted rivers of the JLC, it is clear that the permanent hypoxic/anoxic conditions
389 favors the production of TA and DIC in waters and sediments due to the high TA concentrations in the
390 freshwater end-members in almost all sampling campaigns and stations. The exception was verified in the
391 sampling of Jun-2017 that occurred under conditions of high accumulated precipitation when 3 river stations
392 presented low TA, suggesting dilution during rainy conditions. The rivers of the JLC watershed are inserted in a
393 region of low-carbonate minerals, which contributes with very low concentrations of TA (Meybeck and Ragu
394 2012). The background values of TA in the regions located upstream to the urban influences are low (~ 300-400
395 $\mu\text{mol kg}^{-1}$). Considering that freshwater TA concentrations ranged between 572 to 4,022 $\mu\text{mol Kg}^{-1}$, the
396 contribution of anaerobic processes on generation of TA is estimated at about 30 to 90%. These values are very
397 similar to that found in the polluted Scheldt estuarine basin in the Belgium (Abril and Frankignoulle 2001),
398 where the authors found bicarbonate (HCO_3^-) concentrations 2-10 times higher than the representative
399 concentrations reported in pristine basins. The authors calculated that 22% to 63% of TA concentrations were
400 attributed to process involving nitrogen cycling (ammonification, nitrification and denitrification).

401 The plot between the deviation from the conservative mixing of TA and DIC (ΔTA and ΔDIC) reveals regions of
402 gains and losses of TA and DIC along the lagoon complex (Fig. 4). Data points from the river stations presented
403 always-positive values, consistent with the production of TA and DIC. The distributions of ΔTA and ΔDIC
404 follows mainly the vectors which represent the processes of carbonate dissolution, sulphate reduction and
405 denitrification (see the figure caption for detailed descriptions, and Tab. 3). Carbonate dissolution is unlikely to
406 occur due to the low concentration of carbonate minerals in the watershed, whereas denitrification and sulphate
407 reduction are likely to occur in a significant way. Overall, the highest concentrations of TA were coincident with
408 the highest concentrations of NH_4^+ (Fig. 3c), possibly reflecting the denitrification process. The exception was
409 verified in Jun-2017, which occurred under high rainy conditions (highest accumulated precipitation before 7
410 days of sampling), when TA seemed to be diluted and NH_4^+ concentrations still high possibly reflecting the
411 urban runoff. Overall, the rivers of the JLC presented remarkably high NH_4^+ concentrations, in the same order of
412 magnitude verified only in the high polluted Adyar estuary – India (average between 1,200 and 3,000 $\mu\text{mol L}^{-1}$;
413 Nirmal-Rajkumar et al. 2008), and well above than found in rivers enriched in nitrogen (McMahon and Dennehy
414 1999). These values are comparable to those found in municipal wastewaters (Hammer and Hammer 2012).
415 Denitrification produces DIC and TA which generates nitrogen (N_2), which in turn escapes to the atmosphere
416 (Abril and Frankignoulle 2001; Thomas et al. 2009). This represents an irreversible generation of TA, because
417 the product resists or escapes re-oxidation by oxygen (Thomas et al. 2009). The same is valid for the sulfate
418 reduction, which generates hydrogen sulfite (H_2S) (Thomas et al. 2009). However, TA, NH_4^+ , NO_3^- and DO
419 concentrations in the intermediate salinities suggest that during river-ocean mixing are occurring important
420 processes of re-oxidation that can be a sink for TA compensating the TA generated in the anoxic waters (Hu and
421 Cai 2011; Gustafsson et al. 2019) (see next section of the manuscript).

422 The aerobic respiration can also contribute to the increases of DIC concentrations in heterotrophic waters
423 (Borges and Abril 2011); however, in these polluted and anoxic riverine stations this process seems to be minor
424 compared to anaerobic/anoxic processes. This can be confirmed by looking at the relationship between E-DIC
425 and AOU (Fig. 5b). The data points of the river stations present strong deviation above the 1:1 line, which
426 represents the theoretical quotient between photosynthesis and respiration. This means that additional processes
427 are contributing to the production of DIC that are not linked to the aerobic microbial respiration. This graph
428 shows that the production of DIC can continue even if the oxygen is depleted. These conditions were verified in
429 high $p\text{CO}_2$ estuaries, and attributed mainly to lateral inputs of dissolved CO_2 and anoxic production in waters
430 and sediments (Cai et al. 1999; Abril et al. 2002; Borges and Abril 2011).

431 4.2. The carbonate chemistry in the lagoon waters

432 Contrary to the exposed above for the rivers, the lagoon stations present important losses of TA and DIC along
433 the salinity gradient, with prevalence of negative values of Δ TA and Δ DIC in these more oxygenated waters
434 (Fig. 4). Comparing the covariations of Δ TA and Δ DIC along the salinity gradient, the data points followed
435 mainly the vectors representing the processes of sulphur oxidation, iron oxidation and nitrification that are
436 involved only in the consumption of TA, without net effect on DIC (Abril and Frankignoulle 2001; Baldry et al.
437 2019; Rassmann et al., 2020). In the lagoons, the mixing of anoxic-acid freshwaters with well-oxygenated waters
438 is associated with processes of re-oxidation of reduced by-products of organic matter degradation, generating
439 titration of TA to dissolved CO_2 particularly evident in the middle salinity regions. These intermediate saline
440 waters (10-20) presented the lowest TA concentrations and well-below than freshwater and marine end-
441 members, coincident with minimum concentrations of NH_4^+ , and maximum concentrations of NO_3^- and DO. The
442 nitrification is a process that consumes TA, when NH_4^+ is oxidized to NO_3^- , producing 2H^+ . TA concentrations
443 present an important and inverse relationship with NO_3^- concentrations, corroborating this assumption (Fig. 3b).
444 This suggests that this is an area where nitrification is complete, counter-acting the process of denitrification that
445 occurs in the anoxic freshwaters, compensating the TA generated in anoxic waters. In this way, the lagoon
446 reflects a combination of processes, which are the denitrification and ammonification in anoxic conditions,
447 nitrification in well-oxygenated conditions. Indeed, the complete coupling of ammonification-nitrification-
448 denitrification does not lead to net TA gain (Hu and Cai 2011). In addition, the re-oxidation of all other reduced
449 compounds (H_2S , Fe^{2+} , Mn^{2+} , and also a part of CH_4) is probably also complete. However, it must be stressed
450 that the re-oxidation of reduced species are often complex involving many intermediate steps and side products
451 (Cai et al. 2017). The re-oxidation decreases the TA down to $1,500 \mu\text{mol kg}^{-1}$, much lower than the end-
452 members concentrations. Important re-oxidation processes were described in the high-polluted Scheldt basin,
453 when the ecosystem changes from reducing to oxidizing conditions (Abril and Frankignoulle 2001).

454 The process of primary production is also probably to occur in the mixing zone, with significant changes in DIC
455 concentrations due to the uptake by primary production. Occasional occurrence of phytoplankton blooms were
456 found in the lagoon stations (highest value of Chl *a* of $77 \mu\text{g L}^{-1}$), with decreasing concentrations of DIC, and
457 increasing levels of pH and dissolved oxygen. The process of primary production can be strongly stimulated by
458 high availability of nutrients in the water column, shallow depths, high temperature and high incidence of
459 photosynthetically active radiation (Cotovicz et al. 2015). The influence of biological activities on the carbonate
460 chemistry is apparent comparing the E-DIC versus AOU values (Fig. 5b). Positive E-DIC and AOU values
461 suggest that the system is predominant heterotrophic. The regression line between E-DIC and AOU for the
462 lagoon stations (green line) is very close to the line 1:1, suggesting that the processes of gross primary
463 production and total respiration are coupled in the lagoons (but not in the rivers). This was also showed in the
464 Guanabara Bay (Rio de Janeiro, Brazil), an eutrophic coastal embayment dominated by phytoplankton blooms
465 (Cotovicz et al. 2015) and located close to the JLC. However, for JLC other biogeochemical processes described
466 above like denitrification-nitrification and iron reduction-oxidation can also follow closely the 1:1 line (Tab. 3).
467 The biological influences on the carbonate chemistry are also apparent looking at the relationship between O_2
468 and pH (Fig. 5a). This graph shows a strongly significant and positive relationship between these parameters (R^2
469 = 0.94, $p < 0.0001$). In general, the river stations present very low values of pH coincident with hypoxic/anoxic
470 conditions.

471 4.3. Spatial distributions of dissolved CO_2 and CH_4 in the JLC

472 Inner and low-salinity estuarine regions have been documented as heterotrophic and large CO_2 emitters
473 (Frankignoulle et al. 1998; Silvennoinen et al. 2008). In several coastal waters worldwide, important CO_2
474 changes have been strongly related to eutrophication (Borges and Gypens 2010; Cai et al. 2011; Sunda and Cai
475 2012; Cotovicz et al. 2015; Brigham et al. 2019). Overall, when untreated urban wastewater discharges from
476 megacities reach estuarine waters, they enhance the levels of CO_2 especially in turbidity coastal waters located at
477 the vicinity of outfalls (Frankignoulle et al. 1998; Zhai et al. 2007; Sarma et al. 2012; Brigham et al. 2019).
478 These characteristics of high $p\text{CO}_2$ values are observed in the polluted rivers that compose the drainage basin of
479 the JLC. The averaged values of $p\text{CO}_2$ in these rivers ranged between 6,838 and 13,641 ppmv. These values
480 were verified only in highly impacted estuaries, i. e., Tapti Estuary – India (Sarma et al. 2012), Scheldt Estuary –
481 Belgium (Frankignoulle et al. 1998), Pearl River – China (Guo et al. 2009). The river waters of the JLC
482 presented an extreme oxygen depletion reaching anoxic conditions in surface waters in almost all stations and
483 sampling campaigns, all related to supersaturation of $p\text{CO}_2$. The wastewater contribution is corroborated by the
484 massive NH_4^+ concentrations reaching concentrations measured in municipal wastewaters (Hammer and
485 Hammer 2012).

486 Following the seaward direction, the levels of $p\text{CO}_2$ decreases exponentially with the increases of salinity. This
487 decrease is associate with degassing, biogeochemical processes and mixing with low- $p\text{CO}_2$ waters (Cotovicz et
488 al. 2020). The CO_2 degassing is strongest at the freshwater stations, taking account that the dissolved
489 concentrations are at the highest in this estuarine region, creating a steep gradient between the $p\text{CO}_2$ in the air
490 and in the water. The freshwaters enters in the lagoon with highly reduced conditions, but the mixing with more
491 oxygenated waters creates conditions favoring important processes of re-oxidation, as discussed above. The
492 processes of manganese reduction and iron reduction are linked to the production of CO_2 and consumption of TA
493 in transitional oxic/anoxic estuarine regions (Abril and Frankignoulle 2001). In this way, the $p\text{CO}_2$ values
494 reflects both the physical mixing, and the biogeochemical processes. For intermediate to high-salinities the low
495 values of $p\text{CO}_2$ values are expected due to the mixing with low- $p\text{CO}_2$ seawaters (Chen et al. 2013; Cotovicz et
496 al. 2020), taking account that the adjacent coastal waters present $p\text{CO}_2$ averaging 411 ppmv (Cotovicz et al.,
497 2015). The uptake of CO_2 by primary producers are likely to occur since that phytoplankton blooms occurred in
498 some stations, and also attributed to this marked decline of $p\text{CO}_2$. Overall, $p\text{CO}_2$ values did not present a clear
499 seasonal tendency; however the lowest average of $p\text{CO}_2$ in the rivers were found in June-2017, when the
500 accumulated precipitation of 7 days was at highest levels, probably associate with dilution.

501 Approaching the behavior generally found for CO_2 , CH_4 concentrations are often much greater in the uppermost
502 portion of estuaries (Upstill-Goddard et al. 2000; Middelburg et al. 2002; Upstill-Goddard and Barnes 2016).
503 The methanogenesis is a process of organic matter degradation that is favored when all the other proton
504 acceptors are depleted (i.e., nitrate, sulphate, manganese), occurring in hypoxic/anoxic conditions. High CH_4
505 concentrations are frequently found in water and wastewater throughout integrated urban drainage systems
506 composed of sewer systems, wastewater treatment plants and receiving water bodies (Nirmal-Rajkumar et al.
507 2008; Yu et al., 2017). The primary methanogenic pathways are the conversion of acetate to CO_2 and CH_4 , and
508 reduction of CO_2 with H_2 (Whitman et al. 1992; Matson and Harriss 2009). In severely impacted estuaries, the
509 CH_4 concentrations can span several orders of magnitude spatially and temporally (Nirmal-Rajkumar et al. 2008;
510 Burgos et al. 2015; Cotovicz et al. 2016). The concentrations of dissolved CH_4 found in surface waters of JLC
511 are very high, with an extreme maximum of 288,572 nmol L^{-1} in the river zone. To our best knowledge, this is
512 the second highest concentration measured for any natural river–estuarine system, only behind that measured in
513 the Adyar Estuary (maximum of 386,000 nmol L^{-1} ; Nirmal-Rajkumar et al. 2008). Indeed, a study proposed a
514 rank of averaged dissolved CH_4 concentrations in estuarine environments (Cotovicz et al. 2016). Updating this
515 rank, the waters of JLC presented, on average, the second highest CH_4 estuarine water concentrations worldwide
516 (average of 976 nmol L^{-1}). Only strongly polluted estuaries occupy the other firsts positions: Adyar Estuary –
517 India (2,200 nmol L^{-1} ; Nirmal Rajkumar et al. 2008), Guadalete Estuary – Spain (590 nmol L^{-1} ; Burgos et al.
518 2015) and Guanabara Bay – Brazil (456 nmol L^{-1} ; Cotovicz et al. 2016). The anthropogenic-derived organic
519 carbon in the JLC is likely to be massive taking account that the watershed hosts a huge population and the
520 wastewater treatment covers less than 30% of the total households. The levels of accumulated precipitation were
521 not correlated to the concentrations of CH_4 , however, highest concentrations were observed in Nov-2017 (when
522 the accumulated precipitation of 7 days before sampling was low), preventing the dilution by rain water. Heavy
523 rain events could occur in the region, with possibility to alter the CO_2 and CH_4 concentrations. Climatological
524 and hydrological effects on GHG dynamics needs further investigation.

525 There was a positive correlation between $p\text{CO}_2$ and CH_4 in all campaigns, suggesting a common source of these
526 two gases (Fig. 6). However, for similar $p\text{CO}_2$ values, the concentrations of CH_4 were higher, spanning until one
527 order of magnitude. This was also showed in other estuaries, for example described in tropical mangrove-
528 dominated estuaries of Australia, where the authors attributed this pattern to a mosaic of processes, including the
529 presence of sewage treatment plants, differential groundwater and riverine carbon inputs, and exchange with
530 vegetated coastal habitats (Rosentreter et al. 2018). In JLC, the high presence of untreated domestic effluent
531 discharges associated with strong oxygen depletion seems to enhance disproportionately the production of CH_4
532 compared to CO_2 , particularly in the sampling in Nov-17. According to the analysis of Borges and Abril (2011),
533 and after updated by Cotovicz et al. (2016), there is a positive relationship between CH_4 and $p\text{CO}_2$ in well-mixed
534 estuarine systems, and a marked negative relationship in stratified estuarine systems. In well mixed systems, CH_4
535 and CO_2 present a positive tendency due to degradation of allochthonous organic matter in soils and sediments
536 that are then transported to the estuary, i. e., CO_2 and CH_4 present a same origin. In stratified systems the
537 relationship is negative because the autochthonous organic matter is produced by primary producers in surface
538 waters, lowering the $p\text{CO}_2$. The produced organic matter is further transferred across the pycnocline and
539 promoting anoxic conditions in bottom layers due to organic matter degradation, favoring the methanogenesis in
540 bottom water and sediments (Fenchel et al. 1995; Koné al. 2010). This produced CH_4 is further transported to

541 surface water by advection and diffusion, turning the surface waters enriched in CH₄. However, these tendencies
542 seems to be “perturbed” in anoxic and organic-rich coastal waters, when the CH₄ production is disproportionately
543 favored.

544 4.4. Diffusive emissions of CO₂ and CH₄

545 According to the most recent global compilation of estuarine CO₂ emissions propose by Chen et al. (2013),
546 upper estuaries are sources of CO₂ on the order of 106 mmol C m⁻² d⁻¹, mid-estuaries emit 47 mmol C m⁻² d⁻¹,
547 and lower estuaries with salinities more than 25 are sources of 23 mmol C m⁻² d⁻¹. Considering all JLC, the
548 emissions ranged between 22.00 to 48.67 mmol m⁻² d⁻¹. In this way, the CO₂ emissions in the JLC are very close
549 to the ranges estimated in other estuaries. However, considering only the river stations, the CO₂ outgassing
550 ranged between 199 to 435 mmol C m⁻² d⁻¹. These values are between 2 to 4-fold higher than the averaged
551 emissions of CO₂ by freshwaters and low salinity regions of estuaries. Emissions on this order of magnitude
552 were found only in high-impacted estuaries and carbon-rich environments, for example, in the Cochin Estuary -
553 India (267 mmol C m⁻² d⁻¹; Gupta et al. 2009); Douro, Elbe, Loire, Scheldt, and Sado - European Estuaries
554 (between 155 and 396 mmol C m⁻² d⁻¹; Frankignoulle et al. 1998; Abril et al. 2003); Potou lagoon - Ivory Coast
555 (186.0 mmol C m⁻² d⁻¹; Koné et al 2009); Tapti Estuary – India (362 mmol C m⁻² d⁻¹; Sarma et al. 2012).

556 The air-water CH₄ fluxes to the atmosphere are strongly related to typology of coastal ecosystems, and also the
557 degree of human influence. Concerning diffusion only, the air-water CH₄ fluxes ranges from 0.04 ± 0.17 mmol C
558 m⁻² d⁻¹ for coastal plumes to 1.85 ± 0.99 mmol C m⁻² d⁻¹ for fjords and coastal lagoons, with intermediate values
559 for low salinity zones, marsh and mangrove creeks (Borges and Abril 2011). Considering the ecosystem as a
560 whole, the JLC presented emissions varying between 2.19 to 16.47 mmol m⁻² d⁻¹, which are among the highest
561 documented in estuaries worldwide. The CH₄ emissions on this order of magnitude were found only in high-
562 impacted ecosystems, for example, in the Adyar Estuary – India (4.70 mmol m⁻² d⁻¹; Nirmal-Rajkumar et al.
563 2008); Coastal Lagoon of the Ivory Coast (2.40 mmol m⁻² d⁻¹; Koné et al. 2010) and Guanabara Bay – Brazil
564 (0.24 to 4.79 mmol m⁻² d⁻¹; Cotovicz et al. 2016). The average flux intensities in the JLC are between two and
565 three order of magnitude higher than values normally found in shelf waters (~0.03 mmol m⁻² d⁻¹) and between
566 four and five orders of magnitude higher than values of the open ocean waters (~0.0004 mmol m⁻² d⁻¹) (Borges
567 et al. 2016).

568 We used the global warming potential (GWP) and CO₂-equivalent emissions (CO₂-eq) (IPCC 2013) to compare
569 the fluxes of CH₄ with those of CO₂. This metric was calculated with the gas transfer velocity of RC01. After
570 converting to CO₂-eq, the emissions of CO₂ ranged between 1.11 to 2.94 g CO₂-eq m⁻² d⁻¹. For CH₄ the CO₂-eq
571 emissions ranged between 2.17 to 6.11 g CO₂-eq m⁻² d⁻¹ (Tab. 4). Expressed as CO₂-eq, CH₄ accounted for a
572 major portion of the GHG warming potential in the lagoon (between 46% to 80%) especially in the river stations
573 where the CH₄ was always more important than CO₂. This is unusual since that normally CO₂ is the main GHG
574 in aquatic coastal ecosystems (Campeau et al. 2014; Sadat-Noori et al. 2018). However, studies have suggested
575 that CH₄ can be the main source of CO₂-eq emissions in smaller streams of fluvial network and mangrove
576 ecosystems (Campeau et al. 2014; Sea et al. 2018). Now, we are showing that in extremely impacted ecosystem
577 the CH₄ is the most important GHG in terms of CO₂eq. This study quantified only the diffusive emissions of
578 CH₄, however coastal areas ensures several pathways of CH₄ to the atmosphere, including the ebullition.
579 Ebullition is probable to occur in the JLC, since that the threshold value of 5x10⁴ nmol L⁻¹ of dissolved CH₄
580 beyond which bubbles can forms in aquatic sediments (Chanton et al. 1989) was regularly surpassed in the
581 polluted rivers. Bubble evasion from the surface waters was visually observed in the river stations, which could
582 make CH₄ contribution even stronger.

583 5. Conclusions

584 Our study reveals some of the biogeochemical processes that occur in the case of strongly polluted rivers
585 discharging to coastal lagoons, with considerable effects on carbonate chemistry and emissions of CO₂ and CH₄
586 to the atmosphere. The rivers that compose the watershed are highly polluted, presenting quasi-permanent
587 situations of oxygen depletion. These rivers receive large amounts of anthropogenic-derived organic matter,
588 mostly from domestic effluents, that are discharged “*in natura*” in the waters. This large amount of fresh organic
589 matter contributes to strong oxygen consumption linked to the intense heterotrophic activities reaching
590 conditions of hypoxia and anoxia. Anaerobic processes such as denitrification and sulphate reduction are
591 intrinsically coupled to the transfer of protons, which favor the production of TA. These processes also

592 contribute with production of DIC. The calculated emissions of CO₂ and CH₄ in these polluted rivers are among
593 the highest documented in coastal waters.

594 For the lagoon stations, the deviation from the conservative mixing suggested that additional processes are
595 taking place along the river-ocean continuum. The concentrations of TA, DIC, CO₂ and CH₄ decreased
596 substantially from the rivers to the lagoon waters. The decreases of TA and DIC are attributed to re-oxidation
597 processes such as sulphur oxidation, iron oxidation and nitrification during the mixing of anoxic freshwaters
598 with oxic estuarine waters. The marked decreases of DIC concentrations are also attributed to air-water
599 exchanges (CO₂ outgassing), and primary production. The lagoon waters remains with CO₂ oversaturated
600 conditions, however, the growth of large phytoplankton blooms contributed with occasional conditions of
601 subsaturation, associated with high DO and pH. For CH₄, the main processes are the mixing with low-CH₄
602 seawaters, degassing and CH₄ oxidation. Considering only the lagoon stations, the CO₂ emissions are on the
603 same order of magnitude verified in other ecosystems worldwide, however, for the CH₄ these emissions are
604 among the highest already reported.

605 Compared in terms of CO₂eq, the CH₄ emissions were most important than CO₂, suggesting that ecosystems
606 strongly polluted by anthropogenic-derived organic carbon produces more CH₄ comparatively to CO₂, especially
607 under strong oxygen depletion. These results confirm that severely polluted and eutrophicated coastal lagoons
608 are hotspot of GHG emissions. Therefore, global carbon budgets assertions in coastal regions must include these
609 eutrophicated areas in order to increase the reliability of the proposed estimates. In addition, urgent actions are
610 needed with purposes to reduce the eutrophication in urban coastal ecosystems, in order to mitigate the climate
611 change and to improve the ecosystem health.

612 **Declarations**

613 Ethics approval and consent to participate: Not applicable

614 Consent for publication: Not applicable

615 Availability of data and materials: The datasets used and/or analysed during the current study are available from
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617 Competing interests: The authors declare that they have no competing interests.

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620 Authors' contributions: LCCJr: Conceptualization, Coordination, Execution, Data curation, Formal analysis,
621 Methodology, Writing - original draft. RPR: Laboratorial Analysis, Writing – review. LOV, CRR, DT:
622 Execution, Laboratorial Analysis. MB, RS: Conceptualization, Execution, Writing – review. BAK:
623 Conceptualization, Funding acquisition, Supervision, Writing – review. GA: Conceptualization, Data curation,
624 Formal analysis, Methodology, Supervision, Writing - original draft.

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630 **Figure Captions**

631 **Fig. 1** Map showing the localization of the Jacarepagua Lagoon Complex (JLC). The red squares represent the
632 locations of river stations. The green squares represent the locations of lagoon stations. The yellow line
633 represents the contour of the lagoons and the rivers. The orange line refers to an ecological barrier that impedes
634 the navigation in the landward direction.
635

636 **Fig. 2** Distributions of the main parameters analyzed in this study along the salinity gradient. The red circles
637 represent the river stations, whereas the green circles represent the lagoon stations.

638 **Fig. 3** Scatter plots between: a) NH_4^+ and O_2 ; b) NO_3^- and O_2 ; c) NH_4^+ and TA; d) NO_3^- and TA including all
639 stations and sampling campaigns.

640 **Fig. 4** Deviations from conservative mixing lines of TA (ΔTA) as a function of DIC (ΔDIC) in the river stations
641 (red dots) and lagoon stations (green dots), for all sampling campaigns. The unitless directional vectors
642 representing the slopes of the following processes: (1) iron reduction; (2) carbonate dissolution; (3) sulphate
643 reduction; (4) denitrification; (5) CO_2 influx (ingassing); (6) aerobic respiration; (7) sulphur oxidation, iron
644 oxidation and nitrification; (8) carbonate precipitation, (9) CO_2 efflux (degassing); (9) primary production.

645 **Fig. 5** Graph a) shows the relationship between pH and O_2 , for all sampling campaigns. The black line represents
646 the linear regressions. Graph b) shows the relationship between the excess dissolved inorganic carbon (E-DIC)
647 and apparent utilization of oxygen (AOU). The 1:1 black line represents the quotient between CO_2 and O_2 during
648 the processes of photosynthesis and respiration. The green line represents the linear regressions considering only
649 the lagoon stations. Graph c) shows the relationship between the concentrations of CH_4 and apparent utilization
650 of oxygen (AOU). Note that the y-axis is logarithmic. Red dots are the station in the rivers, and green dots are
651 the stations in the lagoons.

652 **Fig. 6** CH_4 dissolved concentrations vs. average partial pressure of CO_2 ($p\text{CO}_2$) for the sampling campaigns in
653 Mar-2017, Jun-2017 and Nov-2017. For the Mar-2017 the blue line represents the linear regressions. For Mar-
654 2017 and Nov-2017 the relationship showed a linear tendency, whereas for Jun-2017 the relationship followed a
655 non-linear trend, fitting in an exponential growth.

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Table 1 Mean, standard deviation, minimum, and maximum values of the main water properties of JLC investigated in this study, separated in “river” and “lagoon” stations, for all sampling campaigns.

	Temp. (°C)	Salinity	pH (NBS)	Chl <i>a</i> (µg L ⁻¹)	DO (%sat)	TA (µmol kg ⁻¹)	DIC (µmol kg ⁻¹)	<i>p</i> CO ₂ (ppmv)	CH ₄ (nmol L ⁻¹)	N-NH ₄ ⁺ (µmol L ⁻¹)
Mar-2017										
Rivers	26.6 ± 1.1 23.9 / 27.7	1.0 ± 1.1 0.2 / 4.0	7.09 ± 0.07 7.02 / 7.26	7.1 ± 12.9 0.2 / 30.2	2.1 ± 1.7 0.1 / 6.1	3,004 ± 194 2,618 / 3,313	3435 ± 306 3012 / 3846	13,641 ± 3,211 8,931 / 16,974	47,285 ± 22,731 25,573 / 70,913	2,154 ± 990 887 / 3,333
Lagoons	27.5 ± 1.1 25.9 / 29.0	19.3 ± 3.6 11.2 / 24.9	7.90 ± 0.05 7.84 / 7.97	13.9 ± 9.9 5.3 / 30.4	57.4 ± 23.9 24.3 / 86.2	1,868 ± 338 1,431 / 2,263	1802 ± 401 1,385 / 2,233	872 ± 240 577 / 1,226	392 ± 304 92 / 723	312 ± 249 129 / 677
Jun-2017										
Rivers	22.5 ± 0.3 22.2 / 23.4	0.2 ± 0.0 0.2 / 0.3	7.12 ± 0.08 6.93 / 7.22	0.6 ± 0.2 0.3 / 0.9	3.9 ± 0.8 (2.0 5.5)	1,400 ± 836 572 / 3,268	1,663 ± 1,408 652 / 4,028	6,878 ± 7,801 1,927 / 20,417	43,637 ± 17,408 30,677 / 68,336	2,542 ± 432 1,028 / 3,477
Lagoons	22.9 ± 1.0 22.0 / 24.6	16.1 ± 5.2 6.6 / 24.8	8.10 ± 0.43 7.63 / 8.67	17.0 ± 7.1 9.58 / 26.71	81.8 ± 38.9 35.0 / 140.0	1,694 ± 229 1,497 / 2,047	1,599 ± 358 1,267 / 2,032	821 ± 708 109 / 1,603	1,415 ± 1,878 47 / 4,660	104 ± 45 58 / 177
Nov-2017										
Rivers	25.6 ± 0.6 24.9 / 26.7	1.2 ± 1.5 0.2 / 5.1	7.51 ± 0.45 7.13 / 8.64	73.3 ± 153.5 2.1 / 347.9	28.2 ± 42.7 1.0 / 135.0	2,949 ± 466 2,450 / 3,680	3,029 ± 755 2,003 / 3,918	8,127 ± 5,066 218 / 13,742	159,178 ± 105,131 550 / 288,572	3,353 ± 1,721 868 / 5,660
Lagoons	21.6 ± 1.3 20.4 / 24.2	26.9 4.9 21.2 / 31.8	8.12 ± 0.09 8.04 / 8.30	34.6 ± 35.4 3.6 / 77.0	87.4 ± 12.2 73.1 / 112.0	2,169 ± 495 1,449 / 2,567	1,975 ± 515 1,205 / 2,287	523 ± 217 215 / 725	1,121 ± 1,610 199 / 3,528	35 ± 47 3.5 / 105
May-2018										
Rivers	25.9 ± 0.4 25.3 / 26.6	0.6 ± 0.4 0.2 / 1.6	7.18 ± 0.22 6.97 / 7.63	-	1.7 ± 0.4 1.4 / 2.8	2,860 ± 265 2,399 / 3,062	3,226 ± 259 2,853 / 3,560	11,500 ± 5,398 3,856 / 17,096	-	3,126 ± 1,348 768 / 4,078
Lagoons	24.9 ± 1.0 23.7 / 27.2	26.0 ± 5.6 16.0 / 34.0	7.92 ± 0.04 7.84 / 7.97	24.0 ± 5.9 18.3 / 32.7	71.0 ± 9.4 52.4 / 85.6	2,173 ± 326 1,659 / 2,441	2,055 ± 292 1,594 / 2,319	843 ± 117 716 / 981	-	294 ± 332 96 / 876

Table 2 Average values of gas exchange velocity (k_{600}), and air-water CO₂ and CH₄ fluxes calculated according to Wanninkhof (1992), Raymond and Cole (2001) (RC01) and Jiang et al. (2008) (J08), separated by river and lagoon stations, and integrated for entire superficial area, for each sampling campaign.

	k_{600} cm h ⁻¹			CO ₂ flux mmol m ⁻² d ⁻¹			CH ₄ flux mmol m ⁻² d ⁻¹		
	W92	RC01	J08	W92	RC01	J08	W92	RC01	J08
Mar-2017									
Rivers (1.07 Km ²)	2.84	4.88	5.10	363.34	624.33	652.48	38.19	65.63	68.59
Lagoons (12.08 Km ²)	2.24	4.40	4.75	8.95	17.59	18.99	0.24	0.48	0.51
All system area-weighted (13.15 Km ²)				37.78	66.95	70.50	3.33	5.78	6.05
Jun-2017									
Rivers (1.07 Km ²)	2.06	4.24	4.64	126.25	259.86	284.38	22.58	46.47	50.85
Lagoons (12.08 Km ²)	1.12	3.44	4.15	4.46	13.70	16.53	0.38	1.18	1.42
All system area-weighted (13.15 Km ²)				14.36	33.72	38.32	2.19	4.86	5.45
Nov-2017									
Rivers (1.07 Km ²)	0.99	3.32	4.09	72.85	244.32	300.98	44.80	150.27	185.12
Lagoons (12.08 Km ²)	4.50	6.24	6.13	4.27	5.93	5.82	1.12	1.56	1.53
All system area-weighted (13.15 Km ²)				9.85	25.32	29.83	4.68	13.66	16.47
May-2018									
Rivers (1.07 Km ²)	2.24	4.24	4.75	237.85	450.21	504.37			
Lagoons (12.08 Km ²)	2.06	4.40	4.64	7.25	15.49	16.33			
All system area-weighted (13.15 Km ²)				26.01	50.86	56.04			

Table 3 Stoichiometry of main diagenetic reactions that significantly affect TA in the environment. The reactions were separated in positive TA alterations (most common in anaerobic environments), and negative TA alterations (most common in aerobic environments). * Exceptions are the reactions of precipitation and dissolution of CaCO₃, which are not necessarily linked to aerobic/anaerobic conditions.

		Net Change	
		DIC	TA
	Positive TA alterations		
	Chemical Reaction		
1	Ammonification	$R-NH_2H + H_2O + H^+ \rightarrow R-OH + NH_4^+$	0 +2
2	Denitrification	$CH_2O + 0.8NO_3^- + 0.8H^+ \rightarrow CO_2 + 0.4N_2 + 1.4H_2O$	+1 +0.8
3	Iron reduction	$CH_2O + 2Fe_2O_3 + 8H^+ \rightarrow CO_2 + 5H_2O + 4Fe^{2+}$	+1 +8
4	Sulphate reduction	$2CH_2O + SO_4^{2-} + 2H^+ \rightarrow 2CO_2 + 2H_2O + H_2S$	+2 +2
5	Manganese reduction	$CH_2O + 2MnO_2 + 3H^+ \rightarrow HCO_3^- + 2Mn^{2+} + 2H_2O$	+1 +4
6	CaCO ₃ dissolution *	$CaCO_3 \rightarrow 2CO_3^{2-} + 2Ca^{2+}$	+1 +2
			Net Change
	Negative TA alterations		
	Chemical Reaction		
7	Nitrification	$NH_4^+ + 2O_2 \rightarrow NO_3^- + 2H^+ + H_2O$	0 -2
8	Iron oxidation	$Fe^{2+} + O_2 + 10H_2O \rightarrow 4Fe(OH)_3 + 8H^+$	0 -8
9	Sulfide oxidation	$1/2HS^- + O_2 \rightarrow 1/2SO_4^{2-} + 1/2H^+$	0 -1
10	Manganese oxidation	$2Mn^{2+} + O_2 + 4HCO_3^- \rightarrow 2MnO_2 + 4CO_2 + 2H_2O$	0 -4
11	CaCO ₃ precipitation *	$2Ca^{2+} + 2CO_3^{2-} \rightarrow CaCO_3$	-1 -2

Table 4 Average values of CO₂ equivalent emissions (CO₂eq) calculated for CO₂ and CH₄ degassing. The fluxes were calculated for “rivers” and “lagoons” stations, and after integrated for the entire superficial area, for each sampling campaign. The fluxes were calculated using the gas transfer velocity of Raymond and Cole (2001) (RC01).

	CO ₂ emissions in CO ₂ eq g CO ₂ -eq m ⁻² d ⁻¹	CH ₄ emissions in CO ₂ eq * g CO ₂ -eq m ⁻² d ⁻¹	Weight of CO ₂ (%) (in CO ₂ eq)	Weight of CH ₄ (%) (in CO ₂ eq)
Mar-2017				
Rivers(1.07 km ²)	27.47	29.40	48.30	51.70
Lagoons (12.08 km ²)	0.77	0.21	78.23	21.77
All system area-weighted (13.15 km ²)	2.94	2.58	53.21	46.79
Jun-2017				
Rivers	11.43	20.81	35.45	64.55
Lagoons	0.72	0.69	51.01	49.99
All system area-weighted	1.48	2.17	40.51	59.49
Nov-2017				
Rivers	10.73	67.20	13.77	86.23
Lagoons	0.26	0.62	29.42	70.58
All system area-weighted	1.11	6.11	15.40	84.60

* Fluxes of CH₄ multiplied by 28, which represents the GWP of CH₄ (IPCC, 2013).

Fig. 1

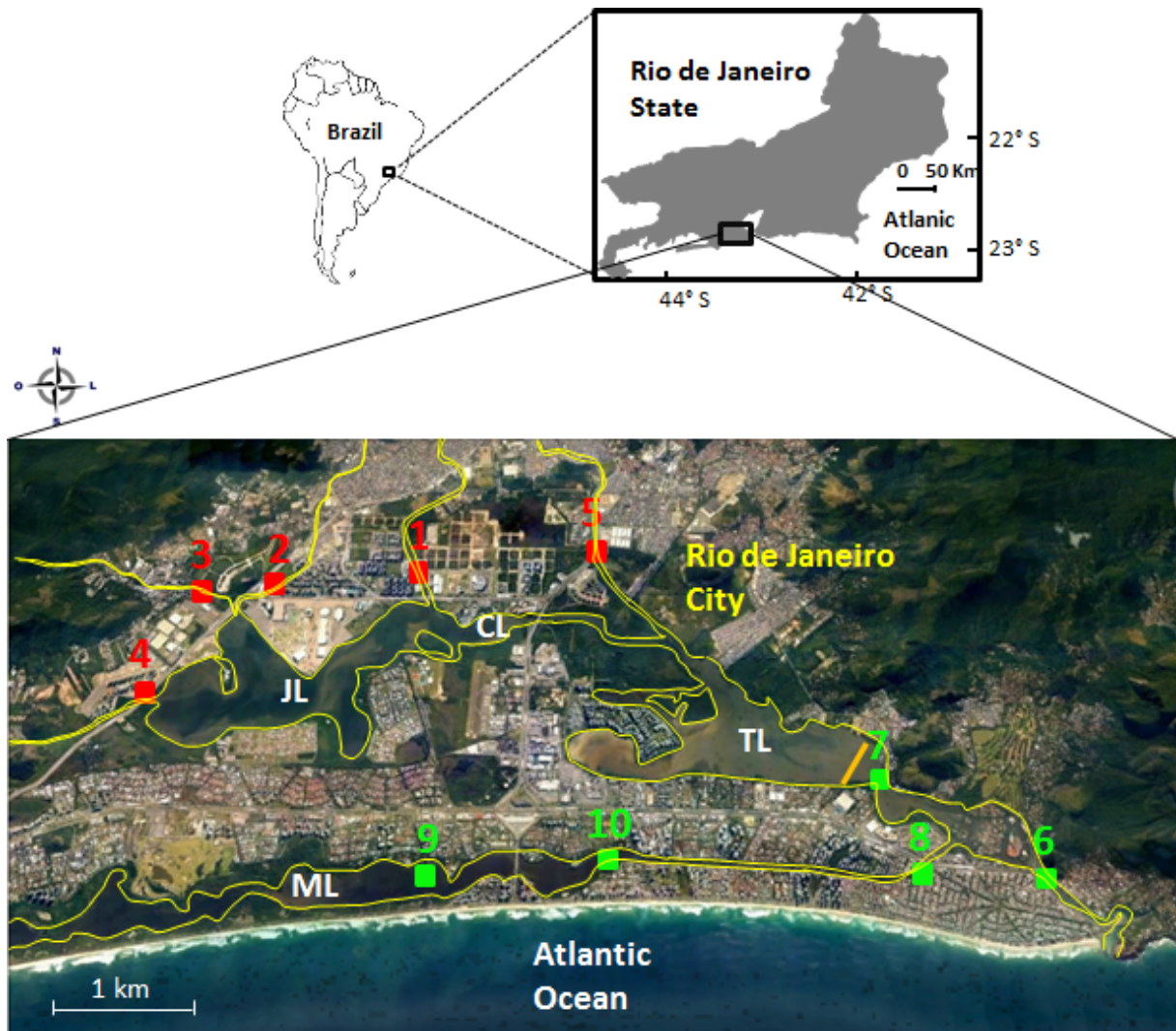


Fig. 2

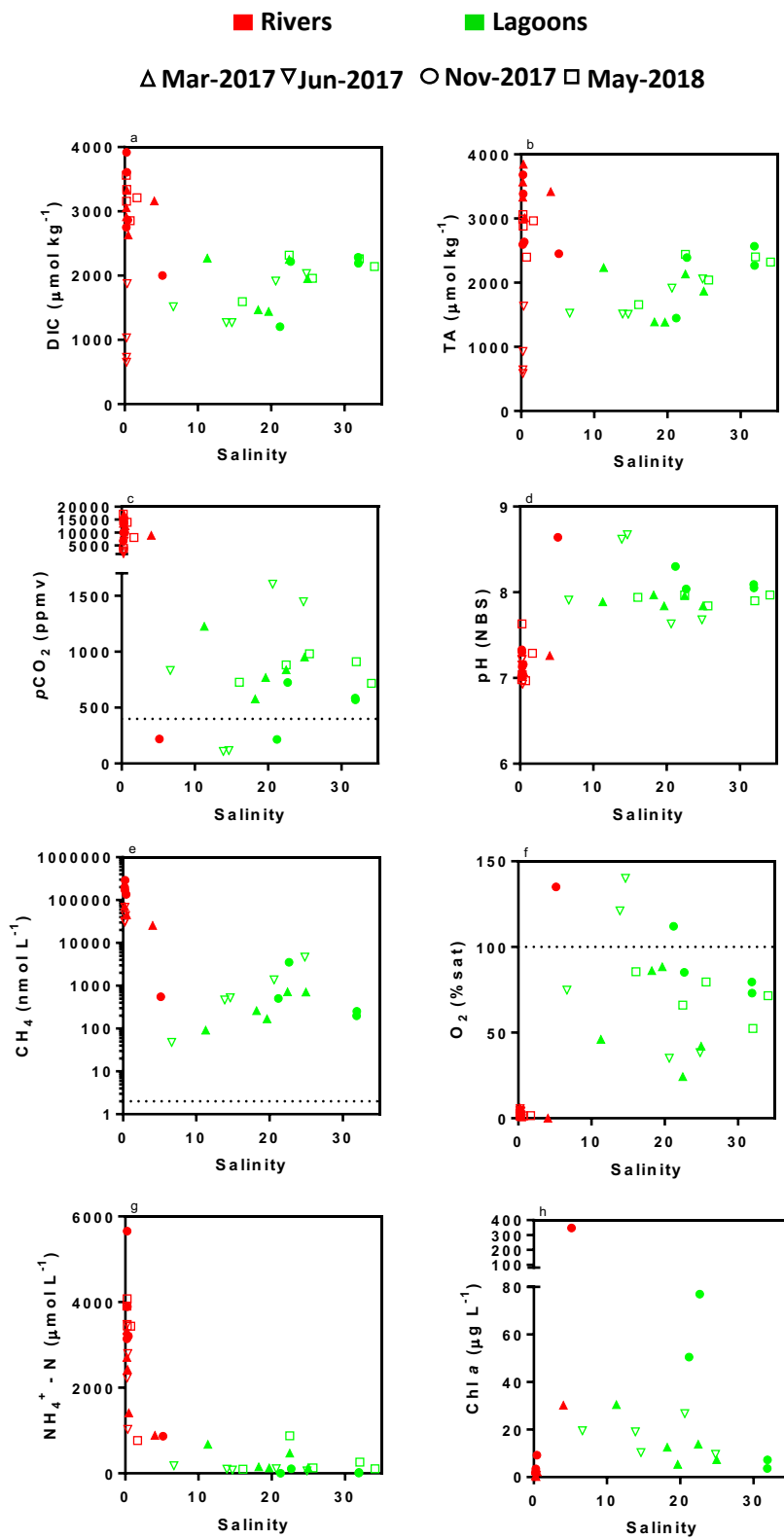


Fig. 3

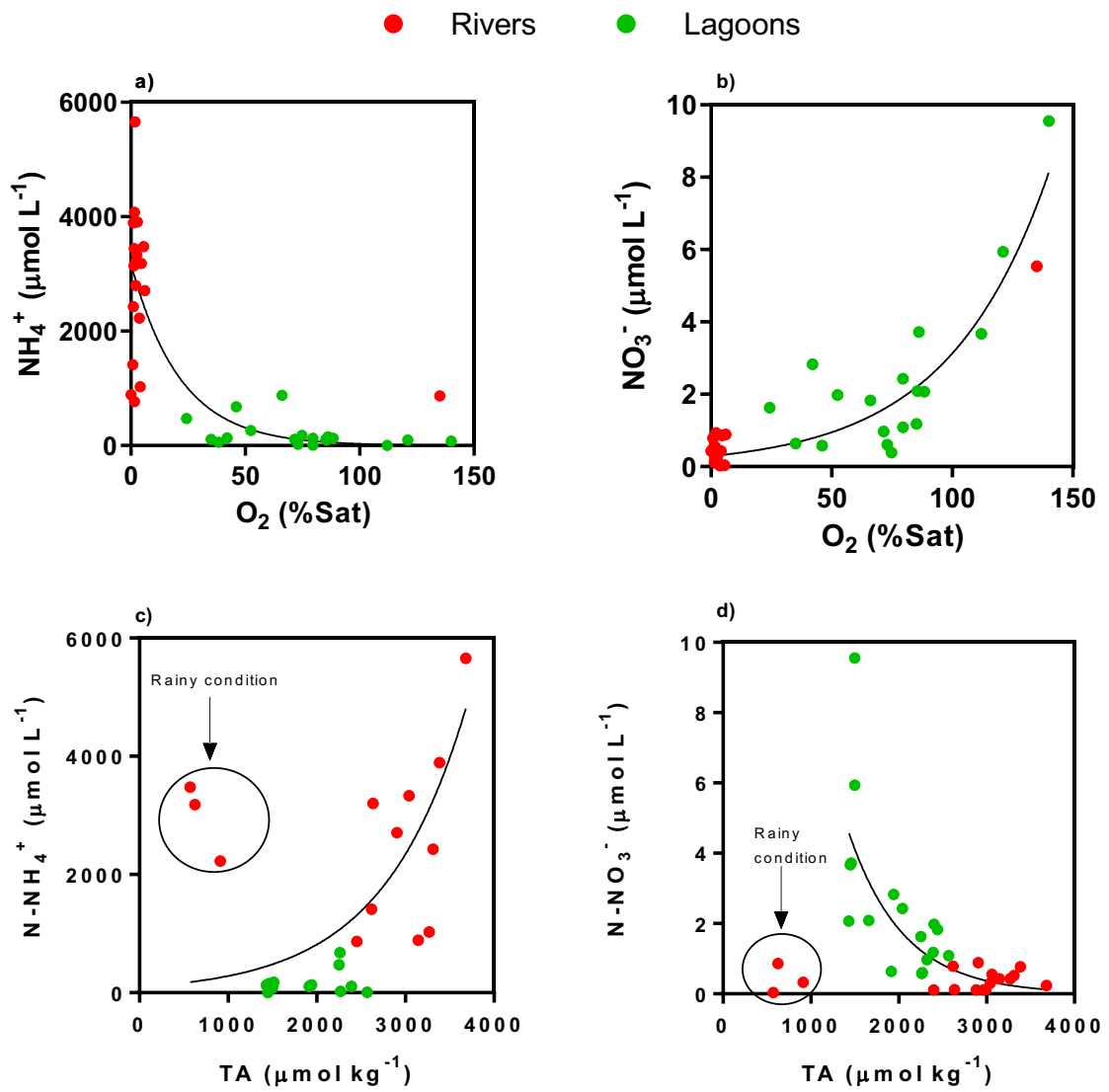


Fig. 4

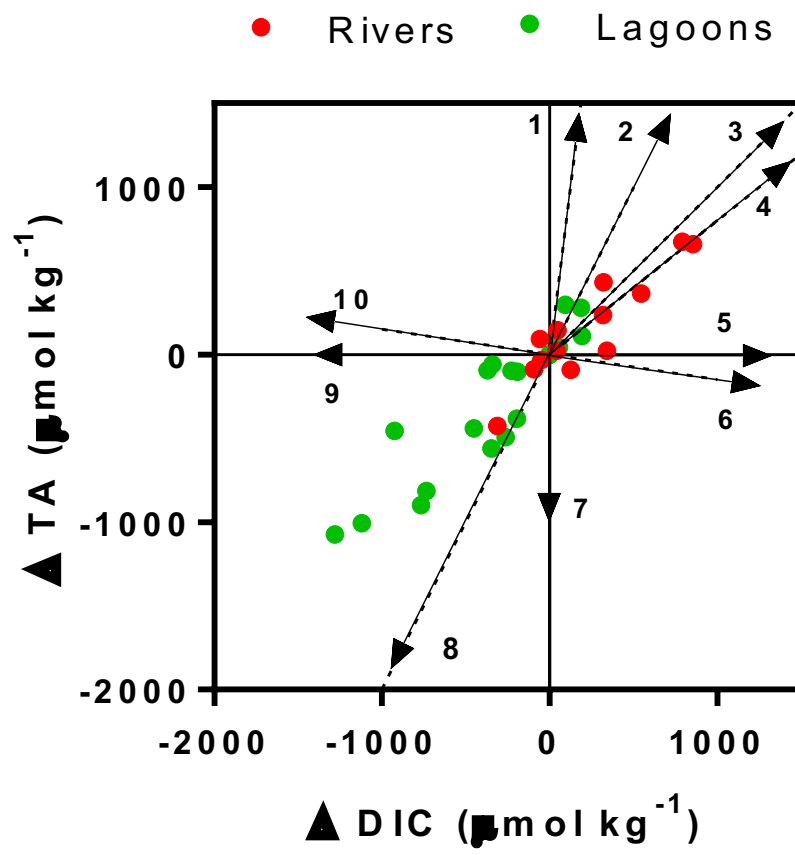


Fig. 5

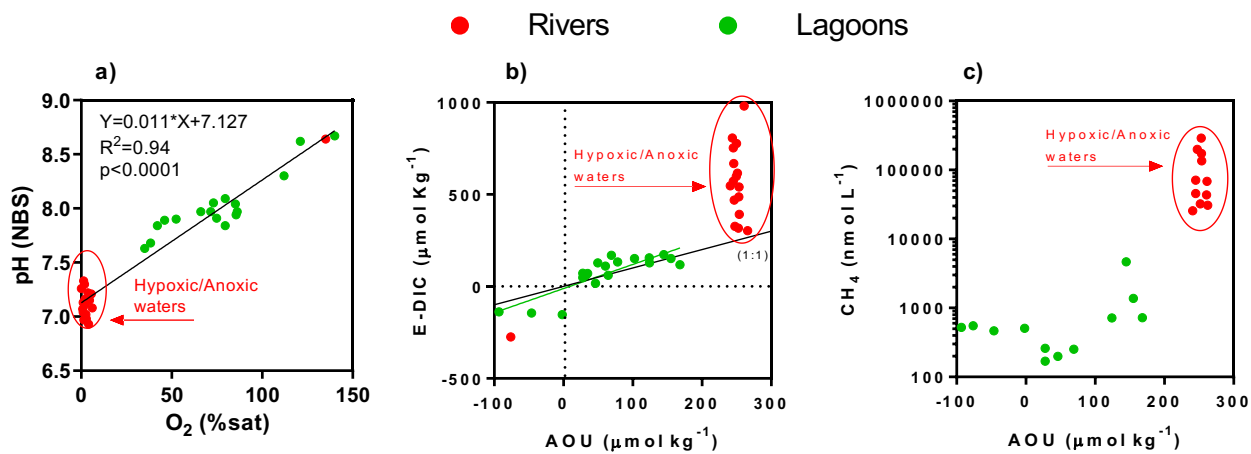
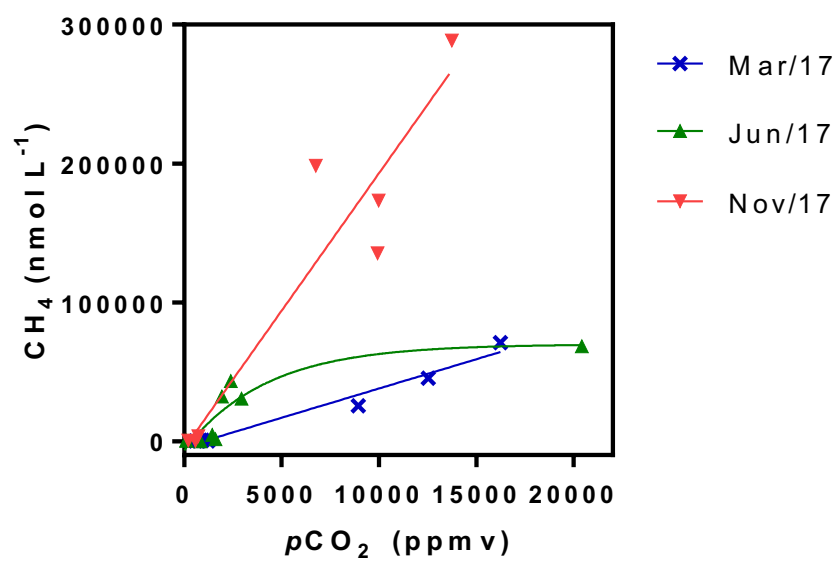


Fig. 6



Greenhouse gas emissions (CO₂ and CH₄) and inorganic carbon in an urban tropical coastal lagoon (Jacarepagua Lagoon Complex, Brazil)

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Fig. S1 Box plots (maximum, percentile 75%, median, percentile 25% and minimum) of the main parameters analyzed in this study for all sampling campaigns, separated by sampling stations (1-10). The horizontal lines in plots b), d), e) represent the atmospheric values.

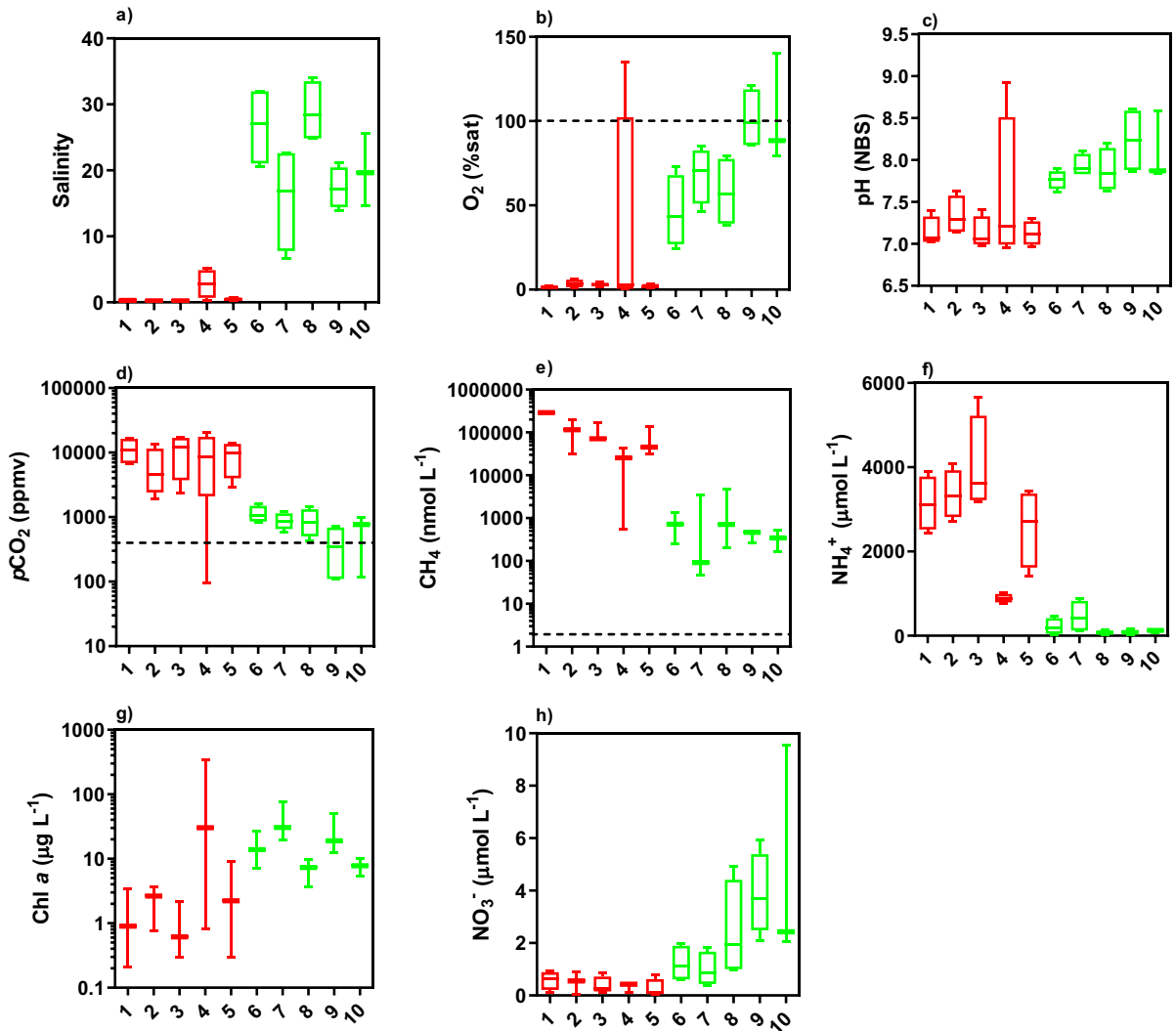


Fig. S2 Emissions of CO_2 and CH_4 calculated averaging the fluxes including the three parameterizations of gas transfer velocity, which were Wanninkhof (1992), Raymond and Cole (2001), Jiang et al. (2008). The fluxes were calculated considering river and lagoon stations separately, and integrated for entire superficial area, comprising all sampling campaigns. Note that graphs are in logarithm scales.

