



HAL
open science

Carbon dioxide sources and sinks in the delta of the Paraíba do Sul River (Southeastern Brazil) modulated by carbonate thermodynamics, gas exchange and ecosystem metabolism during estuarine mixing

Luiz Cotovicz, Luciana Vidal, Carlos Eduardo de Rezende, Marcelo Bernardes, Bastiaan Knoppers, Rodrigo Sobrinho, Renan Cardoso, Marcelo Muniz, Roberto Meigikos dos Anjos, Antoine Biehler, et al.

► **To cite this version:**

Luiz Cotovicz, Luciana Vidal, Carlos Eduardo de Rezende, Marcelo Bernardes, Bastiaan Knoppers, et al.. Carbon dioxide sources and sinks in the delta of the Paraíba do Sul River (Southeastern Brazil) modulated by carbonate thermodynamics, gas exchange and ecosystem metabolism during estuarine mixing. *Marine Chemistry*, 2020, 226, pp.103869. 10.1016/j.marchem.2020.103869 . hal-02931519

HAL Id: hal-02931519

<https://hal.science/hal-02931519v1>

Submitted on 19 Oct 2021

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

1 **Sources and sinks of CO₂ in the delta of the Paraíba do Sul River (Southeastern Brazil)**
2 **modulated by carbonate thermodynamics, gas exchange and ecosystem metabolism during**
3 **estuarine mixing**

4

5 Luiz C. Cotovicz Jr.^{a,b}; Luciana O. Vidal^c; Carlos Eduardo de Rezende^c; Marcelo C. Bernardes^a;
6 Bastiaan A. Knoppers^a; Rodrigo L. Sobrinho^a; Renan P. Cardoso^d; Marcelo Muniz^d; Roberto Meigikos
7 dos Anjos^d; Antoine Biehler^e; Gwenaël Abril^{a,f}

8

9 ^a Programa de Geoquímica, Universidade Federal Fluminense, Niterói, RJ, Brazil

10 ^b Instituto de Ciências do Mar (LABOMAR), Universidade Federal do Ceará, Fortaleza, CE, Brazil

11 ^c Laboratório de Ciências Ambientais, Centro de Biociências e Biotecnologia Universidade Estadual
12 do Norte Fluminense, Campos dos Goytacazes, RJ, Brazil

13 ^d Laboratório de Radioecologia e Alterações Ambientais, Instituto de Física, Universidade Federal
14 Fluminense, Niterói, RJ, Brazil

15 ^e Canada Research Chair in Geochemistry of Coastal Hydrogeosystems, Québec-Océan, Boreas Group
16 on the North Systems, Université du Québec à Rimouski, Rimouski, Canada

17 ^f Biologie des Organismes et Écosystèmes Aquatiques (BOREA), UMR 7208, Muséum National
18 d'Histoire Naturelle, CNRS, IRD, SU, UCN, UA, Paris, France.

19

20 Corresponding author: Luiz C. Cotovicz Jr., lccjunior@id.uff.br

21

22

23 **Marine Chemistry 226 (2020) 103869**

24 **<https://doi.org/10.1016/j.marchem.2020.103869>**

25

26

27

28

29

30

31

32

33 **Abstract**

34 Tropical estuarine deltas generally present poorly buffered waters in their freshwaters. Carbonate
35 chemistry predicts that mixture of such warm freshwater with seawater will create rapid consumption
36 of the freshwater carbon dioxide (CO_2) by the carbonate buffering capacity of the seawater. In this
37 study, we used the Paraíba do Sul River as a laboratory to investigate how thermodynamics compare
38 with biological processes, gas exchange, and tidal advection from mangrove. We conducted three
39 spatial surveys covering the salinity gradient of the main channel and surrounding mangrove waters
40 and one 24-hour mooring in a mangrove creek. In the main channel, dissolved inorganic carbon (DIC)
41 and total alkalinity (TA) showed closely conservative distribution along the salinity gradient,
42 increasing seaward. The partial pressure of CO_2 ($p\text{CO}_2$) followed a bell-shaped curve predicted by
43 carbonate chemistry for conservative mixing of river and ocean endmembers. During high river
44 flow, $p\text{CO}_2$ sharply decreased between salinities 0 and 5 (1800 to 390 ppmv), a $p\text{CO}_2$ drawdown
45 attributed to riverine outgassing and thermodynamics. Indeed, the mixing of TA-poor freshwater (363
46 $\pm 16 \mu\text{mol kg}^{-1}$) with TA-rich seawater creates a deficit of dissolved CO_2 not related to biotic
47 processes. During low river flow, the entire mixing zone was undersaturated in $p\text{CO}_2$ with an
48 increasing trend seaward. However, observed $p\text{CO}_2$ values were slightly above those predicted
49 by conservativity. Approximately half of this deviation was attributed to biological activity (net
50 heterotrophy), and remaining deviation was assigned to the effects of gas exchange (18%) and water
51 heating (36%). The effect of gas exchange was higher in fresh and low salinity waters, reflecting the
52 higher outgassing/ingassing of CO_2 , and lower buffering capacity. Water heating was more important
53 in mid- to high-salinities as a result of diel patterns of solar irradiance. Heterotrophy was slight and not
54 able to outcompete thermodynamics and generate outgassing during estuarine mixing.
55 Consistently, stable isotopic signatures of DIC ($\delta^{13}\text{C-DIC}$) presented slight deviations below the
56 conservative mixing, corroborating net heterotrophy in the main channel. Areas of CO_2 uptake due to
57 phytoplankton activity were identified but restricted to the freshwater endmember during low river
58 flow, with lowest $p\text{CO}_2$ (up to 41 ppmv) and the highest chlorophyll *a* (up to $21.3 \mu\text{g L}^{-1}$). The
59 estuary was a CO_2 sink during low river flow (-1.34 to $-5.26 \text{ mmolC m}^{-2} \text{ d}^{-1}$) and a source during high
60 river flow (5.71 to $19.37 \text{ mmolC m}^{-2} \text{ d}^{-1}$). In the mangrove creek, the $p\text{CO}_2$, DIC, $\delta^{13}\text{C-DIC}$ and TA
61 presented deviations from the conservativity, with slopes between TA and DIC demonstrating organic
62 carbon degradation mediated by aerobic respiration and sulphate reduction. Mangrove creek waters
63 were a CO_2 source (average of $134.81 \text{ mmolC m}^{-2} \text{ d}^{-1}$), exhibiting high values of $p\text{CO}_2$ (up to 21,720
64 ppmv). The results reveal that the low buffering capacity in the main channel of tropical estuarine
65 deltas can be the predominant driver of $p\text{CO}_2$, generating CO_2 undersaturation along the mixing zone,
66 a process overlooked in estuarine systems. Moreover, air-water CO_2 exchange, thermal variability, and
67 biological activities contribute to deviation of the carbonate system from conservative mixing in
68 specific estuarine areas, also modulating $p\text{CO}_2$ variability.

69

70 **Keywords:** carbon dioxide, carbonate chemistry, thermodynamics, tropical coastal deltas

71

72 **1. Introduction**

73 The concentration of carbon dioxide (CO₂) in Earth's atmosphere has been increasing at fast rates, and
74 the current CO₂ level is unprecedented over the past 3 million years (Willeit et al., 2019), changing
75 approximately from 277 ppmv in 1750 (Joos and Spahni, 2008) to 414 ppmv in April 2019 (NOAA,
76 2018), as a result of fossil fuel burning and land-use changes. According to recent estimates, the
77 oceans and the land absorb approximately 23 and 32% of these total emissions, respectively, whereas
78 the remaining 45% accumulate in the atmosphere (Le Quéré et al., 2018). This CO₂ accumulation in
79 the atmosphere is causing global warming, with CO₂ as the most important anthropogenic-derived
80 greenhouse gas (IPCC, 2013). In addition, penetration of CO₂ in the ocean is causing acidification,
81 increasing the surface ocean partial pressure of carbon dioxide (*p*CO₂), with a net decline of pH
82 (Gattuso et al. 2015). While carbon sink in the open ocean is currently estimated with a relative high
83 degree of confidence (2.5 ± 0.5 GtC yr⁻¹; Le Quéré et al., 2018), the air-water CO₂ fluxes and
84 controlling processes remain uncertain in the coastal ocean. Indeed, coastal oceans have not been
85 satisfactory included in global carbon budget calculations, despite their importance in terms of global
86 carbon cycling (Chen and Borges, 2009; Cai, 2011; Bauer et al., 2013).

87 Estuaries are aquatic ecosystems characterized by the mixing of fluvial and marine waters, hosting a
88 large diversity of interfaces and gradients, with distinct physical, geomorphological and biological
89 features (Cai, 2011; Borges and Abril, 2011). Studies have shown that CO₂ emissions by estuarine
90 systems and near-shore coastal waters are globally significant (Chen and Borges, 2009). However, in
91 10 years of global data compilation, CO₂ emission estimates have decreased by a factor of 6. The first
92 global estimate of estuarine CO₂ emissions calculated a degassing of 0.6 PgC yr⁻¹ (Abril and Borges,
93 2004), whereas the two last estimates showed degassing of approximately 0.1 PgC yr⁻¹ (Chen et al.,
94 2013; Laruelle et al., 2013). This decline has been attributed to various factors, mainly the
95 disproportional and insufficient global sampling (poor coverage in tropical regions and the Southern
96 Hemisphere), few studies with direct and continuous measurements of *p*CO₂, and low temporal
97 resolution (semi-diurnal, diurnal, seasonal, and annual) (Borges and Abril, 2011; Cai, 2011; Chen et
98 al., 2013).

99 In general, the upper estuarine regions with low-salinity waters are important sources of CO₂ to the
100 atmosphere. This is normally attributed their net heterotrophy and, to a lesser extent, to inputs of CO₂-
101 enriched freshwater and lateral inputs from intertidal areas such as salt marshes and mangroves (Cai et
102 al., 1999; 2011; Borges and Abril, 2011). However, in some estuaries, the riverine contributions of

103 CO₂ (allochthonous sources) can be greater than contribution of estuarine heterotrophy (autochthonous
104 sources) at certain times of the year (Jiang et al., 2008; Joesoef et al., 2015; Van Dam et al., 2018a).
105 Climatological and hydrological characteristics may change seasonally according to river water
106 discharge, temperature, and formation of vertical stratification, which modulate physical mixing and
107 biological production (Frankignoulle et al., 1998; Salisbury et al., 2008; Borges and Abril, 2011;
108 Dinauer and Mucci, 2017). Downstream in the seaward direction, estuarine mixing zones are
109 considered as moderate CO₂ sources, whereas the marine domain from the river mouth to the shelf
110 break generally behaves as a CO₂ sink (Frankignoulle et al., 1998; Borges and Abril, 2011; Chen et al.,
111 2013). In general, the *p*CO₂ values and CO₂ emissions are much higher in river-dominated estuaries
112 than in marine-dominated estuaries (Jiang et al., 2008; Cotovicz et al., 2015). In addition to the
113 marked and complex natural variability, the coastal ocean hosts approximately 37% of the human
114 population (Cohen et al., 1997), creating human-induced modifications in the metabolism of aquatic
115 ecosystems associated with nutrient enrichment and eutrophication (Frankignoulle et al., 1998; Zhai et
116 al., 2007; Cotovicz et al., 2015; Kubo et al., 2017).

117 Historically, studies addressing estuaries have identified biological processes as predominant drivers
118 on *p*CO₂ distribution and CO₂ fluxes along salinity gradients (Frankignoulle et al., 1998; Cai et al.
119 1999; Borges and Abril, 2011). However, the theory of carbonate chemistry predicts drastic abiotic
120 changes in proportions of dissolved CO₂, bicarbonate (HCO₃⁻), and carbonate (CO₃²⁻) during the
121 mixing of freshwater with seawater. The influence of thermodynamics in the CO₂ system in estuarine
122 waters was first described by the pioneer studies of Mook and Koene (1975) and Whitfield and Turner
123 (1986). These authors showed that modification of the carbonate equilibria in estuarine waters during
124 the mixing of freshwater with seawater results in changes in the *p*CO₂ and, in turn, in the CO₂ fluxes at
125 the air-water interface (Whitfield and Turner 1986; Hu and Cai, 2013; Cai et al., 2013). In particular,
126 the displacement of acid-base equilibrium during the mixing of weakly buffered freshwater (low total
127 TA concentration) with well buffered seawater (high TA concentration) can generate *p*CO₂ values far
128 below that of the atmosphere, with no need for biological uptake (Whitfield and Turner 1986). In this
129 regard, thermodynamic processes would be potentially significant compared with biological processes
130 in oligotrophic/mesotrophic estuaries with short residence times as, for example, estuarine deltas.
131 Thermodynamic changes as the main driver of carbonate chemistry changes along the salinity gradient
132 in estuaries were have been demonstrated in theoretical studies (Hu and Cai, 2003; Salisbury, 2008;
133 Cai et al., 2013), but rarely validated using field data. In the Amazon River plume, *p*CO₂
134 undersaturation has been attributed mainly to phytoplankton productivity (Ternon et al., 2000;
135 Körtzinger, 2003); however, recent findings showed that, from a salinity value of approximately 10,
136 surface water becomes undersaturated as a result of the mixing effect (Lefèvre et al., 2017).

137 The geographical position also exerts influence over CO₂ concentrations and emissions across
138 different latitudes. Estuaries located at low and intermediate latitudes present the largest flux per unit

139 area, whereas those located in regions north of 50° N and south of 50° S present the lowest flux per
140 unit area (Chen et al., 2013). These differences are attributed to local/regional characteristics of the
141 coastal zone, including the mixing of freshwaters (presenting variable levels of $p\text{CO}_2$) with low- $p\text{CO}_2$
142 shelf waters, water temperature, and biogeochemistry complexity (Chen et al., 2013). However, it
143 should be highlighted that studies on carbon cycling conducted in tropical coastal regions are
144 overlooked compared with those in temperate and boreal regions. In addition, tropical rivers present
145 lower TA concentrations than temperate/boreal rivers (Cai et al., 2008), thus the impact of
146 thermodynamic processes during river-ocean mixing can be especially important in tropical estuaries.
147 Estuarine deltas can locally/regionally be the main estuarine type through which significant terrestrial
148 carbon is transported to the ocean (Laruelle et al., 2013). Deltas are mostly located in tropical and sub-
149 tropical regions (Laruelle et al., 2013).

150 The present study aims at investigating the carbonate chemistry and air-water CO_2 exchange in the
151 Paraiba do Sul River estuary (PSRE), southeastern Brazil. This estuary is a tropical mesotrophic
152 ecosystem that has been suffering with increasing eutrophication and construction of dams in its
153 watershed. This ecosystem has a short residence time and low TA concentrations in freshwater,
154 potentially generating $p\text{CO}_2$ undersaturation conditions during mixing with seawater as a result of
155 thermodynamic changes - a fact that is still disregarded globally. Based on high resolution monitoring
156 of carbonate chemistry parameters along the entire salinity gradient, we could differentiate between
157 the biotic and abiotic contributions to water $p\text{CO}_2$ distributions and CO_2 fluxes at the air-water
158 interface; we also analyzed the metabolism of the main channel using $p\text{CO}_2$ distributions and stable
159 isotope data.

160

161 **2. Material and Methods**

162 **2.1 Study Area**

163 The Paraiba do Sul River is an important water resource located in the southeast region of Brazil. The
164 river watershed has an area of approximately 54,400 km^2 , with a length of 1,145 Km, traversing the
165 most industrialized and urbanized region of Brazil (the states of São Paulo, Minas Gerais and Rio de
166 Janeiro). According to previous studies, the river basin is divided into three regions (Ovalle et al.,
167 2013): 1. the upper basin (7,300 km^2), with water sources at 1,800 m of altitude until 600 m in a valley
168 of crystalline rocks; 2. the medium basin (27,500 km^2), with average elevation of 500 m; 3. the lower
169 basin (22,500 km^2), comprising coastal plains, with extensive meanders and islands until the river
170 mouth into the Atlantic Ocean (Fig. 1).

171 The PSRE, located at the north region of the state of Rio de Janeiro (21°37' S; 41°01' W), is composed
172 of a main river channel and a minor secondary channel (Fig. 1). The secondary channel harbors a

173 mangrove forest of approximately 8 km² (Sterza and Fernandes, 2006). The coast is microtidal with
174 high energy of waves, forming an estuarine delta. According to the Köppen's classification, climate in
175 the region is Aw, with wet summers (November to January) and dry winters (July to September)
176 (Cotovicz et al., 2013). The river discharge in the estuary follows a seasonal cycle, with high water
177 flow in summer and early spring and low water flow in winter and early autumn, with discharges
178 averages of 1158 and 444 m³ s⁻¹, respectively. The river discharge modulates the residence time of
179 waters in the mixing zone (Souza et al., 2010) and the extension of the river plume in the adjacent
180 coastal ocean (Rudorff et al., 2011). During low water flow, the plume is reduced and it takes
181 approximately 10 days for the water to reach open ocean (salinity 35), whereas during high water
182 flow, the plume is extended along the shelf and the residence time decreases to 6 days (Souza et al.,
183 2010).

184 The river has undergone increasing anthropogenic influences. The total human population on its
185 watershed is estimated at 5 million inhabitants. Considering only the estuarine region, the surrounding
186 population is estimated at approximately 600,000 inhabitants (IBGE, 2018). In addition, the lower
187 basin presents extensive farming, particularly sugar cane production (Ovalle et al., 2013). The
188 coverage of wastewater treatment plans is still very small in the region, less than 50% of the total
189 households. Therefore, the estuary receives a large amount of industrial, agricultural and domestic
190 effluents, with large inputs of nutrients to the waters, thus presenting mesotrophic characteristics
191 (Cotovicz et al., 2013). Reservoirs and hydroelectric dams have been constructed along the drainage
192 basin (forty-seven different hydroelectric power plants; Ovalle et al., 2013), which have changed
193 hydrological patterns and potentially altered carbon cycling in the estuary.

194 2.2 Sampling Strategy

195 Three extensive spatial surveys were conducted in the estuary on February 17, October 17 and March
196 18. The Feb 17 sampling, historically considered as the rain season, presented an accumulated
197 monthly precipitation of 40 mm, which is 60 mm lower than the historical average, with a 7-day
198 accumulated precipitation before sampling of only 1 mm. The Oct 17 sampling presented an
199 accumulated monthly precipitation of 13 mm (80 mm lower than the historical average), with a 7-day
200 accumulated precipitation before sampling of 4 mm. The Mar 18 sampling presented an accumulated
201 monthly precipitation of 376 mm, which is 267 mm higher than the historical data. Thus, the Feb 17
202 and Oct 17 samplings were considered dry conditions and the Mar 18 sampling was considered wet
203 condition. These climatological characteristics influenced the hydrological pattern. The Feb 17 and
204 Oct 17 samplings were conducted during low river flow, with average discharges of 288 and 178 m³ s⁻¹
205 ¹, respectively (Fig. 1c,d), whereas the Mar 18 collection was performed during high river flow, with
206 average discharge of 1,240 m³ s⁻¹. The mean historical river water discharge (reference period of 95
207 years, 1923-2018) presented higher values than the discharge verified on the sampling days (Fig.

208 1c,d). The regression line of the historical data shows that the river discharge has been decreasing at a
209 rate of $\sim 5 \text{ m}^3 \text{ s}^{-1}$ per year, which means that the mean discharge has already decreased by $475 \text{ m}^3 \text{ s}^{-1}$.

210 In each sampling campaign, continuous and discrete aquatic measurements were performed.
211 Continuous and online measurements were conducted for $p\text{CO}_2$, dissolved oxygen (DO), pH, salinity,
212 and temperature. Surface water was sampled in the mangrove creeks and in the main channel in
213 discrete points distributed regularly along the whole salinity gradient (0 to 35) with approximately
214 three salinity unit increments. Discrete samples were used to analyze TA, Chl *a*, and $\delta^{13}\text{C}$ -DIC. The
215 spatial surveys covered the freshwater domain (upper estuary), the mixing zone (complete salinity
216 gradient), and the external estuary (river plume adjacent to the coastal ocean). The spatial surveys
217 started in the morning, at around 8:30 am, and finished in the early-afternoon, at around 4:00 pm. In
218 addition to the spatial survey screening, an Eulerian time series (24 h of sampling) was conducted in
219 the mangrove tidal creek located in the secondary channel on March 2018 (Fig. 1), combining
220 continuous measurements and discrete water sampling within 2 hours of interval for the same water
221 parameters previously described.

222

223 2.3 Continuous Measurements

224 Continuous samplings were performed from a boat, with real-time measurements of position, $p\text{CO}_2$,
225 DO, pH, salinity, and temperature, at a frequency of 1 min (Frankignoulle et al., 2001, Abril et al.,
226 2014; Cotovicz et al., 2016). Briefly, a water pump placed at a depth of $\sim 0.5 \text{ m}$ provided continuous 6
227 L min^{-1} water flux to the boat. A part of this flux ($\sim 3 \text{ L min}^{-1}$) was directed to an equilibrator to
228 measure the $p\text{CO}_2$. The marble equilibrator consisted of an acrylic tube (60 cm in length; 8 cm in
229 diameter) filled with glass marbles where the water flows from top to bottom and a closed air circuit
230 with a flow of $\sim 1 \text{ L min}^{-1}$ in the opposite direction, from bottom to top. The air is dried using a
231 desiccant (Drierite™) and pumped into a non-dispersive infrared gas analyzer (Li-820 NDIR, LI-
232 COR). Before and after each sampling campaign, the NDIR was calibrated using gas standards with
233 air $p\text{CO}_2$ values of 410, 1007 and 5035 ppmv (White Martins Certified Material, RJ, Brazil). Fresh
234 soda lime was used to set the zero and the standard at 1007 ppmv was used to set the span. The air
235 standards of 1007 and 5035 ppmv were used to verify the system stability. The boat speed was 8-10
236 km h^{-1} during the spatial surveys. The equilibration time of the $p\text{CO}_2$ measurement system is 2-3 min
237 (Cotovicz et al., 2016). This gas equilibration device is ideal for $p\text{CO}_2$ analysis in estuarine waters due
238 to its fast response time (Frankignoulle et al., 2001, Abril et al., 2014; Cotovicz et al., 2016). This
239 time is sufficient to guarantee the equilibration along the estuarine mixing. In the steepest part of the
240 salinity gradient, between salinities 10 and 20, the velocity of the vessel was reduced to less than 2 km
241 h^{-1} before all discrete sampling, this allowed a complete gas equilibration for $p\text{CO}_2$ measurements.
242 Accuracy of the $p\text{CO}_2$ measurements was estimated at ± 5 ppmv. Temperature, salinity, and DO were

243 measured using a calibrated YSI Professional Plus multiparameter meter, and pH was measured using
244 a WTW 3310 pH meter equipped with a Sentix 41 electrode, calibrated with a three-point standard
245 (pH 4.01, pH 7.00 and pH 10.01) according to the National Institute of Standards and Technology
246 (NIST), before and after each sampling campaign. The precision of the pH measurements estimated
247 after seven verifications against standards before and after each sampling campaign was
248 approximately 0.01 NBS units. For the anchored continuous sampling (Eulerian approach), the total
249 duration of sampling was 20 h, encompassing one complete tidal cycle plus one ebb tide period. Two
250 tidal cycles of measurements were not completed due to logistic problems.

251 2.4 Discrete Measurements and Laboratory Analysis

252 Discrete samples were collected at a depth of ~0.5 m using a Niskin bottle and then stored for further
253 laboratory chemical analysis (i.e., fixed and/or kept on ice in the dark). The water was filtered with
254 Whatman[®] grade GF/F glass microfiber filters (pre-combusted at 500 °C for 6 h), followed by
255 determination of TA and Chl *a*. The filters used to analyzed Chl *a* were kept at -18 °C prior to
256 analysis. TA measurements were performed according to the classical Gran (1952) titration in an
257 automated titration system (Metler Toledo model T50) in filtered water samples. The accuracy of this
258 method was better than $\pm 5 \mu\text{mol kg}^{-1}$ (inferred from certified reference material - CRM; A. G.
259 Dickson from Scripps Institution of Oceanography). Chl *a* was extracted from the filters with 90%
260 acetone and quantified by spectrophotometry according to Strickland and Parsons (1972). For $\delta^{13}\text{C}$ -
261 DIC measurement, water was sampled and transferred directly to 150 mL serum vials, which were
262 poisoned by adding 0.2 mL of a HgCl_2 saturated solution, and then sealed. In the laboratory, $\delta^{13}\text{C}$ -DIC
263 was determined following the protocol by Bouillon et al. (2007). A headspace of approximately 40 mL
264 was created with Helium, and 0.2 mL of ultrapure concentrated H_3PO_4 was introduced to convert all
265 inorganic carbon to CO_2 . The samples were shaken and kept in the dark at controlled temperature of
266 25 °C for 12 h. The $\delta^{13}\text{C}$ of CO_2 in the headspace was determined by injecting 0.5-1 mL of headspace
267 gas in an isotopic ratio mass spectrometer (IRMS) equipped with a manual gas injection port. $\delta^{13}\text{C}$ -
268 DIC was calibrated using laboratory standards, which were prepared by adding 45 mg of Na_2CO_3 in a
269 sealed vial flushed with helium and dissolved with 3 mL of 85% H_3PO_4 , as described in Deirmendjian
270 and Abril (2018). This standard was calibrated against a certified standard (NBS 19, -1.96‰) using a
271 dual-inlet IRMS. The isotopic value of the Na_2CO_3 standard was $-4.5 \pm 0.2\text{‰}$. The obtained $\delta^{13}\text{C}$
272 values were corrected for the partitioning of CO_2 between the gaseous (headspace) and water phases in
273 each sample using the algorithm of Miyajima et al. (1995). Repeatability of the analysis was ~0.1‰.
274 The $\delta^{13}\text{C}$ -DIC concentrations are reported in ‰ relative to the standard Vienna Pee Dee Belemnite (V-
275 PDB) scale.

276 2.5 Calculations

277 2.5.1 Carbonate System

278 DIC was calculated from $p\text{CO}_2$, TA, temperature, and salinity using the CO2calc 1.2.9 program
279 (Robbins et al., 2010). We used the dissociation constants for carbonic acid proposed by Mehrbach et
280 al. (1973) refitted by Dickson and Millero (1987), the borate acidity constant from Lee et al. (2010),
281 the dissociation constant for the HSO_4^- ions from Dickson (1990) and the CO_2 solubility coefficient of
282 Weiss (1974). The estimated uncertainty was better than $\pm 6 \mu\text{mol kg}^{-1}$ for DIC (Orr et al., 2018).

283 2.5.2 Excess DIC (E-DIC) and Apparent Utilization of Oxygen (AOU)

284 The excess of DIC (E-DIC, $\mu\text{mol kg}^{-1}$) was calculated according to Abril et al., (2003):

$$285 \text{E-DIC} = \text{DIC}_{\text{sample}} - \text{DIC}_{\text{equilibrium}} \quad (1)$$

286 Where $\text{DIC}_{\text{sample}}$ represents the measured concentration of DIC ($\mu\text{mol kg}^{-1}$) and $\text{DIC}_{\text{equilibrium}}$ is the
287 theoretical DIC at atmospheric equilibrium ($\mu\text{mol kg}^{-1}$). $\text{DIC}_{\text{equilibrium}}$ was calculated from the observed
288 TA and the measured atmospheric $p\text{CO}_2$ during the cruises.

289 The apparent oxygen utilization (AOU, $\mu\text{mol kg}^{-1}$) was calculated as proposed by Benson and Krause
290 (1984):

$$291 \text{AOU} = \text{DO}_{\text{equilibrium}} - \text{DO}_{\text{sample}} \quad (2)$$

292 Where $\text{DO}_{\text{sample}}$ is the measured DO, and $\text{DO}_{\text{equilibrium}}$ is the DO saturation.

293 2.5.4 Diffusive air-water CO_2 fluxes

294 Diffusive fluxes of CO_2 at the air-water interface were calculated according to the following equation:

$$295 \text{FCO}_2 = k_{\text{CO}_2, \text{T}} \cdot k_0 \cdot \Delta p\text{CO}_2 \quad (3)$$

296 Where FCO_2 is the diffusive flux of CO_2 , $k_{\text{CO}_2, \text{T}}$ is the gas transfer velocity of CO_2 at a given
297 temperature (T), k_0 is the solubility coefficient of CO_2 calculated from in situ temperature and salinity
298 (Weiss, 1974), and the $\Delta p\text{CO}_2$ is the difference between the measured water $p\text{CO}_2$ and the measured
299 atmospheric $p\text{CO}_2$. The atmospheric $p\text{CO}_2$ was measured every sampling day at morning, noon and
300 afternoon. The gas transfer velocity of CO_2 $k_{\text{CO}_2, \text{T}}$ was computed as follows (Jähne et al. 1987):

$$301 k_{\text{CO}_2, \text{T}} = k_{600} \times (600 / \text{Sc}_{\text{CO}_2, \text{T}})^n \quad (4)$$

302 where k_{600} is the gas transfer velocity normalized to a Schmidt number of 600 ($\text{Sc} = 600$ for CO_2 at
303 20°C), $\text{Sc}_{\text{CO}_2, \text{T}}$ is the Schmidt number of CO_2 at a given temperature (Wanninkhof, 1992), and n being
304 equal to $2/3$ for wind speed $< 3.7 \text{ m s}^{-1}$ and equal to 0.5 for higher wind speed (Jähne et al., 1987;
305 Guérin et al., 2007).

306 To compute the k_{600} values, we used three different parameterizations proposed by Wanninkhof
307 (1992), Raymond and Cole (2001) and Abril et al. (2009), according to respectively:

308 $k_{600}(W92) = 0.31(U10^2)$ (5)

309 $k_{600}(RC01) = 1.91\exp(0.35U10)$ (6)

310 $k_{600}(A09) = 1.80\exp(-0.0165v + [1.23 + 1.00\text{LOG}(S)]U10)$ (7)

311 where k_{600} is the gas transfer velocity normalized to a Schmidt number of 600 expressed in cm h^{-1} , v is
312 the water current velocity in m s^{-1} , S is the surface area of the specific estuarine section considered in
313 km^2 , and $U10$ is the wind speed at 10m height in m s^{-1} . Water-to-air CO_2 fluxes were calculated using
314 the daily-average $p\text{CO}_2$ for each estuarine domain: low salinity domain (salinities 0-5), mixing domain
315 (salinities 5-25), marine domain (salinities > 25), and mangrove domain. We also differentiated the
316 gas transfer velocities at different moments (morning, afternoon and nighttime). We divided the gas
317 transfer velocities for these periods because the region is strongly impacted by marine breezes, wind
318 speed being stronger during midday/afternoon than during the night/early morning (Amarante et al.,
319 2002; Cotovicz et al., 2015). Wind speed wind velocity ($U10$), accumulated precipitation and
320 atmospheric temperature were recorded in the meteorological station of Campos dos Goytacazes City
321 and were provided by the National Institute for Space Research (INPE). The water current velocities
322 were taken from Ovalle et al. (2013).

323 Rudorff et al. (2011) calculated the spatial coverage of the Paraíba do Sul River plume applying a
324 spectral linear mixture analysis. The authors proposed a linear regression to estimate the surface area
325 of the estuarine plume in the coast as a function of the historical river discharge. We applied this
326 general linear regression to estimate the river plume spatial coverage for our sampling period of
327 maximal river discharge (Mar-18), when the river discharge averaged $1,240 \text{ m}^3 \text{ s}^{-1}$, and the extension
328 of river plume was calculated at about 90.75 km^2 . Accounting for the salinity values along the boat's
329 trajectories, we constructed maps of surface salinity applying the data-interpolating variational
330 analysis (DIVA gridding) using the Ocean Data View Software. The spatial coverages of the salinity
331 zones for each sampling campaign were used to calculate the area-averaged CO_2 flux (Fig. S1,
332 Supplementary file).

333 2.5.5 Mixing Models

334 Two types of mixing models were applied, one for TA, DIC and $\delta^{13}\text{C}$ -DIC in the discrete samples, and
335 one for temperature, salinity and $p\text{CO}_2$, which were recorded continuously.

336 For DIC and TA, the model assumes conservative mixing according to

337 $C_{\text{mix}} = C_{\text{freshwater}}C_{\text{freshwater}} + C_{\text{marine}}(1 - C_{\text{freshwater}})$ (8)

338 Where C_{mix} is the concentration of a given solute during conservative mixing (in our case TA and
339 DIC), and the subscripts freshwater and marine indicate the endmember concentrations in the river and
340 the ocean, respectively. The freshwater fraction ($F_{\text{freshwater}}$) is calculated as:

341 $F_{\text{freshwater}} = 1 - \text{sal}_{\text{sample}}/\text{sal}_{\text{marine}}$ (9)

342 Where sal refer to the salinity, and the subscript sample refers to the *in situ* values for each station.

343 Concerning stable isotope ratios, we calculated the conservative mixing of $\delta^{13}\text{C-DIC}$ ($\delta^{13}\text{C-DIC}_{\text{mix}}$)
 344 according to Mook and Tan (1991), as follows:

345 $\delta^{13}\text{C-DIC}_{\text{mix}} = \text{sal}_{\text{sample}}(\text{DIC}_{\text{freshwater}}\delta^{13}\text{C}_{\text{freshwater}} - \text{DIC}_{\text{marine}}\delta^{13}\text{C}_{\text{marine}}) + \text{sal}_{\text{freshwater}}\text{DIC}_{\text{marine}}\delta^{13}\text{C}_{\text{marine}} -$
 346 $\text{Sal}_{\text{marine}}\text{DIC}_{\text{freshwater}}\delta^{13}\text{C}_{\text{freshwater}} / \text{sal}_{\text{sample}}(\text{DIC}_{\text{freshwater}} - \text{DIC}_{\text{marine}}) + \text{sal}_{\text{freshwater}}\text{DIC}_{\text{marine}} -$
 347 $\text{sal}_{\text{marine}}\text{DIC}_{\text{freshwater}}$ (10)

348 Where $\delta^{13}\text{C}$ is the isotopic signature of DIC, the subscripts freshwater and marine indicate the
 349 endmember concentrations in the river and the ocean, respectively, and the subscript sample indicate
 350 the *in situ* values at each station.

351 The TA and DIC concentrations measured in the discrete samples (see result section) were close to the
 352 conservative mixing line. Thus we could compute these two parameters for each salinity obtained with
 353 the continuous measurements. The theoretical $p\text{CO}_2$ conservative mixing curve ($p\text{CO}_{2\text{mixing}}$) was
 354 obtained by solving the carbonate system using the *in situ* temperature and salinity, and the computed
 355 conservative TA and DIC for each salinity value obtained with the continuous measurements from the
 356 estuary (Jiang et al. 2008; Joesoef et al., 2015). Because the $p\text{CO}_2$ was variable in the freshwater
 357 endmember, we calculate the average and standard deviations for each sampling campaign.

358 In order to allow a full comparison with the observed $p\text{CO}_2$ distribution, two corrections of the
 359 conservative mixing $p\text{CO}_2$ model are necessary: a correction for gas exchange and another for the
 360 effect of heating or cooling in the estuary. In order to correct the mixing $p\text{CO}_2$ curve for gas exchange,
 361 an iterative calculation was applied for each salinity increment. The loss or gain of DIC as CO_2
 362 evasion or invasion between each salinity increment “sal” was calculated as:

363 $\text{DICgain}(\text{sal}) = -\text{FCO}_2(\text{sal}).\text{RT}.\text{H}^{-1}$ (11)

364 Where $\text{FCO}_2(\text{sal})$ is the flux ($\text{mol m}^{-2} \text{h}^{-1}$) for every salinity unit, RT is the residence time (h) during
 365 mixing between salinity (sal) and (sal+1) and H is the water depth (m). $\text{FCO}_2(\text{sal})$ is calculated with
 366 Eq.3, and the conservative mixing $p\text{CO}_2$ (sal). The new corrected DIC concentration at sal+1 is
 367 obtained by adding the $\text{DICgain}(\text{sal}+1)$ to the $\text{DIC}(\text{sal}+1)$ previously deduced from the conservative
 368 mixing of $\text{DIC}(\text{sal})$ with $\text{DIC}_{\text{marine}}$:

369 $\text{Corrected DIC}(\text{sal}+1) = \text{DIC}(\text{sal}+1) + \text{DICgain}(\text{sal})$ (12)

370 Then we recalculate the corrected $p\text{CO}_2(\text{sal}+1)$ from a new mixing lines between corrected $\text{DIC}(\text{sal}+1)$
 371 and $\text{DIC}_{\text{marine}}$, and $\text{TA}(\text{sal}+1)$ and $\text{TA}_{\text{marine}}$. The next iteration consisted in calculating the $\text{FCO}_2(\text{sal}+1)$
 372 from the corrected $p\text{CO}_2(\text{sal}+1)$ and the $\text{DICgain}(\text{sal}+2)$ using Eq.3. The difference between $p\text{CO}_{2\text{gas}}$
 373 exchange and $p\text{CO}_{2\text{mixing}}$ ($\Delta p\text{CO}_{2\text{gas exchange}}$) is attributed to gas exchange.

374 The thermal influence on the $p\text{CO}_2$ (cooling or heating), was calculated from the TA and DIC
375 conservative mixing, and this time by considering not the in situ measured temperature, but the
376 temperature calculated as linearly conservative between the two endmembers. The difference between
377 $p\text{CO}_{2\text{mixing}}$ (calculated with in situ temperature) and the $p\text{CO}_2$ calculated with the endmembers
378 interpolation is attributed to the thermal $p\text{CO}_2$ along the mixing zone ($\Delta p\text{CO}_{2\text{cooling/heating}}$).

379 2.6 Statistical analysis

380 We applied the Shapiro–Wilk test to investigate the normality of the data set. As the data did not
381 follow normal distributions, we applied non-parametric statistics. To compare the differences between
382 averages for the concentrations of biogeochemical parameters in water, we applied the Mann–Whitney
383 test, which compares the distributions of unmatched groups. Linear and non-linear regressions were
384 calculated to analyze the correlations between variables, providing the best-fit slope, the intercept and
385 the goodness of fit (R^2). All statistical analyses were based on $\alpha = 0.05$. The statistical tests and
386 calculations were performed with the Graph Pad Prism 6 program.

387 3. Results

388 3.1 Spatial and temporal variations of carbonate chemistry and ancillary parameters

389 Spatial and temporal variations of $p\text{CO}_2$ and the main parameters analyzed in this study are presented
390 in Table 1 for the four domains. Surface water temperature showed a marked seasonal trend between
391 26.2 and 31.8 °C in summer (Feb 17 and Mar 18 samplings) and between 23.4 and 26.2 °C in winter
392 (Oct 2017 sampling). The highest temperatures were found in freshwaters, with a cooling trend
393 seaward. This decrease in water temperature was slight, with less than 2 °C difference, on average,
394 between the river and marine zones. However, this seaward temperature decrease trend was not linear
395 during estuarine mixing. Intermediate salinities (values from 20 to 30) were generally sampled close to
396 midday, when the solar irradiance is maximum. These intermediate salinities exhibited temperatures
397 higher than that expected for the conservative mixing because of the heating effect (>0.8 °C, on
398 average), reaching 2.2 °C during sampling on March 18. In contrast, waters with temperatures lower
399 than that expected for the conservative mixing (cooling effect) were verified only on the Feb 17
400 sampling in low salinities.

401 The spatiotemporal salinity distribution in surface waters was governed by the river water discharge
402 (Fig. 2; Fig. S1 Supplementary information). This figure shows the boat track for the three sampling
403 campaigns. Note that the boat tracking was not the same for the sampling campaigns. The principal
404 reason for these differences is that the main estuarine channel navigated in the first two trips (Feb 17
405 and Oct 17) became very shallow and dangerous for navigation. For safety reasons, we decided to
406 navigate along the secondary channel during the trip of March 18. During the period of lowest
407 freshwater discharge ($178 \text{ m}^3 \text{ s}^{-1}$), the mixing zone was located close to the river mouth, with an

408 intrusion of brackish water (salinity ≤ 20) until approximately 4 km inside the internal estuary at high
409 tide. Consequently, at low river discharge, the river plume covered a small area ($\sim 30 \text{ km}^2$) in the
410 adjacent shelf waters, with the marine zone (salinity > 30) located closest to the river mouth (between 3
411 and 6 km from the river mouth) (Fig. S1). Contrastingly, during the Mar 18 sampling at high river
412 flow ($1,240 \text{ m}^3 \text{ s}^{-1}$), the mixing zone was located outside the limit of the coast, and no salinity intrusion
413 occurred in the internal estuary (Fig. 2c). During this high flow period, the mixing zone covered the
414 highest surface area ($\sim 63 \text{ km}^2$) in the adjacent shelf (extending to approximately 12 km from the river
415 mouth), with the marine zone located far from the internal estuary ($> 10 \text{ km}$) (Fig. S1).

416 Surface water $p\text{CO}_2$ in the estuary was strongly related to the salinity and followed a distribution close
417 to that predicted for the mixing curve between the river and marine endmembers, with marked
418 differences between the dry and rainy seasons in the low salinity region (Figs. 2 and 3). During low
419 river flow, the low salinity regions (0-5) presented undersaturated $p\text{CO}_2$ conditions compared with the
420 equilibrium with atmosphere in all sampling campaigns, with mean values of $157 \pm 47 \text{ ppmv}$ and 192
421 $\pm 52 \text{ ppmv}$ for the Feb 17 and Oct 17 samplings, respectively (Fig. 2a,b). In the seaward direction,
422 $p\text{CO}_2$ increased with salinity, following a general trend close to the thermodynamic mixing curve
423 (Figs. 2a,b and 3a,b). During the rainy period, the river zone presented high $p\text{CO}_2$ values with
424 permanent oversaturation (mean of $1,946 \pm 252 \text{ ppmv}$). However, $p\text{CO}_2$ showed a sharp decline
425 between salinities 0 and 5, and quickly reached undersaturated conditions at salinity higher than ~ 10 ,
426 with a mean value of $380 \pm 116 \text{ ppmv}$ in the mixing zone (Fig. 2l and 3h). The marine zone (salinity
427 > 30), during the rainy period, showed $p\text{CO}_2$ values close to those found during the dry period, 439 ± 17
428 ppmv , on average. Mangrove-dominated waters (mangrove creek) presented $p\text{CO}_2$ values much higher
429 (up to $11,514 \text{ ppmv}$) than that found in the waters of the main estuarine channel in all sampling
430 campaigns.

431 Strong relationships with salinity were also verified for carbonate chemistry parameters, including TA,
432 DIC, and $\delta^{13}\text{C}$ -DIC (Fig. 4). The TA and DIC concentrations for the freshwater endmember presented
433 small but statistically significant seasonal variation depending on the intensity of river flow (Mann–
434 Whitney test, $p < 0.0001$). The TA and DIC concentrations in the freshwater endmember were 446 ± 89
435 ($n = 4$) and $435 \pm 77 \mu\text{mol kg}^{-1}$ ($n = 3$) during the dry season and 428 ± 101 and $469 \pm 86 \mu\text{mol kg}^{-1}$
436 during the wet season ($n = 4$), respectively. In the mangrove waters, the TA and DIC concentrations
437 were much higher than those in the conservative mixing, and did not follow the linear pattern found in
438 the main channel (Fig. 4a,b,c,d,e,f). Concerning the $\delta^{13}\text{C}$ -DIC signatures, the freshwater endmember
439 showed important seasonal variation according to river discharge (Fig. 4). During low river flow (Feb
440 17 and Oct 17 samplings), freshwater $\delta^{13}\text{C}$ -DIC values showed a mean of $-3.55 \pm 0.43\text{‰}$, and the
441 distributions along the salinity gradient showed slight ^{13}C depletion compared with the conservative
442 mixing curve (Fig. 4). During high river flow, the stable isotope signature mean was $-7.38 \pm 1.49\text{‰}$,
443 and the $\delta^{13}\text{C}$ -DIC distributions along the salinity gradient showed only a minor deviation from the

444 conservative mixing curve. $\delta^{13}\text{C}$ -DIC values in the mangrove creek were more negative than in the
445 main channel during the two dry periods assessed, with mean and minimum values of $-10.96 \pm 1.23\%$
446 and -11.82% , respectively (Fig 4g,h). During the rainy period, the $\delta^{13}\text{C}$ -DIC values in the mangrove
447 creek presented a mean of $-6.43 \pm 1.79\%$, with enrichment in ^{13}C compared with that of the waters of
448 the main channel, and above the conservative mixing curve (Fig. 4i).

449 During the dry period, Chl *a* concentrations were higher in freshwaters (between 3.86 and $21.30 \mu\text{g L}^{-1}$)
450 and showed a marked decrease in the seaward direction (Fig. 4j,k). This decrease in Chl *a*
451 concentrations with increasing salinity is coincident with an increase in $p\text{CO}_2$. Chl *a* and $p\text{CO}_2$ were
452 negatively correlated in the main channel ($R^2 = 0.59$ on Feb 17; $R^2 = 0.60$ on Oct 17; $p < 0.001$) (Fig. 5).
453 On the other hand, for the rainy period, the freshwaters presented the lowest Chl *a* concentrations, and
454 the distributions did not follow a clear pattern along the salinity gradient, not presenting significant
455 correlations with $p\text{CO}_2$ (Figs. 4 and 5). The Chl *a* concentrations in the mangrove tidal creek were
456 high for all the sampling campaigns, reaching a maximum value of $26 \mu\text{g L}^{-1}$ on February 17.

457 3.2 Tidal and diurnal variations of carbonate chemistry in the mangrove creek

458 Results of diurnal variations of the carbonate chemistry parameters in the tidal creek are presented in
459 Table 2 and Figures 6 and 7. We sampled one ebb tide at daytime followed by one flood tide at
460 nighttime and one ebb tide at nighttime. Tidal amplitude was 0.42 m for the first ebb phase (from
461 $\sim 12:00$ pm to $06:30$ pm) and 0.64 m for the second ebb phase (from $\sim 00:30$ am to $07:30$ am). For the
462 first tidal cycle, no statistically significant difference was observed between the ebb and flood tides
463 (Mann Whitney Test; $p > 0.05$); however, the second ebb tide (nighttime) presented higher salinity
464 values than those found in the other sampled periods (Mann Whitney Test; $p < 0.01$), following an
465 atypical pattern. Daytime sampling presented higher average temperature (30.0 ± 0.3 °C) than
466 nighttime sampling (28.3 ± 0.3 °C).

467 In the mangrove creek, $p\text{CO}_2$ values varied drastically along the diurnal time scale, with means of
468 $7,439 \pm 1,390$ ppmv during daytime ebb tide, $11,191 \pm 2,264$ ppmv during nighttime flood tide, and
469 $18,276 \pm 3,408$ ppmv during nighttime ebb tide (Table 2). The maximum $p\text{CO}_2$ value ($21,720$ ppmv)
470 occurred during nighttime ebb tide, whereas the minimum $p\text{CO}_2$ value ($5,318$ ppmv) occurred during
471 daytime ebb tide. The highest $p\text{CO}_2$ values during nighttime ebb tide were coincident with the highest
472 TA, DIC and salinity concentrations and the lowest pH and $\delta^{13}\text{C}$ -DIC values (Figs. 6 and 7). In this
473 way, $p\text{CO}_2$ showed strong negative correlations with DO ($R^2 = 0.99$; $p < 0.0001$) and $\delta^{13}\text{C}$ -DIC ($R^2 =$
474 0.97 ; $p < 0.0001$) (Fig. 7d). Hypoxic and anoxic conditions occurred from the end of the nighttime
475 period until sunrise (between approximately $00:30$ am and $07:30$ am) (Fig. 6c). DO concentrations
476 were also strongly positively correlated with $\delta^{13}\text{C}$ -DIC values ($R^2 = 0.96$; $p < 0.0001$) (Fig. 7c). During
477 the diurnal cycle in the mangrove creek, $\delta^{13}\text{C}$ -DIC values varied between -8.79% (nighttime ebb tide)
478 and -3.27% (daytime flood tide). The TA and DIC distributions followed a nearly linear relationship

479 with salinity (Fig. 7a). Increased TA concentrations followed decreased DO concentrations linearly,
480 but only under hypoxic/anoxic conditions (Fig. 7b). As expected, E-DIC and AOU were well
481 correlated in the mangrove creek, presenting positive concentrations and a high deviation above the
482 line 1:1 in all sampling campaigns, which were different from the main channel pattern (Fig. 8a). The
483 TA and DIC concentrations also showed strong deviation from the conservative mixing (Δ TA and
484 Δ DIC), and different from the pattern observed in the main channel (Fig. 8b).

485 3.3 Gas transfer velocities and CO₂ exchanges at the air-water interface

486 The *k*-wind speed parameterization is one of the most critical parameters to compute the air-sea CO₂
487 fluxes between the *p*CO₂ gradients in the surface ocean and lower atmosphere (Borges and Abril,
488 2011; Wanninkhof, 2014; Call et al., 2015). Diverse formulations of *k*-wind parameterizations are
489 available to estimate the main driving forces of turbulence at the air-sea interface, based on theoretical
490 results from several studies that showed that their performance is more appropriate under certain
491 conditions and environments (Wanninkhof, 2014). Thus, we computed the air-sea CO₂ fluxes using
492 three different *k*-wind parameterizations: two appropriate for estuarine environments (Raymond and
493 Cole, 2001; Abril et al., 2009) and one appropriate for open ocean waters (Wanninkhof, 1992),
494 providing ranges of estimates (Table 3).

495 The calculated gas transfer velocities varied between 0.44 and 21.26 cm h⁻¹ over the morning,
496 afternoon and night periods (Table 3). The *k*₆₀₀ values calculated from the equation of Abril et al.
497 (2009) for estuarine waters, which account for wind velocity, estuarine size and current velocity, were
498 higher than those calculated using the parameterizations proposed by Raymond and Cole (2001) and
499 Wanninkhof (1992), except for wind speeds >6 m s⁻¹, when the equation of Abril et al. (2009)
500 provided lower gas transfer values. The inner estuary current velocities estimated for each estuarine
501 region, considering the water discharge and the cross-sectional area, ranged from 0.1 m s⁻¹, during low
502 river flow, to 1.2 m s⁻¹, during high river flow. For the outer estuary (river plume), the current
503 velocities were measured according to Knoppers et al. (1999). The Oct 17 sampling presented higher
504 gas transfer velocity values compared with those measured on February 17 and March 18 (*p*<0.0001; *t*
505 test) as a result of the higher wind speed averages. Higher computed gas transfer velocities occurred
506 during the afternoon, followed by night and morning (Table 3).

507 Calculated CO₂ fluxes showed high spatiotemporal variability (Table 3) related to salinity and distance
508 from the mangrove forest. The freshwater endmember was a CO₂ sink during low discharge and a CO₂
509 source during high discharge. The highest values of air-water CO₂ uptake in the estuarine zone
510 (between -26.23 and -37.80 mmol C m² d⁻¹) were found during the afternoon, when wind speed was
511 strongest. The mixing zone was also a CO₂ sink, but with smaller intensity compared with fresh and
512 low-salinity waters. The air-water CO₂ fluxes in the mixing zone varied between -0.34 and -18.41
513 mmol C m² d⁻¹. The marine zone acted as a slight CO₂ source, with emissions ranging from 0.12 to

514 5.78 mmol C m² d⁻¹. The mangrove creek waters were a strong CO₂ source, with values ranging from
515 1.97 to 216.14 mmol C m² d⁻¹.

516 Considering all the estuarine areas and time of sampling (morning, afternoon and night), the estuary
517 was a slight CO₂ sink under dry conditions, with weighted surface fluxes ranging from -1.34 to -5.26
518 mmol C m² d⁻¹ (Table 3), representing an uptake between 1.45 and 5.72 t C d⁻¹. During high river
519 discharge (Mar 18), the low salinity region was a strong CO₂ source, with emissions ranging from 6.36
520 to 117.77 mmol C m² d⁻¹, but the mixing zone remained a slight CO₂ sink, with fluxes varying
521 between -0.12 and -2.93 mmol m² d⁻¹. The marine zone was a CO₂ source, but with *p*CO₂ values very
522 close to the equilibrium with the atmosphere and emissions ranging from 0.05 to 1.27 mmol m² d⁻¹.
523 The mangrove tidal creek was a strong source of atmospheric CO₂, with degassing ranging from 9.34
524 to 358.39 mmol m² d⁻¹. Considering the estuary as a whole, the weighted CO₂ surface emissions during
525 high river discharge ranged from 5.71 to 19.37 mmol C m² d⁻¹, representing an efflux between 6.21
526 and 21.09 t C d⁻¹.

527 The riverine inputs of DIC to the estuary calculated by multiplying the DIC concentrations at the river
528 endmember by the river flow were 106 tC d⁻¹, 64 tC d⁻¹ and 488 tC d⁻¹ for the samplings conducted on
529 February 17, October 17 and March 18, respectively. Considering the estuary as a whole, the mean net
530 estuarine fluxes at the air-sea interface were -3.32 tC d⁻¹, -5.72 tC d⁻¹ and 15.88 tC d⁻¹ for the Feb 17,
531 Oct 17 and Mar 18 samplings, respectively. Consequently, the DIC inputs from the river to the estuary
532 were between ~11 and 32 times higher than the carbon influx or efflux at the air-water interface.

533 4. Discussion

534 4.1. Predominance of thermodynamic processes on *p*CO₂ distributions in the main channel and CO₂
535 air-water fluxes

536 Oversaturated *p*CO₂ conditions are usually observed in river-dominated estuaries as a result of the net
537 heterotrophic metabolism sustained by inputs of organic carbon from the catchment (Frankignoulle et
538 al., 1998; Dai et al., 2009; Cai, 2011; Borges and Abril, 2011), river input of dissolved CO₂ (Abril et
539 al. 2000; Jiang et al., 2008; Joesoef et al., 2015; Van Dam et al., 2018a), and of tidal pumping (Maher
540 et al., 2015; Santos et al., 2018). The overall trend of *p*CO₂ decreasing seaward has mostly been
541 described in rivers with moderate to high TA concentrations ($\geq 1000 \mu\text{mol kg}^{-1}$) and moderate to long
542 water residence time (Frankignoulle et al., 1998; Borges and Abril, 2011). However, in the case of
543 many tropical river deltas, TA concentrations are generally low at the riverine endmember (Cai et al.,
544 2008), and these estuaries have relatively short water residence time (Ludwig et al., 1998). Under such
545 conditions, thermodynamic changes during estuarine mixing generate strong *p*CO₂ undersaturation in
546 the low salinity region (Whitfield and Turner, 1986; Cai et al., 2013) that can exceed CO₂ production
547 and consumption by biological processes. Low TA concentrations in the river endmember provide low
548 buffering capacity in fresh and low salinity waters (Egleston et al., 2010; Hu and Cai, 2013; Cai et al.,

549 2013). We calculated the Revelle factor ($\gamma_{\text{DIC}} = \partial \ln(\text{CO}_2) / \partial \text{DIC}$)⁻¹ along the mixing zone of the PSRE
550 to investigate its buffering capacity (Revelle and Suess, 1957; Egleston et al., 2010). The results
551 corroborate this hypothesis, showing that waters with salinities <10 presented the lowest buffering
552 capacity in all sampling campaigns (Fig. S2; Supplementary information).

553 In the PSRE, $p\text{CO}_2$ distributions along the salinity gradient were very close to that predicted by
554 theoretical thermodynamic changes during conservative mixing between the river and marine
555 endmembers, including a $p\text{CO}_2$ minimum much lower than the atmospheric value (Fig. 3). During low
556 river discharge (Feb-17 and Oct-17), the river endmember already presented CO_2 undersaturation with
557 relation to the atmosphere (due to phytoplankton uptake). During high river flow, $p\text{CO}_2$ was high in
558 freshwater, but showed a sharp decrease between salinities 0 and 5 and remained below the
559 atmospheric value along the mixing zone (salinity 0-30). This marked $p\text{CO}_2$ decrease occurred in
560 poorly buffered estuarine waters. The mixing of river water and seawater generates strong equilibrium
561 displacements between species of the carbonate system and strongly alters water $p\text{CO}_2$ values and air-
562 water CO_2 fluxes, creating $p\text{CO}_2$ undersaturation by inorganic processes (Whitfield and Turner, 1986;
563 Cai et al., 2013). In the case of acidic freshwater with low TA and eventually high $p\text{CO}_2$, dissolved
564 CO_2 is absorbed by the buffering capacity of the seawater and immediately incorporated into the
565 HCO_3^- and CO_3^{2-} pools rather than totally emitted to the atmosphere. Because the displacement of
566 chemical equilibriums is an almost instantaneous process, it can occur completely even with the short
567 residence time of waters of few days in the estuary.

568 A previous study discussed these acid-base processes in a theoretically, suggesting that the Amazon
569 River presents a CO_2 deficit along its mixing zone with relation to atmospheric conditions as a result
570 of thermodynamic changes, and the $p\text{CO}_2$ variations are quickly dominated by seawater, sustaining a
571 CO_2 sink along the river-ocean mixing (Cai et al., 2013). In the PSRE, these acid-base processes are
572 confirmed along the mixing zone, showing strong agreement between the theoretical model and *in situ*
573 data. For the three sampling campaigns, however, the $p\text{CO}_2$ values in the salinity gradient remained
574 close but slightly above the theoretical dilution curve ($p\text{CO}_{2 \text{ mixing}}$). The slight deviations of measured
575 $p\text{CO}_2$ compared with $p\text{CO}_{2 \text{ mixing}}$ are attributed to the influence of biological activities, gas exchange,
576 and thermal variability during estuarine mixing, as discussed in the following section.

577

578 4.2 Origin of the observed $p\text{CO}_2$ deviation from conservative mixing

579 Deviations of measured $p\text{CO}_2$ compared with $p\text{CO}_{2 \text{ mixing}}$ are potentially related to gas exchange,
580 thermal effect (heating/cooling), and ecosystem metabolism (estuarine autotrophy/heterotrophy plus
581 tidal pumping) during estuarine mixing (Jiang et al., 2008; Joesoef et al., 2015; Van Dam et al.,
582 2018a). In order to account for these processes, first we binned the measured $p\text{CO}_2$, calculating the
583 means and standard deviations for each salinity increment. Then we calculated the effects of gas

584 exchange and thermal variability on $p\text{CO}_2$ mixing as described in material and methods (section 2.5.5)
585 for the same salinity intervals, assuming a constant and homogeneous residence time along the entire
586 salinity gradient. This way we could calculate different $p\text{CO}_2$ curves during estuarine mixing:
587 measured $p\text{CO}_2$ ($p\text{CO}_2$ measured), conservative $p\text{CO}_2$ ($p\text{CO}_2$ mixing), conservative $p\text{CO}_2$ corrected for gas
588 exchange ($p\text{CO}_2$ gas exchange), and conservative $p\text{CO}_2$ corrected for thermal effects ($p\text{CO}_2$ heating/cooling) (Fig.
589 9). The difference between $p\text{CO}_2$ gas exchange and $p\text{CO}_2$ mixing ($\Delta p\text{CO}_2$ gas exchange) was attributed to gas
590 exchange, whereas the difference between $p\text{CO}_2$ heating/cooling and $p\text{CO}_2$ mixing ($\Delta p\text{CO}_2$ heating/cooling) was
591 attributed to thermal effects. Finally, the residual difference between $p\text{CO}_2$ measured and $p\text{CO}_2$ gas exchange +
592 $p\text{CO}_2$ heating/cooling ($\Delta p\text{CO}_2$ residual) was assigned to ecosystem metabolism (Fig. 9).

593 During low river flow, the values of $\Delta p\text{CO}_2$ gas exchange were positive along the entire salinity gradient in
594 all sampling campaigns, with higher values at low salinities (<10), indicating strong CO_2 invasion that
595 increases the values of $p\text{CO}_2$ in the water (Fig. 9d,e). During the rainy period, the low salinities also
596 showed the highest $\Delta p\text{CO}_2$ gas exchange deviations, but with negative values, indicating the influence of
597 CO_2 evasion that decreases the values of $p\text{CO}_2$ (Fig. 9f). This shows that the maximal influence of gas
598 exchange on $p\text{CO}_2$ variability during estuarine mixing occurs at low salinities. The influence of gas
599 exchange on $p\text{CO}_2$ showed a marked decrease tendency seaward, with nearly negligible influence
600 from salinities >10, as a result of higher buffering capacity and lower air-water $p\text{CO}_2$ gradient. In
601 addition, in intermediate and high salinity waters, $p\text{CO}_2$ values remain very close to air $p\text{CO}_2$ values,
602 minimizing the effect of atmospheric gas exchange. Consequently, during estuarine mixing in the
603 PSRE, the process of gas exchange has a significant impact on DIC concentrations, particularly in the
604 low-buffered waters of the river domain (Fig. S2; Supplementary information). The highest influence
605 of CO_2 invasion was verified on October 17, when the highest wind and gas transfer velocities were
606 observed (Table 3) and $\Delta p\text{CO}_2$ gas exchange reached a value of 50 ppmv (Fig. 9b,e). The highest influence
607 of CO_2 evasion was verified on March 18, when the $\Delta p\text{CO}_2$ gas exchange reached a value of -150 ppmv
608 (Fig 9f). For intermediate and high salinity waters, the influence of gas exchange on $p\text{CO}_2$ variability
609 was minor and nearly negligible, close to that of the marine endmember. Indeed, previous studies have
610 reported lower buffering capacities in regions dominated by freshwaters when the freshwater
611 endmember present low TA concentrations (Hu and Cai, 2013; Cai et al., 2013).

612 The values of $\Delta p\text{CO}_2$ cooling/heating were almost always positive, indicating that the water in the estuarine
613 zone was warmed compared to expected behavior for two endmembers mixing. The highest values of
614 $\Delta p\text{CO}_2$ cooling/heating occurred in mid- to high-salinity waters (salinity values of 20-30). These salinities
615 were generally sampled around midday, when solar irradiance is highest, thus causing this thermal
616 effect. For these salinities of the PSRE, the increase of 1 °C in water temperature tend to increase
617 $p\text{CO}_2$ by ~15 ppmv. As the difference between the temperature measured *in situ* and that predicted by
618 the conservative mixing mean of approximately +0.8 °C, the influence of heating was 12 ppmv, on
619 average; however, the heating effect could reach up ~30 ppmv of $p\text{CO}_2$ under conditions of high

620 intensity solar irradiance during sampling in summer, particularly on the Mar 18 sampling (Fig.9c,f).
621 An exception occurred during sampling on February 17, when water cooling was observed at low
622 salinities (Fig. 9a,d). In addition to local thermal effects occurring at the time scale of estuarine
623 mixing, seasonal variation in temperature induced variations in $p\text{CO}_2$ mainly in waters with salinity
624 >30 , resulting in approximately one half (30 ppmv) of the $p\text{CO}_2$ difference between summer and
625 winter (Takahashi et al. 2002). Indeed, $p\text{CO}_2$ variability in the oligotrophic surface waters of the
626 continental shelf of the Southwestern Subtropical Atlantic Ocean is mainly driven by temperature (Ito
627 et al., 2005). The continental shelf of southeastern Brazil, where the river plume of the PSRE is
628 located, is influenced by the Western Boundary Current, which flows southward along the Brazilian
629 shelf as a section of the South Atlantic Ocean subtropical gyre (Campos et al., 2000). The Brazil
630 Current carries the Tropical Water in the upper layers, the South Atlantic Central Water at
631 intermediate depths, in addition to the Coastal Water in the inner portion of continental shelves, which
632 compose the water masses in the region (Castro and Miranda, 1998).

633 In general, the differences between $p\text{CO}_{2 \text{ measured}}$ and $p\text{CO}_{2 \text{ mixing}}$ were positive for all sampling
634 campaigns, with deviation means of +45 ppmv, +30 ppmv and +32 ppmv for the Feb 17, Oct 17 and
635 Feb 18 samplings, respectively (Fig. 9d,e,f). Together, the gas exchange and thermal effects accounted
636 for nearly half of this difference (with gas exchange and water heating corresponding to approximately
637 18% and 36%, respectively), whereas the other half (residual difference, $\Delta p\text{CO}_{2 \text{ residual}}$) was attributed
638 to the ecosystem metabolism along the mixing zone. These positive deviations reveal a CO_2
639 production along the mixing zone that is not linked to conservative mixing, gas exchange and thermal
640 variability, but rather to net heterotrophy during estuarine mixing. However, some negative $\Delta p\text{CO}_{2 \text{ residual}}$
641 values were also observed in low salinity waters under low river flow conditions, which shows a
642 net biological CO_2 uptake by phytoplanktonic primary production. At low salinities in summer, some
643 autotrophy decreases $p\text{CO}_{2 \text{ measured}}$ values in relation to those of $p\text{CO}_{2 \text{ mixing}}$.

644

645 4.3 Impact of phytoplankton on the river and low salinity region

646 Phytoplankton had an important impact on $p\text{CO}_2$ in the low salinity region of the PSRE, as revealed by
647 the Chl *a* concentrations (Fig. 4j,k,l), the $\delta^{13}\text{C}$ -DIC signatures (Fig. 4g,h,i), and by the mixing model
648 presented in the previous section (Fig. 9). During low river flow, the PSRE presented an atypical
649 pattern of $p\text{CO}_2$ variability along the salinity gradient. In that period, Chl *a* concentrations were higher
650 in the fresh and low salinity waters, with a strong negative correlation with water $p\text{CO}_2$, showing an
651 uptake by planktonic primary production (Fig. 5). This inverse correlation between Chl *a* and $p\text{CO}_2$
652 occurred only during low river flow, when the lower hydrological model forcing provides favorable
653 conditions for phytoplankton growth in freshwaters because of the high availability of nutrients, high
654 incidence of photosynthetically active radiance, increased water residence time, and formation of

655 vertical water column stratification (Souza et al., 2010; Cotovicz et al., 2013). The freshwater
656 discharge contributes to maintaining low dilution and flushing potentials, changing the trophic status
657 in the estuary from oligotrophic to mesotrophic (Cotovicz Jr. et al., 2013). Uptake of CO₂ by
658 phytoplankton is also evidenced by the negative and significant relationship between *p*CO₂, DO, and
659 δ¹³C-DIC signatures (Fig. S3, Supplementary information). During low river flow, *p*CO₂ values were
660 lower, whereas DO concentrations and δ¹³C-DIC signatures were higher, indicating prevalence of net
661 autotrophy. During photosynthesis, plants preferentially utilize the lighter carbon isotope (¹²C) rather
662 than the heavier carbon isotope (¹³C), making the remaining DIC pool ¹³C enriched (Finlay and
663 Kendall, 2007; Cotovicz et al., 2019). A previous study showed that the stable isotope composition of
664 the dissolved CO₂ (δ¹³C-DOC) also presented a marked seasonal signal in the PSRE, with more ¹³C
665 depletion in the rainy season (minimum of -25.7 ‰) than in the dry season (maximum of -20.0 ‰)
666 (Marques et al., 2017). These authors suggested that algae could be a potential source of isotopically
667 heavier DOC to the river zone during the dry season, as our data of low *p*CO₂ values and high δ¹³C-
668 DIC signatures and Chl *a* concentrations also suggest.

669 The Paraíba do Sul River receives large amounts of domestic and industrial effluents along its course,
670 which drains one of the most urbanized and industrialized regions of Brazil (Cotovicz et al., 2013).
671 Low *p*CO₂ levels due to nutrient enrichment and phytoplankton blooms development has been
672 previously shown for other coastal bays surrounded by large urban areas, e.g., the tropical Guanabara
673 Bay (Cotovicz et al., 2015) and in the temperate Tokyo Bay (Kubo et al., 2017). However, this is very
674 uncommon in river-dominated estuaries, which are considered important CO₂ sources globally
675 (Borges and Abril, 2011). To the best of our knowledge, this pattern of low *p*CO₂ in freshwater was
676 only reported in the temperate Merrimack Estuary, located in a highly industrialized region of the
677 United States, which experienced a rapid population growth (Salisbury et al., 2008).

678 Large phytoplankton biomass is observed in the freshwaters of the PSRE during low river flow, but it
679 shows a marked decline seaward (Fig. 4j,k,l). Indeed, estuarine deltas with short residence times are
680 characterized by rapid salinity changes in water masses, which hinder the installation of phytoplankton
681 communities because of osmotic stress (Lancelot and Muylaert, 2011). Salinity and turbulent mixing
682 are often reported as the major factors determining phytoplankton distribution (Cloern, 1996; Lancelot
683 and Muylaert, 2011). In addition to osmotic stress, the community structure, biomass production,
684 species succession, and magnitude of the phytoplankton bloom along the estuary are also related to
685 small availability and short residence time (Roubeix et al., 2008; Flöder et al., 2010). Thus, sharp
686 salinity changes, high turbulence, turbidity, and short residence time create conditions unfavorable for
687 phytoplankton production.

688 During high river flow, the phytoplankton community is probably flushed and dies in the main
689 channel. The river discharge is stronger than the tidal prism, and the mixing occurs offshore.

690 According to Lucas et al. (2009), the phytoplankton biomass can increase in an estuary only if the net
691 specific growth rates exceed the water residence time and flushing time in the estuary. In general,
692 development of phytoplankton blooms in estuaries is inversely correlated to river water discharge
693 (Strayer et al., 2008). However, during the flood on May 18, part of the phytoplankton was apparently
694 trapped in the low salinity mangrove creeks, where the observed Chl *a* concentrations reached $\sim 70 \mu\text{g}$
695 L^{-1} (Table 2). Mangrove creek provided ideal conditions for phytoplankton refuge due to low salinity
696 stress. This created a special case in this estuary - a low salinity mangrove creek enriched with
697 phytoplankton. Phytoplankton activity and the influence on DIC and $\delta^{13}\text{C}$ -DIC concentrations are
698 evident in the mangrove creek within the diurnal variations (Fig. 6). During the diel sampling in the
699 mangrove creek, phytoplankton biomass was high, and managed to drawdown $p\text{CO}_2$ during the
700 afternoon compare with nighttime, making $\delta^{13}\text{C}$ -DIC less negative due to a preferential uptake of ^{12}C
701 from the DIC pool during photosynthesis. Similar processes have been described in a hypertrophic
702 lake (Lake Taihu, China; Van Dam et al., 2018b) and in a tropical eutrophic coastal embayment
703 (Guanabara Bay, Brazil, Cotovicz Jr. et al., 2019), but not in mangrove creeks. During the rainy
704 period, the mangrove creek presented more ^{13}C -enriched signatures than the expected for conservative
705 mixing (Fig. 4g,h,i) and related to this phytoplankton activity. However, this pattern in the mangrove
706 creek was not verified during the dry period, when Chl *a* concentration do not exceed $14.6 \mu\text{g L}^{-1}$, and
707 $\delta^{13}\text{C}$ -DIC signatures were ^{13}C -depleted more than would be expected for conservative mixing, a
708 distribution generally found in mangrove-dominated waters because of enhanced respiratory processes
709 (Bouillon et al., 2007; 2011; Miyajima et al., 2009; Sippo et al., 2016).

710 4.4. Evidence of heterotrophy in the mixing zone

711 Multiplication of the residual $p\text{CO}_2$ difference attributed to biological activities ($\Delta p\text{CO}_2_{\text{residual}}$) with gas
712 transfer velocity (Eq. 3) provides an estimate of the community production (NCP) (Table 4). The gas
713 transfer velocity parameterization of Raymond and Cole (2001), which resulted in intermediate values
714 of air-water fluxes (Table 3), was chosen for this calculation. For the entire estuarine mixing zone,
715 average NCP was $-1.70 \text{ mmol m}^{-2} \text{ d}^{-1}$ on February 17, $-1.13 \text{ mmol m}^{-2} \text{ d}^{-1}$ on October 17, and -0.58
716 $\text{mmol m}^{-2} \text{ d}^{-1}$ on February 18. NCP values in the PSRE are in the lower range of NCP and ecosystem
717 metabolism in the European coastal zone (Gazeau et al., 2004). These low NCP values observed along
718 the mixing zone of the PSRE confirm the moderate influence of biological activities, with microbial
719 respiration not being sufficient to create CO_2 oversaturation in relation to the atmosphere. During low
720 river flow, the entire mixing zone was already undersaturated, and the net heterotrophy was also not
721 sufficient to generate CO_2 outgassing. This created a very special condition in the mixing zone of the
722 estuary, with concomitant $p\text{CO}_2$ undersaturation and heterotrophic metabolism. During high river
723 flow, the heterotrophic metabolism was also apparent in the freshwater owing to $p\text{CO}_2$ values above
724 the atmospheric equilibrium, DO concentrations below the atmospheric equilibrium, and more
725 negative $\delta^{13}\text{C}$ -DIC signatures, all indicating prevalence of microbial respiration over primary

726 production (Fig. S3, Supplementary information). However, as previously shown (Fig 9f),
727 heterotrophic metabolism was modest in the estuary during high discharge, and thus the river input
728 was a major contributor to the high CO₂ concentrations, at least in the region dominated by
729 freshwaters (0-5 salinity). Riverine CO₂ inputs represent the major CO₂ source in other river-
730 dominated estuaries (Jiang et al., 2008; Joesoef et al., 2015; Van Dam et al., 2018a).

731 The covariations of $\Delta\delta^{13}\text{C-DIC}$ and ΔDIC , considering only the main river channel, also reveal net
732 heterotrophy, with values of $\delta^{13}\text{C-DIC}$ showing slight ¹³C-depleted signatures (negative $\Delta\delta^{13}\text{C-DIC}$)
733 compared with the conservative mixing (Fig. 10). This graph is divided in four quadrants that
734 represent the processes of primary production/outgassing of CO₂ (quadrant PP/OG), carbonate
735 precipitation (quadrant CP), organic carbon degradation (quadrant DC), and carbonate dissolution
736 (quadrant CD) (Alling et al., 2012; Samanta et al., 2015; Cotovicz et al., 2019). The red arrows
737 represent the directions of slopes in which data points would move in relation to a specific process,
738 whereas the grey lines represent the directions in which samples would move in relation to the effects
739 of more than one process (see figure caption for further details). The data points of the PSRE are
740 mostly located in the quadrant of organic carbon degradation (DC), and to a lesser extent in the
741 quadrant of carbonate precipitation (CP). The process of organic carbon degradation increases the DIC
742 concentrations in water (positive ΔDIC) and decreases the isotopic signature of DIC (negative $\Delta\delta^{13}\text{C-}$
743 DIC) (Alling et al., 2012; Samanta et al., 2015). The respiration of organic carbon produces CO₂ with
744 approximately the same isotopic signature than that of the respired organic matter, which is generally
745 ¹³C depleted; consequently, the DIC pool tends to be more depleted in ¹³C when the organic matter
746 respiration rates are high and prevalent in phytoplankton uptake (Kendall et al., 2004; Bouillon et al.,
747 2011; Borges et al., 2018). The process of carbonate precipitation is unlikely to occur, because this
748 estuary is not known to host high levels of calcifying fauna and flora. However, as pointed out, DIC
749 and $\delta^{13}\text{C-DIC}$ can be subjected to more than one process at same time. This means that if one sample
750 was subjected to organic carbon degradation followed by CO₂ outgassing, it could also be located in
751 the quadrant of carbonate precipitation (Samanta et al., 2015). This probably occurs in regions that are
752 sources of CO₂ to the atmosphere: the mixing region with very low salinities on March 18 and in
753 offshore waters on Feb 17 and Mar 18 (Figs. 9 and 10). These deviations of $\delta^{13}\text{C-DIC}$ signatures and
754 DIC concentrations from the conservative mixing are thus very consistent with the approach,
755 considering the differences between $p\text{CO}_2_{\text{measured}}$ and $p\text{CO}_2_{\text{mixing}}$ (Fig. 9).

756 The marked seaward decrease of Chl *a* concentrations along the mixing zone in the main channel
757 suggests that these phytoplankton cells are dying, providing labile organic material for decomposition
758 by heterotrophic bacteria. However, heterotrophy remains weak probably because of the short water
759 residence time in the mixing zone, a crucial factor for bacterial growth in estuaries (Del Giorgio and
760 Bouvier, 2002; Crump et al., 2004), and because of salinity stress in the bacterioplankton, since that
761 freshwater bacteria could remain active in the estuary, but at a reduced rate (Crump et al., 2004). The

762 Δ TA and Δ DIC values along the salinity gradient in the main channel were low (generally $<50 \mu\text{mol}$
763 kg^{-1} ; Fig. 8b), which correspond to less than 5% of the DIC and TA pools, confirming a modest
764 biological influence in the main channel.

765

766 4.5 Tidal pumping in the mangrove creek

767 Water $p\text{CO}_2$ values in the mangrove creek were much higher than those in the main channel, as well as
768 than those predicted by the conservative mixing curve (Fig.3). In addition, the mean $p\text{CO}_2$ values
769 observed in the mangrove creeks were within the high range of values reported in other mangroves
770 worldwide. The maximum $p\text{CO}_2$ value reported here was 22,000 ppmv and, to the best of our
771 knowledge, only one study reported a higher maximum $p\text{CO}_2$ value (27,000 ppmv; Australian micro-
772 tidal system, Call et al. 2015). Our measured $p\text{CO}_2$ values are similar to those observed in some micro-
773 , meso- (Koné and Borges, 2008; Call et al., 2015; Rosentreter et al., 2018) and macro-tidal (Call et
774 al., 2019) mangrove creeks. The mangrove waters presented higher values of Δ TA and Δ DIC
775 compared with those of the main channel (Fig. 8b). The slope of the linear regression of Δ TA vs.
776 Δ DIC in the mangrove creek was 0.73, a value within the theoretical slopes of organic matter aerobic
777 degradation (0.2), denitrification (0.8), sulfate reduction (0.9), and calcium carbonate (CaCO_3)
778 dissolution (2.0) (Borges et al., 2003; Bouillon et al., 2007). Denitrification is likely to be minor in
779 mangrove ecosystems due to the low concentrations of inorganic N-species (Alongi et al., 2000;
780 Maher et al., 2016). CaCO_3 dissolution is unlike to be important in this mangrove that does not receive
781 important amounts of CaCO_3 from adjacent ecosystems. This slope is rather similar to those found in
782 the mangrove tidal creeks of Papua New Guinea (Borges et al., 2003), Kenya (Bouillon et al. 2007)
783 and Australia (Sippo et al., 2016) and in the secondary channels of the Mekong Delta (Borges et al.,
784 2018), suggesting that the main processes responsible for TA and DIC production are sulphate
785 reduction and aerobic degradation of organic matter. TA production occurs when DO presents
786 saturation $<30\%$ (Fig. 7b), and it is maximal under hypoxic/anoxic conditions. These results reveal
787 that the mangrove creek in the PSRE is producing and exporting DIC and TA to mangrove
788 surrounding waters, a process recently reported in a number of other mangroves that still needs precise
789 quantification (Sippo et al., 2016; and references there in). Important correlations of radon (^{222}Rn) with
790 DIC and TA in several mangrove creeks located at different coastal latitudes have evidenced an
791 important production of TA and DIC in mangrove sediment pore waters with export mediated by
792 tidally induced processes (Santos et al., 2018; Call et al., 2019 and references therein).

793 The relationship between E-DIC and AOU (Fig. 08a) exhibited important deviations above the 1:1 line
794 that occurred almost exclusively in the mangrove creek. This high deviation above the 1:1 line in the
795 mangrove creek could be associated with anaerobic organic matter degradation in sediments and
796 lateral transfer via tidal pumping. Because the process of sulphate reduction is a dominant

797 mineralization pathway of organic carbon in mangroves (Borges et al., 2003; Bouillon et al., 2007;
798 Sippo et al., 2016), secondary metabolites such as Fe(II) and sulfides escape re-oxidation by oxygen
799 through the formation of pyrite (Alongi et al., 2000; Hu and Cai, 2011), resulting in net consumption
800 of protons and net production of TA.

801 Tidal variation also seems to be important considering the modulation of CO₂ production and
802 consumption in the mangrove tidal creek (Figs. 6 and 7). On May 2017, CO₂ uptake occurred during
803 daytime, making the waters enriched in δ¹³C-DIC, with drawdown of *p*CO₂ and production of DO,
804 even during ebb tide. This explains the low *p*CO₂ values at ebb tide (daytime), which are not common
805 in mangrove waters (Bouillon et al., 2011; Sippo et al., 2016). The maximal CO₂ concentrations were
806 found during ebb tide in early morning, concomitant with the highest concentrations of TA and DIC
807 and the highest ¹³C depletion, evidencing the carbon respiration accumulated overnight and the
808 influence of diagenetic processes. Tidal pumping is facilitated, during ebb tide, by the semi-diurnal
809 flushing of crab burrows that are considerably enriched in dissolved carbon due to the diffusion and
810 advection of pore water from the soils (Borges et al., 2003; Call et al., 2015; Maher et al., 2015). This
811 *p*CO₂ pattern peaking at the nighttime ebb tide is consistent with findings of previous studies that
812 suggest a pore water source of surface water *p*CO₂ (Bouillon et al., 2007; Kristensen et al., 2008; Linto
813 et al., 2014; Call et al., 2019).

814

815 4.6 CO₂ fluxes in the PSRE compared with those of other estuaries

816 Estuarine systems and mangrove surrounding waters are sources of CO₂ to the atmosphere and
817 significant for regional and global carbon budgets (Bouillon et al., 2008; Maher et al., 2013; Chen et
818 al., 2013; Laruelle et al., 2013). According to the most recent global compilation of estuarine CO₂
819 emissions propose by Chen et al. (2013), upper estuaries are CO₂ sources of the order of 106 mmol C
820 m⁻² d⁻¹, mid-estuaries emit 47 mmol C m⁻² d⁻¹, and lower estuaries with salinities >25 emit 23 mmol C
821 m⁻² d⁻¹. These values are much higher than those found in the PSRE, which partially acts as a CO₂
822 sink, with annual CO₂ emission of only 1.63 to 11.98 mmol C m⁻² d⁻¹ (Table 3). The low CO₂ fluxes in
823 the PSRE are consistent with those found in the continental shelf of the subtropical Atlantic Ocean
824 (0.3-9.8 mmol C m⁻² d⁻¹; Ito et al., 2005). Considering only the dry period, the estuary as a whole was
825 a CO₂ sink, with fluxes ranging from -0.34 to -5.26 mmol C m⁻² d⁻¹. These values are close to those
826 reported in the tropical Aby Lagoon (-7.39 mmolC m⁻² d⁻¹; Koné et al., 2008), subtropical southeast
827 Australian estuaries (-3.28 to -12.05 mmolC m⁻² d⁻¹; Maher and Eyre, 2012), the tropical eutrophic
828 Guanabara Bay (-26.3 to -50.1 mmolC m⁻² d⁻¹; Cotovicz et al., 2015), the temperate Tokyo Bay (-8.8
829 mmolC m⁻² d⁻¹; Kubo et al., 2017) and the Liminganlahti Bay (-2.46 mmolC m⁻² d⁻¹; Silvennoinen et
830 al., 2008), in addition to some fjords (Takahashi et al., 2012). All these systems are marine-dominated
831 estuaries, different from the PSRE, which is a river-dominated estuary. To the best of our knowledge,

832 only the temperate Kennebec River ($-1.36 \text{ mmol C m}^{-2} \text{ d}^{-1}$; Takahashi et al., 2012) and the New
833 River/USA (-0.5 to $5.4 \text{ mmol C m}^{-2} \text{ d}^{-1}$; Crosswell et al., 2017) are river-dominated estuaries that
834 exhibited CO_2 sink at least in certain periods of the year. Recent findings in the mixing zone of the
835 Amazon River estuary also calculated a net CO_2 sink (maximum of $-9.2 \text{ mmol C m}^{-2} \text{ d}^{-1}$), attributed to
836 mixing and biological activity, although the Amazon River and the tropical Atlantic are net sources
837 (Lefèvre et al., 2017). Considering only the rainy period, the PSRE was a CO_2 source of
838 approximately 5.71 to $19.37 \text{ mmol C m}^{-2} \text{ d}^{-1}$. These CO_2 emissions are much lower than the average
839 global emissions in estuaries (Chen et al., 2013) due to the fact that, even under high river flow
840 conditions, the mixing zone of the PSRE is a permanent CO_2 sink due to the prevalence of
841 thermodynamic processes. However, considering only the river domain during the rainy season, the
842 PSRE presents emission of approximately $60 \text{ mmol C m}^{-2} \text{ d}^{-1}$, a degassing rate close to those reported
843 in other river-dominated estuaries (Frankignoulle et al., 1998; Chen et al., 2013).

844 The CO_2 degassing rate in the mangrove tidal creek (average of $135 \text{ mmol C m}^{-2} \text{ d}^{-1}$) is above global
845 average of CO_2 flux emissions from surrounding mangrove waters ($56 \text{ mmol C m}^{-2} \text{ d}^{-1}$; Rosentreter et
846 al., 2018). Our mean values and ranges of CO_2 degassing are close to those found in mangroves in
847 Vietnam (Kiên Vàng and Tam Giang mangroves, 32 to $155 \text{ mmol C m}^{-2} \text{ d}^{-1}$; Koné and Borges, 2008),
848 Andaman Islands (Kalighat mangrove, 23 to $173 \text{ mmol C m}^{-2} \text{ d}^{-1}$; Linto et al., 2014), Australia
849 (Moreton Bay mangrove tidal creek, $202 \text{ mmol C m}^{-2} \text{ d}^{-1}$; Call et al., 2015), and the Amazon region
850 (62 to $437 \text{ mmol C m}^{-2} \text{ d}^{-1}$; Call et al., 2019). These high CO_2 emissions in mangrove tidal creeks, in
851 addition to the mangrove production of TA and DIC and transport to surrounding waters, can represent
852 an important fraction of the carbon that is fixed by mangrove vegetation, with high significance in
853 mangrove carbon budgets on a global scale (Bouillon et al., 2008; Maher et al., 2013, Call et al.,
854 2015).

855 Comparison between the amount of DIC delivered by the river and the CO_2 exchanges at the air-sea
856 interface in the mixing zone shows that the river contributes ~ 18 to 520 times more inorganic carbon
857 to the adjacent continental shelf compared with the estuarine carbon sink. This means that the air-
858 water exchange of CO_2 is much slower than the acid-base equilibration of DIC during mixing in the
859 estuary, increasing the importance of thermodynamic processes and decreasing the importance of air-
860 water exchanges and biological activities. It is worth highlighting that many of the world's largest
861 river systems are located in tropical regions, which provide $\sim 40\%$ of global freshwater discharge to the
862 oceans (Dai and Thenberth, 2002). Overall, large tropical rivers present low TA concentrations, such
863 as the Amazon, Congo and Orinoco Rivers (Cai et al., 2008; Moore-Maley et al., 2018).
864 Consequently, the CO_2 concentrations at the estuarine mixing zone of large and poorly buffered rivers
865 can be largely overestimated due to this still overlooked process.

866

867 5. Conclusions

868 Overall, the ecosystem showed aquatic sources and sinks of CO₂ considering specific estuarine
869 regions, which were modulated by carbonate thermodynamics, gas exchange, thermal effects, and
870 biological activities. The *p*CO₂ and carbonate chemistry parameters in the PSRE showed marked
871 spatiotemporal variations governed by processes somewhat different from those reported so far in the
872 literature:

873 i) In the freshwater domain, biological effects were prevalent. During high river flow, the waters
874 presented higher *p*CO₂ values and lower DO concentrations and δ¹³C-DIC signatures, as a result of
875 heterotrophic processes in the river. In contrast, under dry conditions, the waters presented low *p*CO₂
876 values and high δ¹³C-DIC signatures as a result of phytoplankton growth.

877 ii) In the mixing zone, the thermodynamic processes during estuarine mixing was the most important
878 driver of *p*CO₂ variations, with measured *p*CO₂ following a distribution close to the theoretical
879 conservative curve predicted by the mixing of the river and marine endmembers. During the rainy
880 period, the *p*CO₂ values decreased sharply as a result of rapid absorption by the acid-base buffering
881 capacity of high TA seawaters. During the dry period, the *p*CO₂ values were below the atmospheric
882 *p*CO₂ in freshwater and increased in seaward, also consistent with the theoretical thermodynamic
883 mixing.

884 iii) The δ¹³C-DIC signatures were slightly below the conservative mixing curve, indicating a
885 heterotrophic metabolism at intermediate to high salinities. The biological activity contributed to
886 approximately half of the deviation of measured *p*CO₂ from *p*CO_{2 mixing}. The other half was attributed
887 to gas exchange (~18%) and water heating (~36%) during estuarine mixing.

888 iv) In the mangrove creek, the waters presented high CO₂ values in all sampling campaigns, with
889 strong oversaturation attributed to production of DIC and TA in the water and pore waters by aerobic
890 and anaerobic processes, and transport by diffusion and convection via tidal pumping. Interesting to
891 point out that, during high river flow, the mangrove-dominated waters presented higher δ¹³C-DIC
892 signatures than the main estuarine channel, attributed to phytoplankton growth and fractionation of
893 DIC.

894 Considering the entire area of the PSRE, the estuary was a CO₂ sink at low freshwater discharge (air-
895 water CO₂ fluxes ranging from -0.34 to -5.26 mmol C m⁻² d⁻¹) and a CO₂ source at high freshwater
896 discharge (5.71-19.37 mmol C m⁻² d⁻¹). These fluxes are lower and different from those reported in
897 other river-dominated estuaries worldwide, which are normally strong CO₂ sources. The construction
898 of dams in the upper sections of Paraíba do Sul River has decreased its water flow and, associated with
899 increased anthropogenic-derived nutrient inputs to the river, can potentially change the functioning of
900 this ecosystem, from an annual CO₂ source to an annual CO₂ sink. These results also have implications

901 on global carbon budgets, showing that tropical river-dominated estuaries could absorb CO₂ along the
902 river and mixing domains as a result of the poor buffering capacity during estuarine mixing. Low TA
903 concentrations are a property of many large tropical rivers (Amazon, Congo, Orinoco), suggesting that
904 this process can be important globally and needs further investigation.

905 **Acknowledgments**

906 The authors are grateful for the support from the Laboratory of Environmental Sciences and to the
907 Graduate Program in Ecology and Natural Resources of the State University of Norte Fluminense
908 Darcy Ribeiro. This study was financed in part by the Coordenação de Aperfeiçoamento de Pessoal de
909 Nível Superior -Brazil (CAPES)-Finance Code 001, and by the Carlos Chagas Foundation for
910 Research Support of the State of Rio de Janeiro (FAPERJ; proc. no. E-26/202.785/2016). Luiz C.
911 Cotovicz Jr. is a postdoctoral researcher of the Carlos Chagas Foundation for Research Support of the
912 State of Rio de Janeiro (FAPERJ; proc. no. E-26202.785/2016). Carlos E. Rezende thanks the
913 financial support of CNPq (305217/2017-8) and FAPERJ (E-26/202.916/2017 and 210.883/2016).
914 B.A. Knoppers is a senior scientist of CNPq (proc. no. 301572/2010-0). Luciana O. Vidal is a
915 postdoctoral researcher of the Foundation for the Coordination of Higher Education and Graduate
916 Training (CAPES; proc. no. 88882.314551/2019-01). This research was also conducted with the
917 support of the International Research Project VELITROP (Vulnerability of littoral tropical ecosystems
918 to eutrophication) funded by the French Institute of Environment and Ecology INEE-CNRS.

919 **References**

920

921 Abril, G., Etcheber, H., Delille, B., Frankignoulle, M., Borges, A.V., 2003. Carbonate dissolution in
922 the turbid and eutrophic Loire estuary. *Mar. Ecol-Prog. Ser.* 259, 129–138.
923 <https://doi.org/10.3354/meps259129>.

924 Abril, G., Borges, A.V., 2004. Carbon dioxide and methane emissions from estuaries, in: Tremblay,
925 A., Varfalvy, L., Roehm, C., Garneau, M. (Eds.), *Greenhouse Gases Emissions from Natural*
926 *Environments and Hydroelectric Reservoirs: Fluxes and Processes*. Springer, Berlin, pp. 187–207.

927 Abril, G., Commarieu, M.-V., Sottolichio, A., Bretel, P., Guérin, F., 2009. Turbidity limits gas
928 exchange in a large macrotidal estuary. *Estuar. Coast. Shelf Sci.* 83, 342–348.
929 <https://doi.org/10.1016/j.ecss.2009.03.006>

930 Abril, G., Martinez, J.-M., Artigas, L.F., Moreira-Turcq, P., Benedetti, M.F., Vidal, L., Meziane, T.,
931 Kim, J.-H., Bernardes, M.C., Savoye, N., Deborde, J., Albéric, P., Souza, M.F.L., Souza, E.L., Roland,
932 F., 2014. Amazon River Carbon Dioxide Outgassing fueled by Wetlands. *Nature* 505, 395–398.
933 <https://doi.org/10.1038/nature12797>

934 Alling, V., Porcelli, D., Mörth, C.M., Anderson, L.G., Sanchez-Garcia, L., Gustafsson, Ö., Andersson,
935 P.S., Humborg, C., 2012. Degradation of terrestrial organic carbon, primary production and out-
936 gassing of CO₂ in the Laptev and East Siberian Seas as inferred from ¹³C values of DIC. *Geochim.*
937 *Cosmochim. Acta* 95, 143–159. <https://doi.org/10.1016/j.gca.2012.07.028>

938 Alongi, D.M., Tirendi, F., Trott, L.A., Xuan, T.T., 2000. Benthic decomposition rates and pathways in
939 plantations of the mangrove *Rhizophora apiculata* in the Mekong delta, Vietnam. *Mar. Ecol-Prog. Ser.*
940 194, 87-101. <https://doi.org/10.3354/meps194087>

941 Amarante, O.A., Silva, F.J., Rios Filho, L.G., 2002. Atlas Eólico, Estado do Rio de Janeiro. Secretaria
942 de Estado da Energia, da Indústria Naval e do Petróleo, Rio de Janeiro.
943 http://www.cresesb.cepel.br/publicacoes/download/atlas_eolico/AtlasEolicoRJ.pdf (accessed 15 April
944 2019).

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

947 Benson, B.B., Krause, D., 1984. The concentration and isotopic fractionation of oxygen dissolved in
948 freshwater and seawater in equilibrium with the atmosphere. *Limnol. Oceanogr.* 29, 620–632.
949 <https://doi.org/10.4319/lo.1984.29.3.0620>

950 Borges, A.V., Djenidi, S., Lacroix, G., Theate, J., Delille, B., Frankignoulle, M., 2003. Atmospheric
951 CO₂ flux from mangrove surrounding waters. *Geophys. Res. Lett.* **30**, 1558.
952 <https://doi.org/10.1029/2003GL017143>

953 Borges, A.V., Abril, G., 2011. Carbon dioxide and methane dynamics in estuaries, in: Wolanski, E.,
954 McLusky, D. (Eds.), *Treatise on estuarine and coastal science*, vol 5. Academic Press, Amsterdam, pp.
955 119–161.

956 Borges, A.V., Abril, G., Bouillon, S., 2018. Carbon dynamics and CO₂ and CH₄ outgassing in the
957 Mekong delta. *Biogeosciences* 15, 1093-1114. <https://doi.org/10.5194/bg-15-1093-2018>.

958 Bouillon, S., Dehairs, F., Schiettecatte, L.-S., Borges, A.V., 2007. Biogeochemistry of the Tana
959 estuary and delta (northern Kenya). *Limnol. Oceanogr.* 52, 46–59.
960 <https://doi.org/10.4319/lo.2007.52.1.0046>

961 Bouillon, S., Borges, A.V., Castañeda-Moya, E., Diele, K., Dittmar, T., Duke, N.C., Kristensen, E.,
962 Lee, S.Y., Marchand, C., Middelburg, J.J., Rivera-Monroy, V., Smith, T.J., Twilley, R.R., 2008.
963 Mangrove production and carbon sinks: a revision of global budget estimates. *Glob. Biogeochem. Cy.*
964 22, GB2013. <https://doi.org/10.1029/2007GB003052>.

965 Bouillon, S., Connolly, R.M., Gillikin, D.P., 2011. Use of stable isotopes to understand food webs and
966 ecosystem functioning in estuaries, in: Wolanski, E., McLusky, D. (Eds.), *Treatise on Estuarine and*
967 *Coastal Science*. Academic Press, Amsterdam, pp. 143–173.

968 Cai, W.-J., Pomeroy, L.R., Moran, M.A., Wang, Y., 1999. Oxygen and carbon dioxide mass balance
969 for the estuarine–intertidal marsh complex of five rivers in the southeastern U.S. *Limnol. Oceanogr.*
970 *44*, 639–649. <https://doi.org/10.4319/lo.1999.44.3.0639>.

971 Cai, W.-J., Guo, X., Chen, C.-T.A., Dai, M., Zhang, L., Zhai, W., Lohrenz, S.E., Yin, K., Harrison,
972 P.J., Wang, Y., 2008. A comparative overview of weathering intensity and HCO₃⁻ flux in the world’s
973 major rivers with emphasis on the Changjiang, Huanghe, Zhujiang (Pearl) and Mississippi Rivers.
974 *Cont. Shelf Res.* *28*, 1538–1549. <https://doi.org/10.1016/j.csr.2007.10.014>

975 Cai, W.-J., 2011. Estuarine and coastal ocean carbon paradox: CO₂ sinks or sites of terrestrial carbon
976 incineration? *Ann. Rev. Mar. Sci.* *3*, 123–145. <https://doi.org/10.1146/annurev-marine-120709-142723>

977 Cai, W.-J., Hu X., Huang, W.-J., Murrell, M.C., Lehrter, J.C., Lohrenz, S.E., Chou, W.-C., Zhai, W.,
978 Hollibaugh, J.T., Wang, Y., 2011. Acidification of subsurface coastal waters enhanced by
979 eutrophication. *Nat. Geosci.* *4*, 766–770. <https://doi.org/10.1038/ngeo1297>

980 Cai, W. -J., Chen, C.-T.A., Borges A.V., 2013. Carbon dioxide dynamics and fluxes in coastal waters
981 influenced by river plumes, in: Bianchi, T., Allison, M., Cai, W.-J. (Eds.), *Biogeochemical Dynamics*
982 *at Major River-Coastal Interfaces: Linkages with Global Change*. Cambridge University Press,
983 Cambridge, pp. 155-173.

984 Call, M., Maher, D.T., Santos, I.R., Ruiz-Halpern, S., Mangion, P., Sanders, C.J., Erler, D.V., Oakes,
985 J.M., Rosentreter, J., Murray, R., Eyre, B.D., 2015. Spatial and temporal variability of carbon dioxide
986 and methane fluxes over semi-diurnal and spring–neap–spring timescales in a mangrove creek.
987 *Geochim. Cosmochim. Acta* *150*, 211–225. <https://doi.org/10.1016/j.gca.2014.11.023>

988 Call, M., Santos, I.R., Dittmar, T., Rezende, C.E., Asp, N.E., Maher, D.T., 2019. High pore-water
989 derived CO₂ and CH₄ emissions from a macro-tidal mangrove creek in the Amazon region. *Geochim.*
990 *Cosmochim. Acta* *247*, 106-120. <https://doi.org/10.1016/j.gca.2018.12.029>

991 Campos, E.J.D., Velhote, D., Silveira, I.C.A., 2000. Shelf break upwelling driven by Brazil current
992 cyclonic meanders. *Geophys. Res. Lett.* *27*, 751–754. <https://doi.org/10.1029/1999GL010502>

993 Castro, B.M., Miranda, L.B., 1998. Physical oceanography of the western Atlantic continental shelf
994 located between 4°N and 34°S, in: Robinson, A.R., Brink, K.H. (Eds.), *The Sea*. John Wiley,
995 Hoboken, pp. 209–251.

- 996 Chen, C.T.A., Borges, A.V., 2009. Reconciling opposing views on carbon cycling in the coastal
997 ocean: continental shelves as sinks and near-shore ecosystems as sources of atmospheric CO₂. *Deep*
998 *Sea Res. Part 2 Top. Stud. Oceanogr.* 56, 578-590. <https://doi.org/10.1016/j.dsr2.2009.01.001>.
- 999 Chen C.-T.A., Huang, T.-H., Chen, Y.-C., Bai, Y., He, X., Kang, Y., 2013. Air–sea exchanges of CO₂
1000 in the world’s coastal seas. *Biogeosciences* 10, 6509–6544. <https://doi.org/10.5194/bg-10-6509-2013>
- 1001 Cloern, J.E., 1996. Phytoplankton bloom dynamics in coastal ecosystems: a review with some general
1002 lessons from sustained investigation of San Francisco Bay, California. *Rev Geophys.* 2, 127–168.
1003 <https://doi.org/10.1029/96RG00986>
- 1004 Cohen, J.E., Small, C., Mellinger, A., Gallup, J., Sachs, J., Vitousek, P.M., Mooney, H.A., 1997.
1005 Estimates of coastal populations. *Science* 278, 1209–1213.
1006 <https://doi.org/10.1126/science.278.5341.1209c>
- 1007 Cotovicz, Jr., L.C., Brandini, N., Knoppers, B.A., Mizerkowski, B.D., Sterza, J.M., Ovalle, A.R.C.,
1008 Medeiros, P.R.P., 2013. Assessment of the trophic status of four coastal lagoons and one estuarine
1009 delta, eastern Brazil. *Environ. Monit. Assess.* 185, 3297-3311. <https://doi.org/10.1007/s10661-012->
1010 2791-x
- 1011 Cotovicz, Jr., L.C., Knoppers, B.A., Brandini N., Costa Santos, S.J., Abril, G., 2015. A strong CO₂
1012 sink enhanced by eutrophication in a tropical coastal embayment (Guanabara Bay, Rio de Janeiro,
1013 Brazil). *Biogeosciences* 12, 6125–6146. <https://doi.org/10.5194/bg-12-6125-2015>
- 1014 Cotovicz, Jr., L.C., Libardoni, B., Brandini, N., Knoppers, B., Abril, G., 2016. Comparações entre
1015 medições em tempo real da pCO₂ aquática com estimativas indiretas em dois estuários tropicais
1016 contrastantes: o estuário eutrofizado da Baía de Guanabara (RJ) e o estuário oligotrófico do Rio São
1017 Francisco (AL). *Quím. Nova* 39, 1206–1214. <http://dx.doi.org/10.21577/0100-4042.20160145>
- 1018 Cotovicz, Jr., L.C., Knoppers, B.A., Deirmendjian, L., Abril, G., 2019. Sources and sinks of dissolved
1019 inorganic carbon in an urban tropical coastal bay revealed by δ¹³C-DIC signals. *Estuar. Coast. Shelf*
1020 *Sci.* 220, 185-195. <https://doi.org/10.1016/j.ecss.2019.02.048>
- 1021 Crosswell, J.R., Anderson, I.C., Stanhope, J.W., Van Dam, B., Brush, M.J., Ensign, S., Piehler, M.F.,
1022 McKee, B., Bost, M., Paerl, H.W., 2017. Carbon budget of a shallow, lagoonal estuary:
1023 Transformations and source-sink dynamics along the river-estuary-ocean continuum. *Limnol.*
1024 *Oceanogr.* 62, S29–S45. <http://doi.org/10.1002/lno.10631>
- 1025 Crump, B.C., Hopkinson, C. S., Sogin, M. L., Hobbie, J.E., 2004. Microbial biogeography along an
1026 estuarine salinity gradient: combined influences of bacterial growth and residence time. *Appl. Environ.*
1027 *Microbiol.* 70, 1494-1505.2 <https://doi.org/10.1128/aem.70.3.1494-1505.2004>

1028 Dai, A., Trenberth, K.E., 2002. Estimates of Freshwater Discharge from Continents: Latitudinal and
1029 Seasonal Variations . *J. Hydrometeorol.* 3, 660-687. [https://doi.org/10.1175/1525-](https://doi.org/10.1175/1525-7541(2002)003<0660:EOFDFC>2.0.CO;2)
1030 [7541\(2002\)003<0660:EOFDFC>2.0.CO;2](https://doi.org/10.1175/1525-7541(2002)003<0660:EOFDFC>2.0.CO;2)

1031 Dai, M., Lu, Z., Zhai, W., Chen, B., Cao, Z., Zhou, K., Cai, W.-J., Chen, C.A., 2009. Diurnal
1032 variations of surface seawater pCO₂ in contrasting coastal environments. *Limnol. Oceanogr.* 54, 735–
1033 745. <https://doi.org/10.4319/lo.2009.54.3.0735>.

1034 Del Giorgio, P.A., Bouvier, T., 2002. Linking the physiologic and phylogenetic successions in free-
1035 living bacterial communities along an estuarine salinity gradient. *Limnol. Oceanogr.* 47, 471-486.
1036 <https://doi.org/10.4319/lo.2002.47.2.0471>

1037 Deirmendjian, L., Abril, G., 2018. Carbon dioxide degassing at the groundwater-stream-atmosphere
1038 interface: isotopic equilibration and hydrological mass balance in a sandy watershed. *J. Hydrol.* **558**,
1039 129–143. <https://doi.org/10.1016/j.jhydrol.2018.01.003>

1040 Dickson, A.G., 1990. Thermodynamics of the dissociation of boric acid in synthetic seawater from
1041 273.15 to 318.15 K. *Deep-Sea Res. I Oceanogr. Res. Pap.* 37, 755–766. [https://doi.org/10.1016/0198-](https://doi.org/10.1016/0198-0149(90)90004-F)
1042 [0149\(90\)90004-F](https://doi.org/10.1016/0198-0149(90)90004-F)

1043 Dickson, A.G., Millero, F.J., 1987. A comparison of the equilibrium constants for the dissociation of
1044 carbonic acid in seawater media. *Deep-Sea Res.* 34, 1733–1743. [https://doi.org/10.1016/0198-](https://doi.org/10.1016/0198-0149(87)90021-5)
1045 [0149\(87\)90021-5](https://doi.org/10.1016/0198-0149(87)90021-5)

1046 Dinauer, A., Mucci, A., 2017. Spatial variability in surface-water pCO₂ and gas exchange in the
1047 world’s largest semi-enclosed estuarine system: St. Lawrence Estuary (Canada). *Biogeosciences* 14,
1048 3221-3237. <https://doi.org/10.5194/bg-14-3221-2017>

1049 Egleston, E.S., Sabine, C.L., Morell, F.M., 2010. Revelle revisited: Buffer factors that quantify the
1050 response of ocean chemistry to changes in DIC and alkalinity. *Glob. Biogeochem. Cy.* 24, GB1002.
1051 <http://dpo.org/10.1029/2008GB003407>, 2010

1052 Finlay, J.C., Kendall, C., 2007. Stable isotope tracing of temporal and spatial variability in organic
1053 matter sources to freshwater ecosystems, in: Michener, R., Lajtha, K. (Eds.), *Stable Isotopes in*
1054 *Ecology and Environmental Science*. Blackwell Publishing, Hong Kong, pp. 283-333.

1055 Flöder, S., Jaschinski, S., Wells, G., Burns, C.W., 2010. Dominance and compensatory growth in
1056 phytoplankton communities under salinity stress. *J. Exp. Mar. Bio. Ecol.* 395, 223–231.
1057 <https://doi.org/10.1016/j.jembe.2010.09.006>

1058 Frankignoulle, M., Abril, G., Borges, A., Bourge, I., Canon, C., Delille, B., Libert, E., Theate, J.M.,
1059 1998. Carbon Dioxide Emission from European Estuaries. *Science* 282, 434–436.
1060 <https://doi.org/10.1126/science.282.5388.434>

1061 Frankignoulle, M., Borges, A., Biondo, R., 2001. A new design of equilibrator to monitor carbon
1062 dioxide in highly dynamic and turbid environments. *Water Res.* 35, 1344–1347.
1063 [https://doi.org/10.1016/S0043-1354\(00\)00369-9](https://doi.org/10.1016/S0043-1354(00)00369-9)

1064 Gattuso, J.-P., Magnan, A., Billé, R., Cheung, W.W.L., Howes, E.L., Joos, F., Allemand, D., Bopp, L.,
1065 Cooley, S.R., Eakin, C.M., Hoegh-Guldberg, O., Kelly, R.P., Pörtner, H.-O., Rogers, A.D., Baxter,
1066 J.M., Laffoley, D., Osborn, D., Rankovic, A., Rochette, J., Sumaila, U.R., Treyer, S., Turley, C., 2015.
1067 Contrasting futures for ocean and society from different anthropogenic CO₂ emissions scenarios.
1068 *Science* 349, aac4722. <https://doi.org/10.1126/science.aac4722>

1069 Gazeau, F., Smith, S.V., Gentili, B., Frankignoulle, M., Gattuso, J.-P., 2004. The European coastal
1070 zone: characterization and first assessment of ecosystem metabolism. *Estuar. Coast. Shelf Sci.* 60,
1071 673–694. <https://doi.org/10.1016/j.ecss.2004.03.007>

1072 Gran, G., 1952. Determination of the equivalence point in potentiometric titrations-Part II. *Analyst* 77,
1073 661–671.

1074 Guérin, F., Abril, G., Serç,a D., Delon, C., Richard, S., Delmas, R., Tremblay, A., Varfalvy, L. 2007.
1075 Gas transfer velocities of CO₂ and CH₄ in a tropical reservoir and its river downstream. *J. Mar. Syst.*
1076 66, 161–172. <https://doi.org/10.1016/j.jmarsys.2006.03.019>.

1077 Hu, X., Cai, W.-J., 2011. An assessment of ocean margin anaerobic processes on oceanic alkalinity
1078 budget. *Global Biogeochem. Cy.* 25, GB3003. <https://doi.org/10.1029/2010GB003859>

1079 Hu, X., Cai, W.-J., 2013. Estuarine acidification and minimum buffer zone—A conceptual study.
1080 *Geophys. Res. Lett.* 40, 5176-5181. <https://doi.org/10.1002/grl.51000>

1081 IBGE., 2018. Instituto Brasileiro de Geografia e Estatística.
1082 <https://cidades.ibge.gov.br/brasil/rj/panorama/> (Accessed December 13, 2018).

1083 IPCC., 2013. Climate Change 2013: The Physical Science Basis, in: Stocker et al. (Eds.), Contribution
1084 of Working Group I to the Fifth Assessment Report of the Intergovernmental Panel on Climate
1085 Change. Cambridge Univ. Press., Cambridge. <https://doi.org/doi:10.1017/CBO9781107415324>

1086 Ito, R.G., Scheider, B., Thomas, H., 2005. Distribution of surface fCO₂ and air–sea fluxes in the
1087 Southwestern subtropical Atlantic and adjacent continental shelf. *J. Mar. Syst.* 56, 227-242.
1088 <https://doi.org/10.1016/j.jmarsys.2005.02.005>

1089 Jähne, B., Munnich, K.O., Bosinger, R., Dutzi, A., Huber, W., Libner, P., 1987. On parameters
1090 influencing air-water exchange. *J. Geophys. Res.* 92, 1937–1949.
1091 <https://doi.org/10.1029/JC092iC02p01937>

- 1092 Jiang, L.-Q., Cai, W.-J., Wang, Y., 2008. A comparative study of carbon dioxide degassing in river-
1093 and marine-dominated estuaries. *Limnol. Oceanogr.* 53, 2603–2615.
1094 <https://doi.org/10.4319/lo.2008.53.6.2603>
- 1095 Joesoef, A., Huang, W.-J., Gao, Y., Cai, W.-J., 2015. Air–water fluxes and sources of carbon dioxide
1096 in the Delaware Estuary: spatial and seasonal variability. *Biogeosciences* 12, 6085–6101.
1097 <https://doi.org/10.5194/bg-12-6085-2015>
- 1098 Joos, F., Spahni, R., 2008. Rates of change in natural and anthropogenic radiative forcing over the past
1099 20,000 years. *Proc. Natl. Acad. Sci.* 105, 1425–1430. <https://doi.org/10.1073/pnas.0707386105>
- 1100 Kendall, C., Doctor, D.H., Holland, H.D., Turekian, K.K., 2004. Stable isotope applications in
1101 hydrologic studies. *Surf. Gr. Water, Weather. Soils* 5, 319–364. <https://doi.org/10.1016/B0-08-043751-6/05081-7>
- 1103 Knoppers, B.A., Ekau, W., Figueiredo, A.G., 1999. The coast and shelf of East and Northeast Brazil
1104 and material transport. *Geo-Marine Letters*, 19, 171-178. <https://doi.org/10.1007/s003670050106>
- 1105 Koné, Y.J.M., Abril, G., Kouadio, K.N., Delille, B., Borges, A.V., 2008. Seasonal Variability of
1106 Carbon Dioxide in the Rivers and Lagoons of Ivory Coast (West Africa). *Estuar. Coast.* 32, 246–260.
1107 <https://doi.org/10.1007/s12237-008-9121-0>
- 1108 Koné, Y.J.M., Borges, A.V., 2008. Dissolved inorganic carbon dynamics in the waters surrounding
1109 forested mangroves of the Ca Mau Province (Vietnam). *Estuar. Coast. Shelf Sci.* 77, 409–421.
1110 <https://doi.org/10.1016/j.ecss.2007.10.001>
- 1111 Körtzinger, A., 2003. A significant sink of CO₂ in the tropical Atlantic Ocean associated with the
1112 Amazon River plume. *Geophys. Res. Lett.* 30, 2287. <https://doi.org/10.1029/2003GL018841>
- 1113 Kristensen, E., Flindt, M.R., Ulomi, S., Borges, AV., Abril, G., Bouillon, S., 2008. Emission of CO₂
1114 and CH₄ to the atmosphere by sediments and open waters in two Tanzanian mangrove forests. *Mar.*
1115 *Ecol. Prog. Ser.* 370, 53-67. <https://doi.org/10.3354/meps07642>
- 1116 Kubo, A., Maeda, Y., Kanda, J., 2017. A significant net sink for CO₂ in Tokyo Bay. *Sci. Rep.* 7,
1117 44355. <https://doi.org/10.1038/srep44355>
- 1118 Lancelot, C., Muylaert, K., 2011. Trends in Estuarine Phytoplankton Ecology., in: McLusky, D.S.,
1119 Wolanski, E., (Eds.), *Treatise on estuarine and coastal science*. Academic Press, Amsterdam, pp. 5-15.
- 1120 Laruelle, G.G., Dürr, H.H., Lauerwald, R., Hartmann, J., Slomp, C.P., Goossens, N., Regnier, P.,
1121 2013. Global multi-scale segmentation of continental and coastal waters from the watersheds to the
1122 continental margins. *Hydrol. Earth Syst. Sci.* 17, 2029–2051. <https://doi.org/10.5194/hess-17-2029-2013>
- 1123 2013

- 1124 Le Quéré, C., Andrew, R.M., Friedlingstein, P., Sitch, S., Hauck, J., Pongratz, J., Pickers, P.A.,
1125 Korsbakken, J.I., Peters, G.P., Canadell, J.G., Arneth A., Arora, V.K., Barbero, L., Bastos, A., Bopp,
1126 L., Chevallier, F., Chini, L.P., Ciais, P., Doney, S.C., Gkritzalis, T., Goll, D.S., Harris, I., Haverd, V.,
1127 Hoffman, F.M., Hoppema, M., Houghton, R.A., Hurtt, G., Ilyina, T., Jain, A.K., Johannessen, T.,
1128 Jones, C.D., Kato, E., Keeling, R.F., Goldewijk, K.K., Landschützer, P., Lefèvre, N., Lienert, S., Liu,
1129 Z., Lombardozi, D., Metzl, N., Munro, D.R., Nabel, J.E.M.S., Nakaoka, S.-I., Neill, C., Olsen, A.,
1130 Ono, T., Patra, P., Peregon, A., Peters, W., Peylin, P., Pfeil, B., Pierrot, D., Poulter, B., Rehder, G.,
1131 Resplandy, L., Robertson, E., Rocher, M., Rödenbeck, C., Schuster, U., Schwinger, J., Séférian, R.,
1132 Skjelvan, I., Steinhoff, T., Sutton, A., Tans, P.P., Tian, H., Tilbrook, B., Tubiello, F.N., van der Laan-
1133 Luijkx, I.T., van der Werf, G.R., Viovy, N., Walker, A.P., Wiltshire, A.J., Wright, R., Zaehle, S.,
1134 Zheng, B., 2018. Global Carbon Budget 2018, *Earth Syst. Sci. Data* 10, 2141-2194.
1135 <https://doi.org/10.5194/essd-10-2141-2018>
- 1136 Lee, K., Kim, T.W., Byrne, R.H., Millero, F.J., Feely, R.A., Liu, Y.M., 2010. The universal ratio of
1137 boron to chlorinity for the North Pacific and North Atlantic oceans. *Geochim. Cosmochim. Acta* 74,
1138 1801–1811. <https://doi.org/10.1016/j.gca.2009.12.027>
- 1139 Lefèvre, N., Montes, M.F., Gaspar, F.L., Rocha, C., Jiang, S., Araujo, M., Ibanhez, S., 2017. Net
1140 heterotrophy in the Amazon Continental Shelf changes rapidly to a sink of CO₂ in the outer Amazon
1141 Plume. *Front. Mar. Sci.* 4, 1-16. <https://doi.org/10.3389/fmars.2017.00278>
- 1142 Linto, N., Barnes, J., Ramachandran, R., Divia, J., Ramachandran, P., Upstill-Goddard, R.C., 2014.
1143 Carbon Dioxide and Methane Emissions from Mangrove-Associated Waters of the Andaman Islands,
1144 Bay of Bengal. *Estuar. Coast.* 37, 381–398. <https://doi.org/10.1007/s12237-013-9674-4>
- 1145 Lucas, L.V., Thompson, J.K., Brown, L.R., 2009. Why are diverse relationships observed between
1146 phytoplankton biomass and transport time? *Limnol. Oceanogr.* 54, 381–390.
1147 <https://doi.org/10.4319/lo.2009.54.1.0381>
- 1148 Ludwig, W., Amiotte-Suchet, P., Munhoven, G., Probst, J.-L., 1998. Atmospheric CO₂ consumption
1149 by continental erosion: Present-day controls and implications for the last glacial maximum Global
1150 Planet. Change, 17, 107– 120. [https://doi.org/10.1016/S0921-8181\(98\)00016-2](https://doi.org/10.1016/S0921-8181(98)00016-2).
- 1151 Maher, D.T., Eyre, B.D., 2012. Carbon budgets for three autotrophic Australian estuaries: Implications
1152 for global estimates of the coastal air-water CO₂ flux. *Global Biogeochem. Cy.* 26, GB1032.
1153 <https://doi.org/10.1029/2011GB004075>
- 1154 Maher, D.T., Santos, I.R., Golsby-Smith, L., Gleeson, J., Eyre, B.D., 2013. Groundwater-derived
1155 dissolved inorganic and organic carbon exports from a mangrove tidal creek: The missing mangrove
1156 carbon sink? *Limnol. Oceanogr.* 58, 475–488. <https://doi.org/doi:10.4319/lo.2013.58.2.0475>

1157 Maher, D.T., Cowley, K., Santos, I.R., Macklin, P., Eyre, B.D., 2015. Methane and carbon dioxide
1158 dynamics in a subtropical estuary over a diel cycle: Insights from automated in situ radioactive and
1159 stable isotope measurements. *Mar. Chem.* 168, 69–79. <https://doi.org/10.1016/j.marchem.2014.10.017>

1160 Maher, D.T., Sippo, J., Tait, D., Holloway, C., Santos, I.R., 2016. Pristine mangrove creek waters are
1161 a sink of nitrous oxide. *Scientific Reports*, 6, 25701. <https://doi.org/10.1038/srep25701>

1162 Marques, J.S.J., Dittmar, T., Niggemann, J., Almeida, M.G., Gomez-Saez, G.V., Rezende, C.E., 2017.
1163 Dissolved Black Carbon in the Headwaters-to-Ocean Continuum of Paraíba Do Sul River, Brazil.
1164 *Front. Earth Sci.* 5, 1–12. <https://doi.org/10.3389/feart.2017.00011>

1165 Mehrbach, C., Cuberson, C.H., Hawley, J.E., Pytkowicz, R.M., 1973. Measurements of the apparent
1166 dissociation constants of carbonic acid in seawater at atmospheric pressure. *Limnol. Oceanogr.* 18,
1167 897–907. <https://doi.org/10.4319/lo.1973.18.6.0897>

1168 Miyajima, T., Miyajima, Y., Hanba, Y.T., Yoshii, K., Koitabashi, T., Wada, E., 1995. Determining the
1169 stable isotope ratio of total dissolved inorganic carbon in lake water by GC/C/IRMS. *Limnol.*
1170 *Oceanog.* 40, 994–1000. <https://doi.org/10.4319/lo.1995.40.5.0994>.

1171 Miyajima, T., Tsuboi, Y., Tanaka, Y., Koike, I., 2009. Export of inorganic carbon from two Southeast
1172 Asian mangrove forests to adjacent estuaries as estimated by the stable isotope composition of
1173 dissolved inorganic carbon. *J. Geophys. Res. Biogeosciences* 114, 1–12.
1174 <https://doi.org/10.1029/2008JG000861>

1175 Mook, W.G., Koene, B.K., 1975. Chemistry of dissolved inorganic carbon in estuarine and coastal
1176 brackish waters. *Estuar. Coast. Mar. Sci.* 3, 325-336.

1177 Mook, W.G., Tan, F.C., 1991. Stable carbon isotopes in rivers and estuaries, in: Degens, E.T., Kempe,
1178 S., Richey, J.E., (Eds.), *Biogeochemistry of Major World Rivers*. John Wiley and Sons, Chichester,
1179 pp. 245–264.

1180 Moore-Maley, B., Ianson, D., Allen, S.E., 2018. The sensitivity of estuarine aragonite saturation state
1181 and pH to the carbonate chemistry of a freshet-dominated river. *Biogeosciences* 15, 3743-3760.
1182 <https://doi.org/10.5194/bg-15-3743-2018>

1183 NOAA, 2019. National Oceanic and Atmospheric Administration. Earth System Research Laboratory.
1184 Global Monitoring Division. <https://www.esrl.noaa.gov/gmd/ccgg/trends/graph.html> (Accessed 24
1185 July 2019).

1186 Orr, J.C., Epitalon, J.-M., Dickson, A.G., Gattuso, J.-P., 2018. Routine uncertainty propagation for the
1187 marine carbon dioxide system. *Mar. Chem.* 207, 84–107.
1188 <https://doi.org/10.1016/j.marchem.2018.10.006>

1189 Ovalle, A.R.C., Silva, C.F., Rezende, C.E., Gatts, C.E.N., Suzuki, M.S., Figueiredo, R.O., 2013. Long-
1190 term trends in hydrochemistry in the Paraíba do Sul River, southeastern Brazil. *J. Hydrol.* 481, 191–
1191 203. <https://doi.org/10.1016/j.jhydrol.2012.12.036>

1192 Raymond, P.A., Cole, J.J., 2001. Gas Exchange in Rivers and Estuaries: Choosing a Gas Transfer
1193 Velocity. *Estuaries* 24, 312-317. <https://doi.org/10.2307/1352954>

1194 Revelle, R., Suess, H.E., 1957. Carbon dioxide exchange between atmosphere and ocean and the
1195 question of an increase of atmospheric CO₂ during the past decades. *Tellus*, 9, 18– 27.

1196 Robbins, L.L., Hansen, M.E., Kleypas, J.A., Meylan, S.C., 2010. CO₂ Calc: a user-friendly seawater
1197 carbon calculator for Windows, Max OS X, and iOS (iPhone), U.S. Geological Survey Open-File
1198 Report, 2010–1280, 1–17. <http://pubs.usgs.gov/of/2010/1280/> (accessed 07 November 2018).

1199 Rosentreter, J.A., Maher, D.T., Erler, D.V., Murray, R., Eyre, B.D., 2018. Seasonal and temporal CO₂
1200 dynamics in three tropical mangrove creeks – A revision of global mangrove CO₂ emissions.
1201 *Geochim. Cosmochim. Acta* 222, 729–745. <https://doi.org/10.1016/j.gca.2017.11.026>

1202 Roubex V., Rousseau V., Lancelot C. (2008) Diatom succession and silicon removal from freshwater
1203 in estuarine mixing zones: from experiment to modelling. *Estuar. Coast. Shelf Sci.* 78, 14–26

1204 Rudorff, N.M., Kampel, M., Rezende, C.E., 2011. Spectral mapping of the Paraíba do Sul River plume
1205 (Brazil) using multitemporal Landsat images. *J. App. Rem. Sens.* 5, 053550-053550-19.
1206 <https://doi.org/10.1117/1.3630220>

1207 Salisbury, J.E., 2008. Coastal Acidification by Rivers: A Threat to Shellfish? *Eos* 89, 513-528.
1208 <https://doi.org/10.1029/2008EO500001>

1209 Salisbury, J.E., Vandemark, D., Hunt, C.W., Campbell, J.W., McGillis, W.R., McDowell, W.H., 2008.
1210 Seasonal observations of surface waters in two Gulf of Maine estuary-plume systems: Relationships
1211 between watershed attributes, optical measurements and surface pCO₂. *Estuar. Coast. Shelf Sci.* 77,
1212 245–252. <https://doi.org/10.1016/j.ecss.2007.09.033>

1213 Samanta, S., Dalai, T.K., Pattanaik, J.K., Rai, S.K., Mazumdar, A., 2015. Dissolved inorganic carbon
1214 (DIC) and its ¹³C in the Ganga (Hooghly) River estuary, India: Evidence of DIC generation via organic
1215 carbon degradation and carbonate dissolution. *Geochim. Cosmochim. Acta* 165, 226–248.
1216 <https://doi.org/10.1016/j.gca.2015.05.040>

1217 Santos, I.R., Maher, D.T., Eyre, B.D., 2012. Coupling automated radon and carbon dioxide
1218 measurements in coastal waters. *Environ. Sci. Technol.* 46, 7685–91.
1219 <https://doi.org/10.1021/es301961b>

- 1220 Santos, I.R., Maher, D.T., Larkin, R., Webb, J., Sanders, C.J., 2018. Carbon outwelling and outgassing
1221 vs. burial in an estuarine tidal creek surrounded by mangrove and saltmarsh wetlands. *Limnol.*
1222 *Oceangr.* 64, 996-1013. <https://doi.org/10.1002/lno.11090>
- 1223 Silvennoinen, H., Liikanen, A., Rintala, J., Martikainen, P.J., 2008. Greenhouse gas fluxes from the
1224 eutrophic Temmesjoki River and its Estuary in the Liminganlahti Bay (the Baltic Sea).
1225 *Biogeochemistry* 90, 193–208. <https://doi.org/10.1007/s10533-008-9244-1>
- 1226 Sippo, J.Z., Maher, D.T., Tait, D.R., Holloway, C., Santos, I.R., 2016. Are mangroves drivers or
1227 buffers of coastal acidification? Insights from alkalinity and dissolved inorganic carbon export
1228 estimates across a latitudinal transect. *Global Biogeochem. Cy.* 30, 753–766.
1229 <https://doi.org/10.1002/2015GB005324>
- 1230 Souza, T.A., Godoy, J.M., Godoy, M.L.D.P., Moreira, I., Carvalho, Z.L., Salomão, M.S.M.B.,
1231 Rezende, C.E., 2010. Use of multitracers for the study of water mixing in the Paraíba do Sul River
1232 estuary. *J. Environ. Radioact.* 101, 564–570. <https://doi.org/10.1016/j.jenvrad.2009.11.001>
- 1233 Sterza, J.M., Fernandes, L.L., 2006. Distribution and abundance of cladocera (brachiopoda) in the
1234 Paraíba do Sul River Estuary, Rio de Janeiro, Brazil. *Braz. J. Oceanogr.* 54, 193-204.
1235 <http://dx.doi.org/10.1590/S1679-87592006000300003>
- 1236 Strayer, D.L., Pace, M.L., Caraco, N.F., Cole, J.J., Findlay, S., 2008. Hydrology and grazing jointly
1237 control a large-river food web. *Ecology* 89, 12–18. <https://doi.org/10.1890/07-0979.1>
- 1238 Strickland, J.D.H., Parsons, T.R., 1972. A practical handbook of seawater analysis. Fisheries Research
1239 Board of Canada Bulletin, Ottawa.
- 1240 Takahashi, T., Sutherland, S.C., Sweeney, C., Poisson, A., Metzl, N., Tilbrook, B., Bates, N.,
1241 Wanninkhof, R., Feely, R.A., Sabine, C., Olafsson, J., Nojiri, Y., 2002. Global sea-air CO₂ flux based
1242 on climatological surface ocean pCO₂, and seasonal biological and temperature effects. *Deep. Sea Res.*
1243 *Part II* 49, 1601–1622. [https://doi.org/10.1016/S0967-0645\(02\)00003-6](https://doi.org/10.1016/S0967-0645(02)00003-6).
- 1244 Takahashi, T., Sutherland, S.C., Kozyr, A., 2012. Global ocean surface water partial pressure of CO₂
1245 database: Measurements performed during 1957–2011 (Version 2011), Oak Ridge, Tennessee.
1246 [https://doi.org/10.3334/CDIAC/OTG.NDP088\(V2013\)](https://doi.org/10.3334/CDIAC/OTG.NDP088(V2013))
- 1247 Ternon, J.F., Oudot, C., Dessier, A., Diverrès, D., 2000. A seasonal tropical sink for atmospheric CO₂
1248 in the Atlantic ocean: the role of the Amazon River discharge. *Mar. Chem.* 68, 183–201.
1249 [https://doi.org/10.1016/S0304-4203\(99\)00077-8](https://doi.org/10.1016/S0304-4203(99)00077-8)
- 1250 Van Dam, B. R., Crosswell, J. R., Anderson, I. C., Paerl, H. W., 2018a. Watershed-scale drivers of air-
1251 water CO₂ exchanges in two lagoonal North Carolina (USA) estuaries. *J. Geophys. Res.*
1252 *Biogeosciences*, 123, 1-17. <https://doi.org/10.1002/2017JG004243>

1253 Van Dam, B.R., Tobias, C., Holbach, A., Paerl, H.W., Zhu, G., 2018b. CO₂ limited conditions favor
1254 cyanobacteria in a hypereutrophic lake: An empirical and theoretical stable isotope study. *Limnol.*
1255 *Oceanogr.* 63, 1643–1659. <https://doi.org/10.1002/lno.10798>

1256 Wanninkhof, R., 1992. Relationship Between Wind Speed and Gas Exchange. *J. Geophys. Res.* 97,
1257 7373–7382. <https://doi.org/10.1029/92JC00188>

1258 Wanninkhof, R., 2014. Relationship between wind speed and gas exchange over the ocean revisited.
1259 *Limnol. Oceanogr. Methods* 12, 351–362. <https://doi.org/10.4319/lom.2014.12.351>

1260 Weiss, R.F., 1974. Carbon dioxide in water and seawater: the solubility of a non-ideal gas. *Mar.*
1261 *Chem.* 2, 203–215. [https://doi.org/10.1016/0304-4203\(74\)90015-2](https://doi.org/10.1016/0304-4203(74)90015-2)

1262 Whitfield, M., Turner, D.R., 1986. The carbon dioxide system in estuaries – An inorganic perspective.
1263 *Sci. Total Environ.* 49, 235-255. [https://doi.org/10.1016/0048-9697\(86\)90243-3](https://doi.org/10.1016/0048-9697(86)90243-3)

1264 Willeit, M., Ganopolski, A., Calov, R., Brovkin, V., 2019. Mid-Pleistocene transition in glacial cycles
1265 explained by declining CO₂ and regolith removal. *Sci. Adv.* 5, 1–9. doi:10.1126/sciadv.aav7337

1266 Zhai, W., Dai, M., Guo, X., 2007. Carbonate system and CO₂ degassing fluxes in the inner estuary of
1267 Changjiang (Yangtze) River, China. *Mar. Chem.* 107, 342–356.
1268 <https://doi.org/10.1016/j.marchem.2007.02.011>

1269

Table 1 Mean (\pm standard deviation), minimum and maximum values of the principal physicochemical properties on the waters of the PSRE, separated by sampling campaigns and estuarine zones.

Salinity Interval / Estuarine Region	Sal.	Temp. (°C)	$p\text{CO}_2$ (ppmv)	DIC ($\mu\text{mol kg}^{-1}$)	pH (NBS)	TA ($\mu\text{mol kg}^{-1}$)	$\delta^{13}\text{C-DIC}$ (‰)	Chl <i>a</i> ($\mu\text{g L}^{-1}$)	DO (%sat)
Feb. – 17									
0 – 5	0.8 \pm 1.0 (0.0 / 4.9)	30.8 \pm 0.4 (28.1 / 31.8)	157 \pm 47 (41 / 321)	428 \pm 72 (357 / 655)	8.40 \pm 0.36 (7.29 / 9.36)	441 \pm 91 (347 / 670)	-3.64 \pm 0.56 (-4.81 / -2.30)	15.3 \pm 4.7 (8.0 / 21.3)	110 \pm 6 (91 / 122)
5 – 30	19.0 \pm 6.9 (5.3 / 29.8)	29.1 \pm 0.5 (27.3 / 30.7)	306 \pm 83 (121 / 446)	1982 \pm 79 (1902 / 2061)	8.12 \pm 0.08 (7.61 / 8.61)	1234 \pm 362 (747 / 1882)	0.27 \pm 1.07 (-2.12 / 1.93)	7.0 \pm 1.4 (4.3 / 9.2)	92 \pm 4 (86 / 102)
> 30	31.8 \pm 1.6 (30.3 / 33.5)	27.9 \pm 1.0 (26.2 / 28.2)	459 \pm 8 (402 / 472)	1884 \pm 130 (1689 / 2061)	8.04 \pm 0.01 (8.00 / 8.06)	2239 \pm 96 (2143 / 2336)	2.46 \pm 0.11 (2.34 \pm 2.57)	1.14 \pm 0.88 (0.26 / 2.02)	88.4 \pm 0.9 (84.1 / 89.5)
Mangrove Creek	1.2 \pm 0.3 (0.5 / 1.7)	30.7 \pm 0.2 (30.3 / 31.3)	1479 \pm 606 (456 / 2840)	784 \pm 137 (647 / 922)	7.49 \pm 0.11 (7.29 / 7.88)	719 \pm 120 (599 / 839)	-7.47 \pm 0.64 (-8.11 / -6.82)	12.8 \pm 1.1 (10.5 / 14.6)	99.1 \pm 0.7 (98.4 / 100.1)
Oct. – 17									
0 – 5	1.1 \pm 1.2 (0.0 / 4.9)	25.4 \pm 0.3 (24.6 / 26.2)	192 \pm 52 (91 / 300)	440 \pm 81 (347 / 558)	8.40 \pm 0.15 (8.06 / 8.77)	458 \pm 86 (352 / 573)	-3.47 \pm 0.36 (-4.23 / -2.89)	6.04 \pm 1.38 (3.86 / 11.86)	107 \pm 9 (82 / 119)
5 – 30	19.4 \pm 6.0 (5.1 / 29.9)	25.6 \pm 0.3 (24.4 / 26.2)	275 \pm 62 (102 / 414)	1158 \pm 228 (713 / 1629)	8.47 \pm 0.05 (8.05 / 8.66)	1306 \pm 266 (777 / 1874)	0.46 \pm 0.80 (-1.51 / 1.71)	2.49 \pm 0.31 (1.54 / 3.14)	89 \pm 7 (79 / 116)
> 30	32.0 \pm 0.9 (30.1 / 33.0)	24.0 \pm 0.5 (23.4 / 25.0)	390 \pm 14 (356 / 429)	1895 \pm 38 (1818 / 1941)	8.40 \pm 0.01 (8.37 / 8.44)	2211 \pm 47 (2120 / 2274)	2.19 \pm 0.23 (1.91 / 2.50)	1.64 \pm 1.30 (0.31 / 4.24)	92 \pm 5 (86 / 111)
Mangrove Creek	5.1 \pm 1.1 (0.1 / 7.2)	24.5 \pm 0.1 (24.0 / 25.2)	4016 \pm 2643 (525 / 11514)	1755 \pm 1172 (753 / 4687)	7.44 \pm 0.15 (7.13 / 7.98)	1019 \pm 211 (700 / 1467)	-8.96 \pm 1.53 (-11.82 / -7.00)	6.05 \pm 1.63 (3.83 / 9.65)	80 \pm 14 (48 / 112)
Mar. – 18									
0 – 5	0.1 \pm 0.13 (0.0 / 4.4)	29.0 \pm 0.4 (28.1 / 31.1)	1946 \pm 252 (1187 / 2411)	469 \pm 86 (381 / 667)	7.10 \pm 0.13 (6.43 / 8.20)	428 \pm 101 (337 / 663)	-7.38 \pm 1.49 (-9.07 / -4.64)	1.81 \pm 0.37 (0.85 / 2.72)	58 \pm 3 (58 / 80)
5 – 30	17.4 \pm 6.6 (5.1 / 30)	29.5 \pm 0.8 (27.3 / 31.8)	380 \pm 96 (309 / 668)	1198 \pm 215 (747 / 1628)	8.21 \pm 0.14 (7.79 / 8.42)	1322 \pm 266 (766 / 1846)	0.22 \pm 0.86 (-2.87 / 1.56)	4.03 \pm 1.60 (0.53 / 7.57)	87 \pm 6 (73 / 107)
> 30	33.7 \pm 2.2 (30.1 / 36.2)	28.4 \pm 0.5 (27.5 / 29.3)	439 \pm 17 (384 / 469)	1895 \pm 129 (1765 / 2024)	8.27 \pm 0.01 (8.24 / 8.32)	2170 \pm 160 (2010 / 2331)	2.08 \pm 0.25 (1.83 / 2.34)	1.74 \pm 1.09 (0.65 / 2.83)	88 \pm 3 (84 / 94)
Mangrove Creek	0.6 \pm 0.3 (0.1 / 2.1)	28.7 \pm 0.2 (28.3 / 30.1)	8988 \pm 2325 (3931 / 13344)	1555 \pm 195 (1071 / 2407)	6.92 \pm 0.09 (6.75 / 7.78)	1177 \pm 356 (822 / 2055)	-6.43 \pm 1.79 (-9.04 / -3.27)	22.70 \pm 2.51 (19.31 / 26.55)	29 \pm 16 (3 / 70)

Table 2 Results of the anchored station at the mangrove creek showing the diurnal variability (mean, standard deviation, minimum and maximum) for the principal physicochemical properties k, separated by time of sampling (ebb tide daytime, flood tide nighttime, ebb tide nighttime).

	Ebb tide daytime	Flood tide nighttime	Ebb tide nighttime
Temperature (°C)	30.3 ± 0.3 28.8 - 31.0	29.0 ± 0.7 28.1 - 30.0	27.6 ± 0.03 27.6 - 27.7
Salinity	0.38 ± 0.00 0.38 - 0.42	0.41 ± 0.02 0.39 - 0.44	0.72 ± 0.07 0.58 - 0.80
<i>p</i> CO ₂ (ppmv)	7,439 ± 1,390 5,318 - 11,600	11,191 ± 2,264 7,366 - 13,919	18,276 ± 3,408 6,358 - 21,720
DIC (μmol kg ⁻¹)	1,105 ± 32 1,071 - 1,143	1,259 ± 77 1,103 - 1,335	2,213 ± 210 1,791 - 2,407
TA (μmol kg ⁻¹)	860 ± 36 805 - 912	931 ± 34 885 - 981	1,582 ± 169 1,246 - 1,749
pH (NBS)	7.06 ± 0.06 6.84 - 7.61	6.92 ± 0.10 6.81 - 7.07	6.89 ± 0.03 6.80 - 6.93
δ ¹³ C-DIC (‰)	-4.10 ± 0.95 -6.00 to -3.27	-5.99 ± 1.12 -7.65 to -4.45	-8.57 ± 0.15 -8.79 to -8.28
Chl a (μmol kg ⁻¹)	66.7 ± 4.0 61.3 - 72.1	19.0 ± 3.4 15.5 - 22.4	-
DO (%sat)	59.8 ± 10.8 5.2 - 80.3	39.2 ± 14.2 23.9 - 62.0	4.9 ± 4.3 0.2 - 13.1

Table 3 Calculated mean values for gas exchange coefficient (k_{600}) and CO_2 fluxes at the air-water interface in each estuarine regions of the PSRE, as well as, the spatial time-integrated fluxes for the whole system. The periods M, A, and N represents the morning, afternoon and night. W92 is the data calculated according to k_{600} of Wanninkhof (1992), RC01 is the data calculated according to k_{600} of Raymond and Cole (2001), and A09 is data calculated according to k_{600} of Abril et al. (2009).

	Period	FCO_2 (mmol C m ⁻² d ⁻¹) W92	FCO_2 (mmol C m ⁻² d ⁻¹) RC01	FCO_2 (mmol C m ⁻² d ⁻¹) A09	K_{600} (cm h ⁻¹) W92	K_{600} (cm h ⁻¹) RC01	K_{600} (cm h ⁻¹) A09
Feb – 17							
0-5 (21.50 km ²)	M	-1.61	-7.44	-11.52	0.69	3.21	4.98
	A	-12.07	-18.46	-19.49	5.21	7.97	8.42
	N	-2.30	-8.18	-12.46	1.00	3.54	5.38
5-30 (49.00 km ²)	M	-0.34	-1.56	-2.78	0.69	3.21	5.76
	A	-2.52	-3.86	-5.11	5.21	7.97	10.56
	N	-0.48	-1.70	-3.05	1.00	3.54	6.32
> 30 (20.00 km ²)	M	0.38	1.75	3.14	0.69	3.21	5.76
	A	2.86	4.37	5.78	5.21	7.97	10.56
	N	0.55	1.94	3.46	1.00	3.54	6.32
Mangrove Creek (0.25 km ²)	M	1.97	28.56	34.92	0.17	2.47	3.02
	A	14.35	44.30	48.82	1.24	3.82	4.22
	N	2.88	30.07	41.18	0.25	2.6	3.56
All Estuary (90.75 km ²) are-averaged	M	-0.48	-2.14	-3.43			
	A	-3.55	-5.38	-5.98			
	N	-0.67	-2.35	-3.72			
		-1.34	-3.05	-4.22			
Oct – 17							
0-5 (12.90 km ²)	M	-5.64	-10.34	-12.86	3.17	5.82	7.23
	A	-26.23	-37.80	-21.55	14.75	21.26	12.12
	N	-9.26	-14.16	-14.98	5.21	7.97	8.42
5-30 (30.60 km ²)	M	-2.74	-5.04	-7.70	3.17	5.82	8.9
	A	-12.77	-18.41	-13.61	14.75	21.26	15.73
	N	-4.51	-6.91	-9.14	5.21	7.97	10.56
> 30 (47.00 km ²)	M	0.12	0.22	0.34	3.17	5.82	8.9
	A	0.55	0.82	0.60	14.75	21.26	15.73
	N	0.19	0.31	0.41	5.21	7.97	10.56
Mangrove Creek (0.25 km ²)	M	23.09	107.40	131.16	0.69	3.21	3.92
	A	126.82	216.14	171.31	3.79	6.46	5.12
	N	41.50	127.80	141.19	1.24	3.82	4.22
All Estuary (90.75 km ²) area-averaged	M	-1.61	-2.76	-3.89			
	A	-7.39	-10.56	-6.86			
	N	-2.62	-3.84	-4.61			
		-3.55	-5.26	-4.99			
Mar – 18							
0-5 (21.50 km ²)	M	6.36	41.76	66.17	0.44	2.89	4.58
	A	68.06	107.35	117.77	4.71	7.43	8.15
	N	12.86	49.70	75.72	0.89	3.44	5.24
5-30 (62.00 km ²)	M	-0.12	-0.82	-1.49	0.44	2.89	5.21
	A	-1.34	-2.14	-2.93	4.71	7.43	10.19
	N	-0.26	-0.98	-1.75	0.89	3.44	6.13
> 30 (7.00 km ²)	M	0.05	0.36	0.65	0.44	2.89	5.21
	A	0.60	0.94	1.27	4.71	7.43	10.19
	N	0.12	0.43	0.77	0.89	3.44	6.13

Mangrove	M	9.34	198.72	219.84	0.11	2.34	3.38
Creek	A	105.31	324.41	358.39	1.24	3.82	4.22
(0.25 km ²)	N	26.33	228.46	289.08	0.31	2.69	3.63
All Estuary		1.46	9.91	15.50			
(90.75 km ²)		15.55	24.94	26.98			
area-averaged		2.95	11.76	17.64			
		5.71	14.59	19.37			

Table 4 Net Community Production (NCP) estimated for the mixing zone. The NCP was estimated as the difference between (ΔFCO_2), ($\Delta\text{FCO}_{2\text{mixing corrected}}$) and ($\Delta\text{FCO}_{2\text{cooling/heating}}$). FCO_2 , $\text{FCO}_{2\text{mixing corrected}}$ and $\text{FCO}_{2\text{cooling/heating}}$ were calculated with the values of $p\text{CO}_{2\text{measured}}$, $p\text{CO}_{2\text{mixing corrected}}$ and $p\text{CO}_{2\text{cooling/heating}}$. See the section 3.55 in material and methods and 4.3 in discussion for further details.

	Mixing Zone
Feb – 17	
$\Delta\text{FCO}_2 = \text{FCO}_{2\text{mixing}} - \text{FCO}_2$ (mmol C m ⁻² d ⁻¹)	-2.18
$\Delta\text{FCO}_{2\text{mixing corrected}} = \text{FCO}_{2\text{mixing}} - \text{FCO}_{2\text{mixing corrected}}$ (mmol C m ⁻² d ⁻¹)	-0.18
$\Delta\text{FCO}_{2\text{cooling/heating}} = \text{FCO}_{2\text{mixing}} - \text{FCO}_{2\text{cooling/heating}}$ (mmol C m ⁻² d ⁻¹)	-0.30
NCP = (ΔFCO_2) – ($\Delta\text{FCO}_{2\text{mixing corrected}}$) – ($\Delta\text{FCO}_{2\text{cooling/heating}}$)	-1.70
Oct – 17	
$\Delta\text{FCO}_2 = \text{FCO}_{2\text{mixing}} - \text{FCO}_2$ (mmol C m ⁻² d ⁻¹)	-2.95
$\Delta\text{FCO}_{2\text{mixing corrected}} = \text{FCO}_{2\text{mixing}} - \text{FCO}_{2\text{mixing corrected}}$ (mmol C m ⁻² d ⁻¹)	-1.02
$\Delta\text{FCO}_{2\text{cooling/heating}} = \text{FCO}_{2\text{mixing}} - \text{FCO}_{2\text{cooling/heating}}$ (mmol C m ⁻² d ⁻¹)	-0.79
NCP = (ΔFCO_2) – ($\Delta\text{FCO}_{2\text{mixing corrected}}$) – ($\Delta\text{FCO}_{2\text{cooling/heating}}$)	-1.13
Mar – 18	
$\Delta\text{FCO}_2 = \text{FCO}_{2\text{mixing}} - \text{FCO}_2$ (mmol C m ⁻² d ⁻¹)	-0.46
$\Delta\text{FCO}_{2\text{mixing corrected}} = \text{FCO}_{2\text{mixing}} - \text{FCO}_{2\text{mixing corrected}}$ (mmol C m ⁻² d ⁻¹)	0.69
$\Delta\text{FCO}_{2\text{cooling/heating}} = \text{FCO}_{2\text{mixing}} - \text{FCO}_{2\text{cooling/heating}}$ (mmol C m ⁻² d ⁻¹)	-0.57
NCP = (ΔFCO_2) – ($\Delta\text{FCO}_{2\text{mixing corrected}}$) – ($\Delta\text{FCO}_{2\text{cooling/heating}}$)	-0.58

Figure Captions

Figure 1. Map 1a shows the localization of the state of Rio de Janeiro. The river basins are shown in shades of grey. Map 1b shows the localization of the PSRE and adjacent shelf waters. The colored lines represent the boat track with online and continuous measurements of $p\text{CO}_2$, DO, pH, temperature, and salinity. Note that the boat track varied in each sampling campaign: light green, dark green and blue represent Feb 17, Oct 17 and Mar-18, respectively. Along the boat track, discrete stations were sampled (the exact localization of the sampling stations exhibited variations between sampling campaigns according to the boat track and the salinity gradient). The yellow star represents the localization of the anchoring station (Eulerian time-series data). Graph c shows a comparison between the river water discharge for the year of sampling (2017/2018) and the historical average. The red arrows are the sampling months. Graph d shows a historical tendency of decreasing river flow (average monthly values).

Figure 2. Maps of continuous measurements of a) salinity, b) pH, c) DO, and d) $p\text{CO}_2$ in surface waters of the PSRE for all sampling campaigns.

Figure 3. Distribution of $p\text{CO}_2$ along the salinity gradient in the PSRE separated by sampling campaigns. Graphs a), c), e) and g) include all the data, with the main estuarine channel and the mangrove creek. Graphs b), d), f) and h) include only the data in the main estuarine channel.

Figure 4. Distributions of TA, DIC, $\delta^{13}\text{C}$ -DIC, and Chl *a* in discrete samples along the salinity gradient. The black dots are the main estuarine channel and the green dots are the mangrove creek. The dashed blue lines represent the theoretical models of conservative mixing endmembers.

Figure 5. Relationship between the concentrations of Chl *a* vs. $p\text{CO}_2$ along the main channel of the PSRE. The different symbols in the figure represent the sampling campaigns, as indicated in the caption. The terms “river” and “ocean” represent the values found in the river and ocean endmembers, respectively, for the different sampling campaigns.

Figure 6. Eulerian time-series data of the mangrove creek. The shaded area symbolizes the nighttime sampling.

Figure 7. Scatter plots between a) TA or DIC and salinity, b) TA and DO, c) $\delta^{13}\text{C}$ -DIC and DO, d) $\delta^{13}\text{C}$ -DIC and $p\text{CO}_2$ in the mangrove creek throughout the 20 h cycle on Mar 18. Red dots characterize hypoxic condition with $\text{DO}_{\text{sat}}\% < 25\%$ observed in early morning and low tide.

Figure 8. Graph a shows the relationship between the excess dissolved inorganic carbon (E-DIC) and apparent oxygen utilization (AOU) in the PSRE main channel and mangrove creek for the three sampling campaigns. Green dots are the stations in the mangrove creek and blue dots are the stations in the main estuarine channel. The 1:1 line represents the quotient between CO_2 and O_2 during the processes of photosynthesis and respiration. Graph b) shows the deviations from conservative mixing

lines of total alkalinity (ΔTA) as a function of dissolved inorganic carbon (ΔDIC), including the three sampling campaigns. Green dots are the stations in the mangrove creek and blue dots are the stations in the main estuarine channel. α indicates the slope of the linear regression line.

Figure 9. Comparison between mixing model and pCO_2 measured in the mixing zone, including corrections performed for gas exchange and thermal variability and deviations from the conservative mixing. Graphs a), c) and e) show the means and standard deviations of pCO_2 measured (black dots), pCO_2 mixing (blue dots), pCO_2 gas exchange (green dots) and pCO_2 cooling/heating (red dots) for each salinity unit. Graphs b), d) and f) show the difference between pCO_2 measured and pCO_2 mixing (ΔpCO_2 measured), pCO_2 gas exchange and pCO_2 mixing (ΔpCO_2 gas exchange), and the cumulative difference between pCO_2 gas exchange + pCO_2 cooling/heating and pCO_2 mixing (ΔpCO_2 gas exchange + cooling/heating). The green arrow indicates the effect of gas exchange compared with pCO_2 mixing (influx or efflux of CO_2). The red arrow indicates the effect of thermal variability (cooling and heating). The grey arrow indicates the residual difference between pCO_2 measured and pCO_2 mixing attributed to biological activities.

Figure 10. Deviations from conservative mixing lines of stable isotope composition of DIC ($\Delta\delta^{13}C$ -DIC) as a function of DIC (ΔDIC) for the main channel. Different colors represent the sampling campaigns. The origin represents the conservative mixing with sample values equal to the ocean endmember value. The four quadrants (PP/OG, CP, DC, and CD) in the graph indicate the processes that could influence the DIC and $\delta^{13}C$ -DIC distributions. Quadrant PP/OG represents the primary production/outgassing of CO_2 , when DIC concentrations increase and $\delta^{13}C$ -DIC values decrease. Quadrant CP represents the carbonate precipitation, when DIC concentrations and $\delta^{13}C$ -DIC values decrease. Quadrant DC represents the degradation of organic carbon, when DIC concentrations increase and $\delta^{13}C$ -DIC decrease. Quadrant CD represents the carbonate dissolution, when the DIC concentrations and $\delta^{13}C$ -DIC values increase. The red vectors represent the slopes of specific processes affecting the DIC and $\delta^{13}C$ -DIC distributions: primary production (slope = -24.0‰), CO_2 outgassing (slope = -8.4‰), and organic carbon degradation using the $\delta^{13}C$ -DIC value of river water (-16.0‰). The grey arrows represent the direction that the samples will follow if they are subject to more than one process (organic matter degradation followed by primary production, which is drawn parallel to vector of primary production; and organic carbon degradation followed by CO_2 outgassing, which is drawn parallel to the vector of CO_2 outgassing). Details about the formulations and calculations of these vectors can be found in Alling et al. (2012), Samanta et al. (2015), and Cotovicz Jr. et al. (2019).

Figure 1

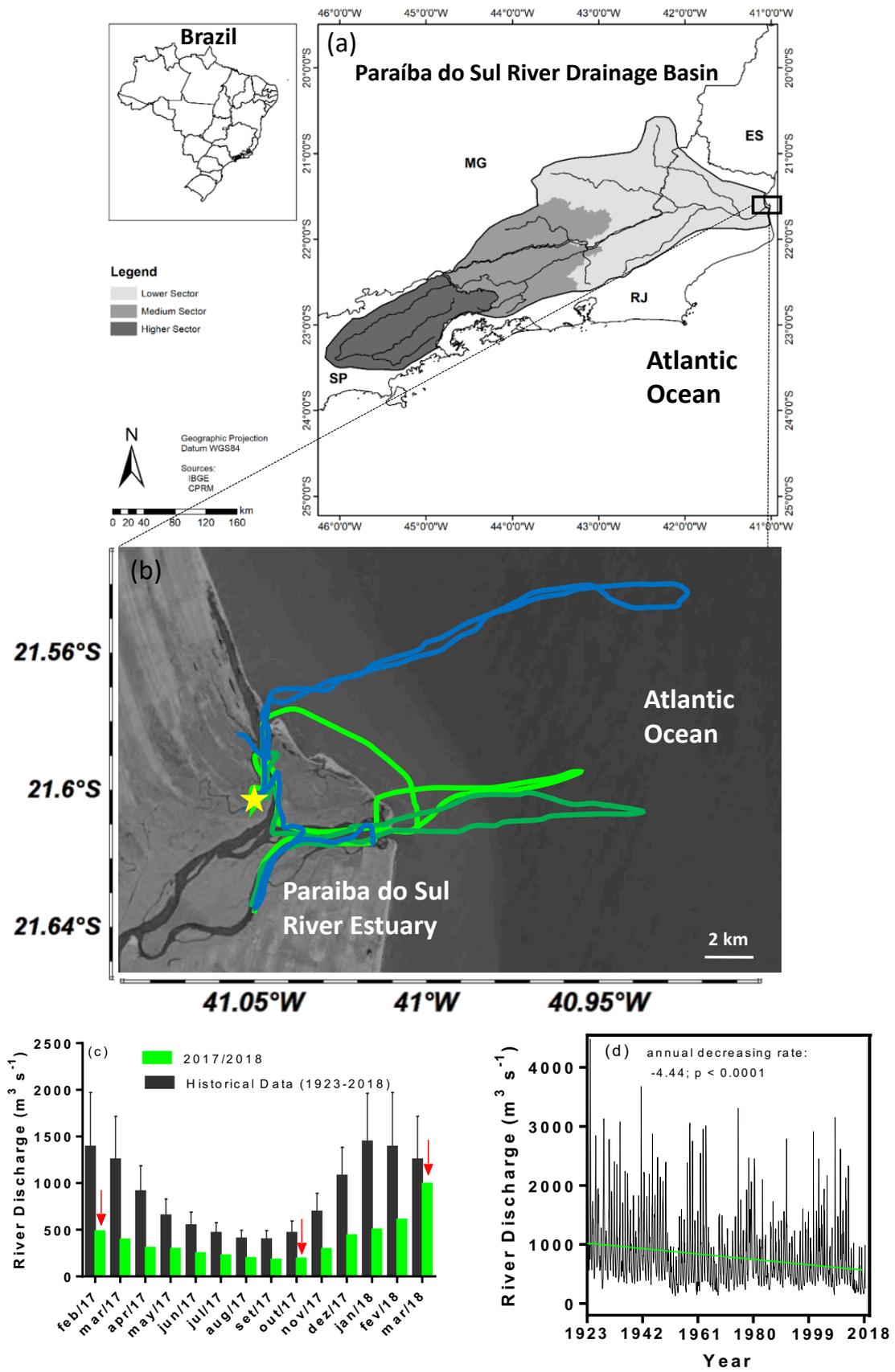


Figure 2

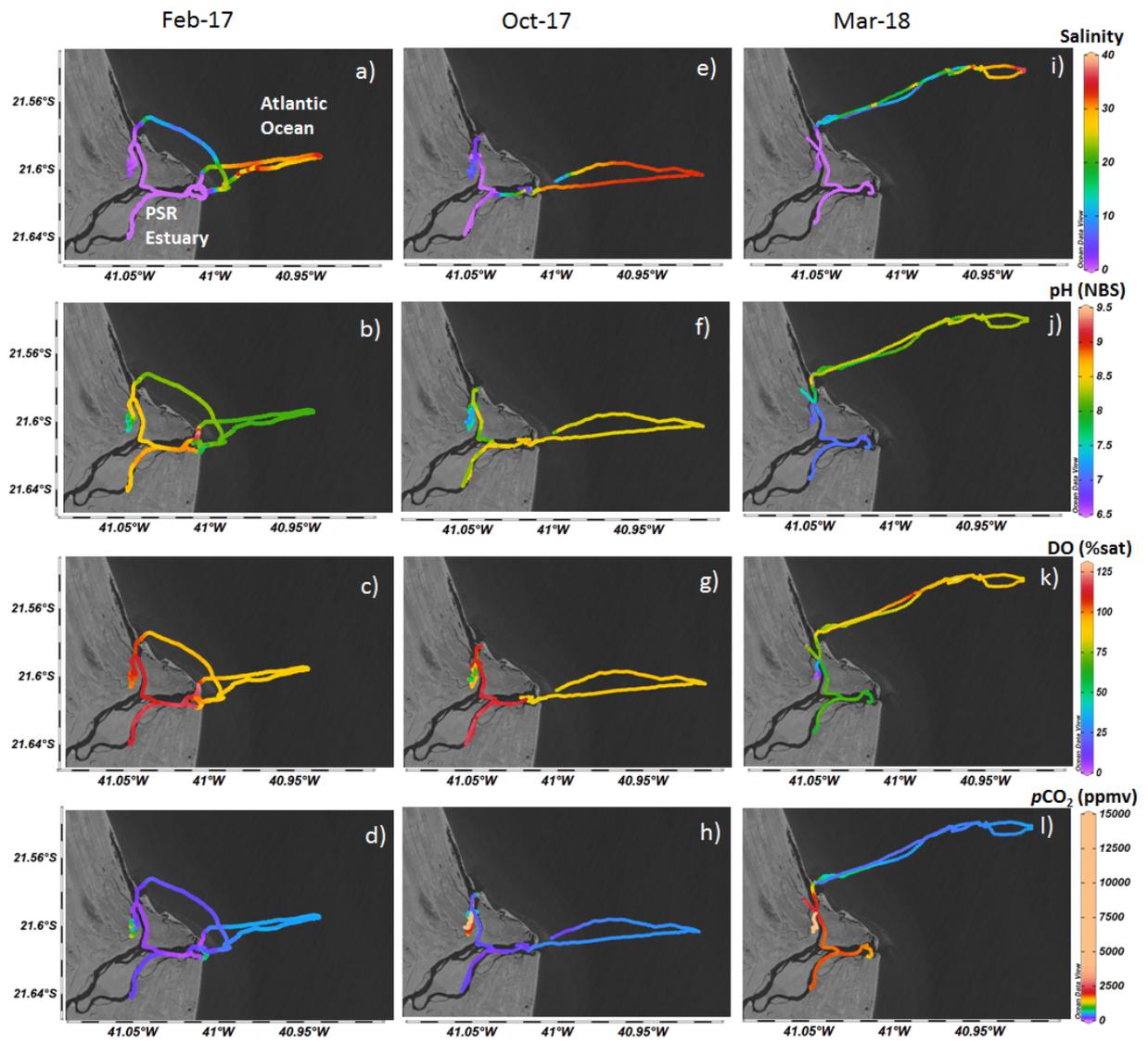


Figure 3

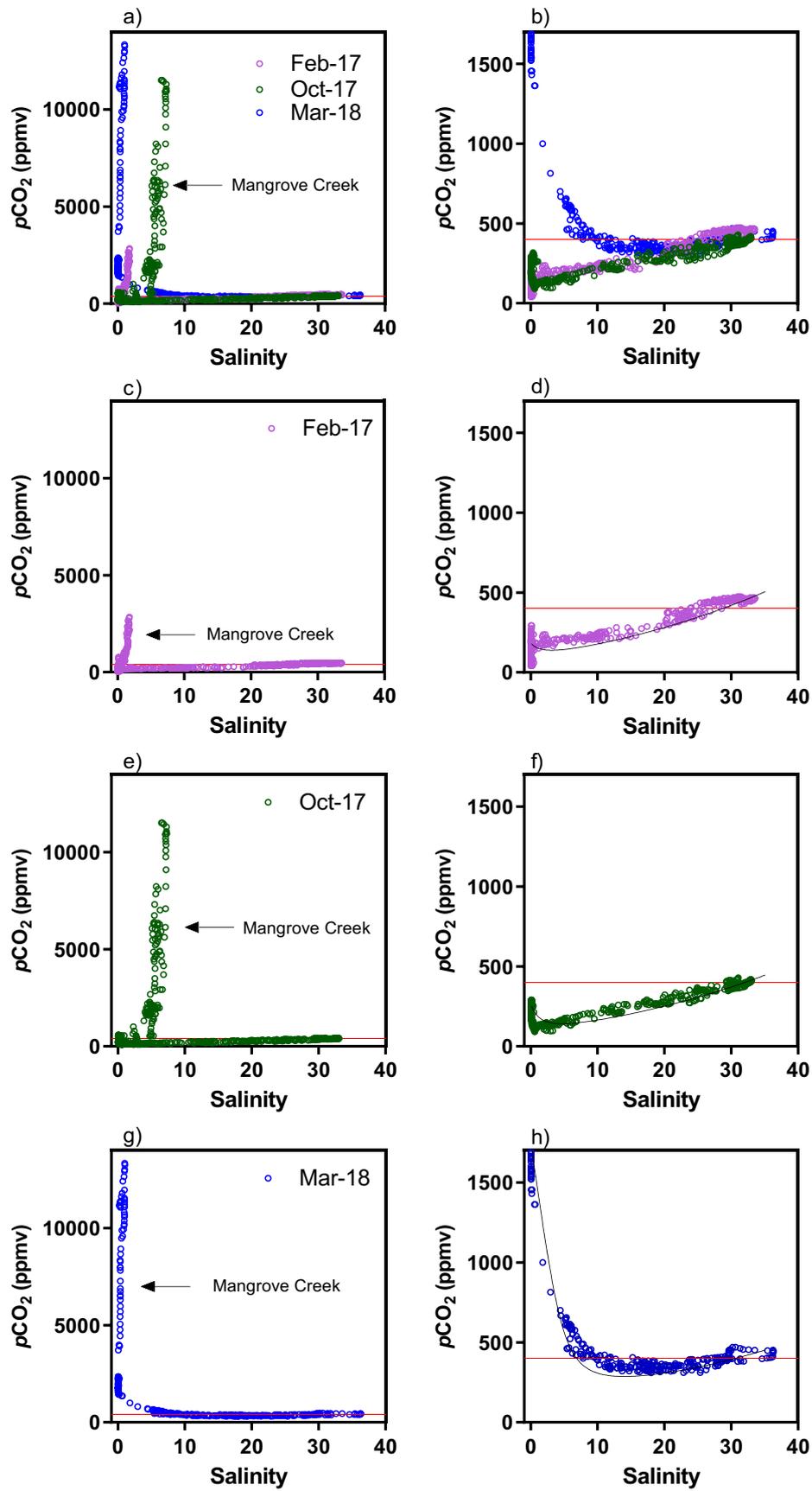


Figure 4

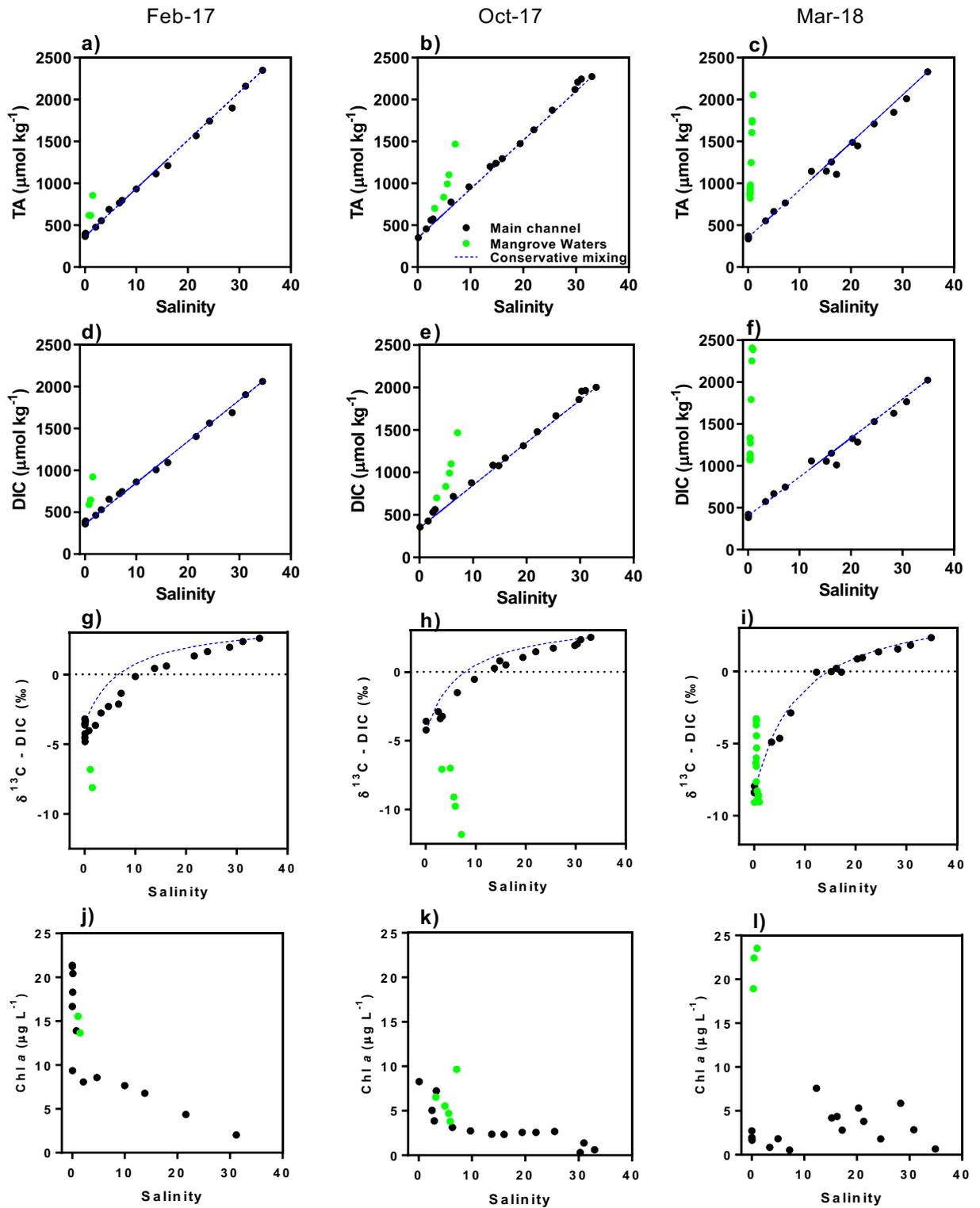


Figure 5

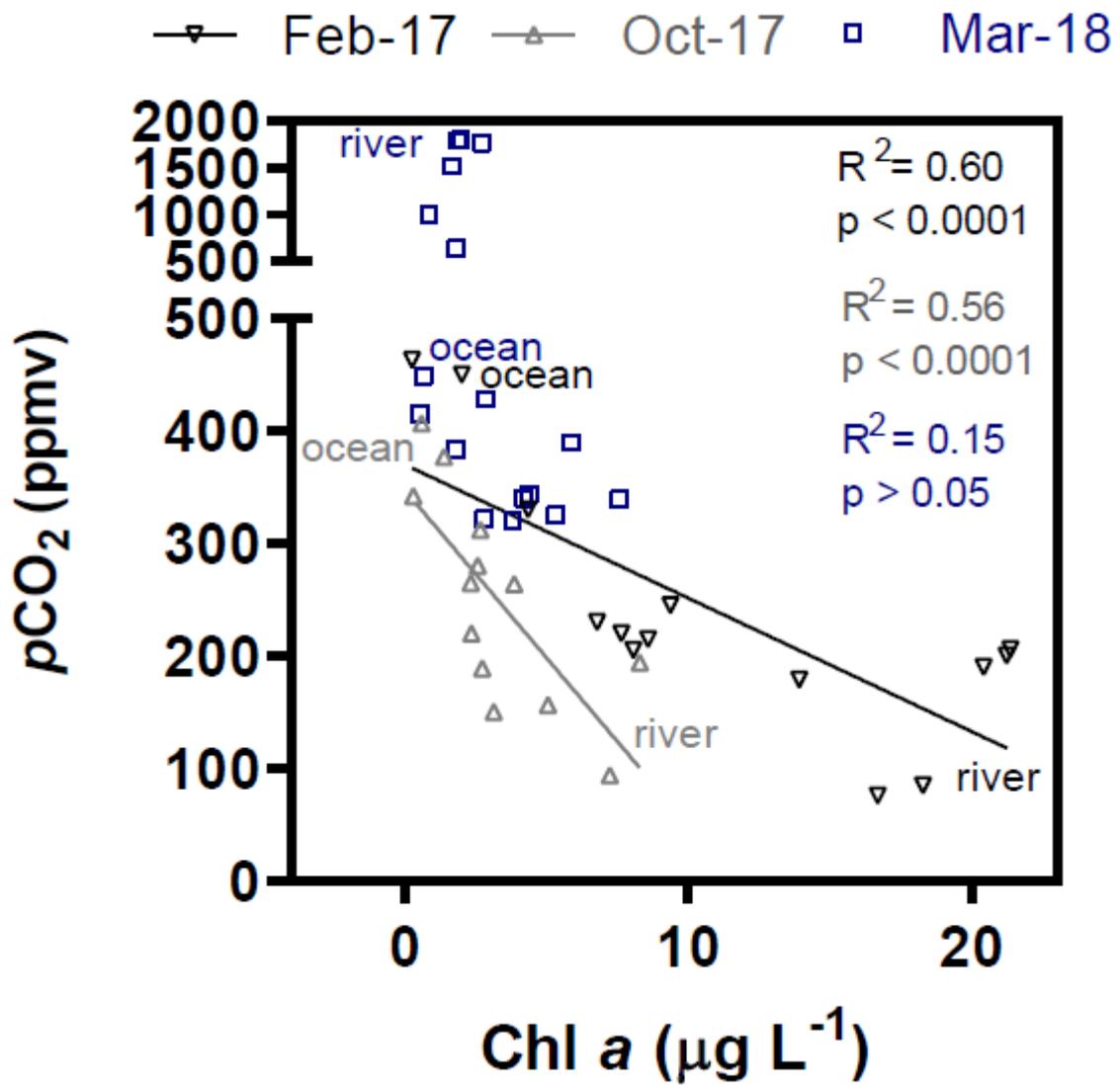


Figure 6

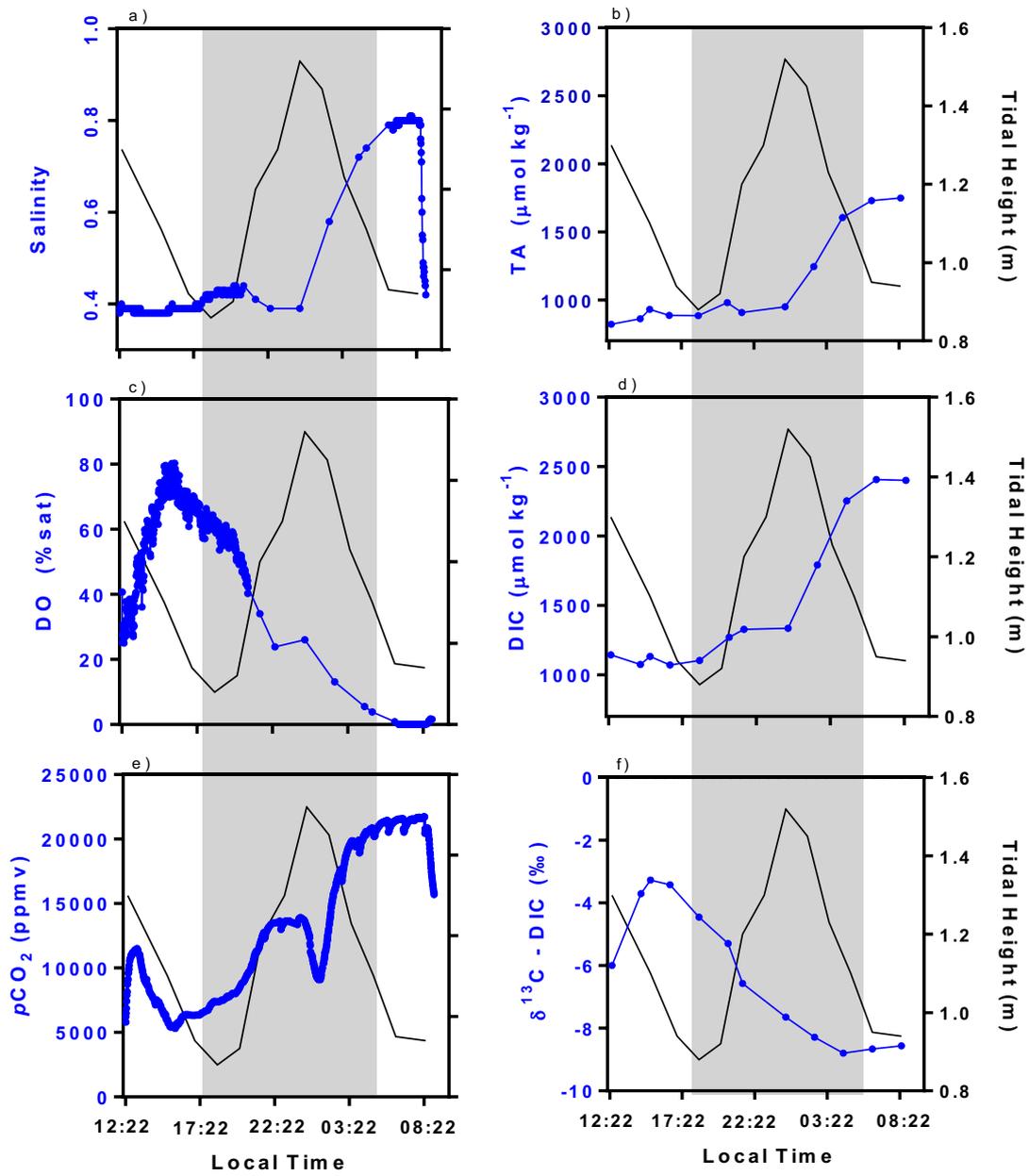


Figure 7

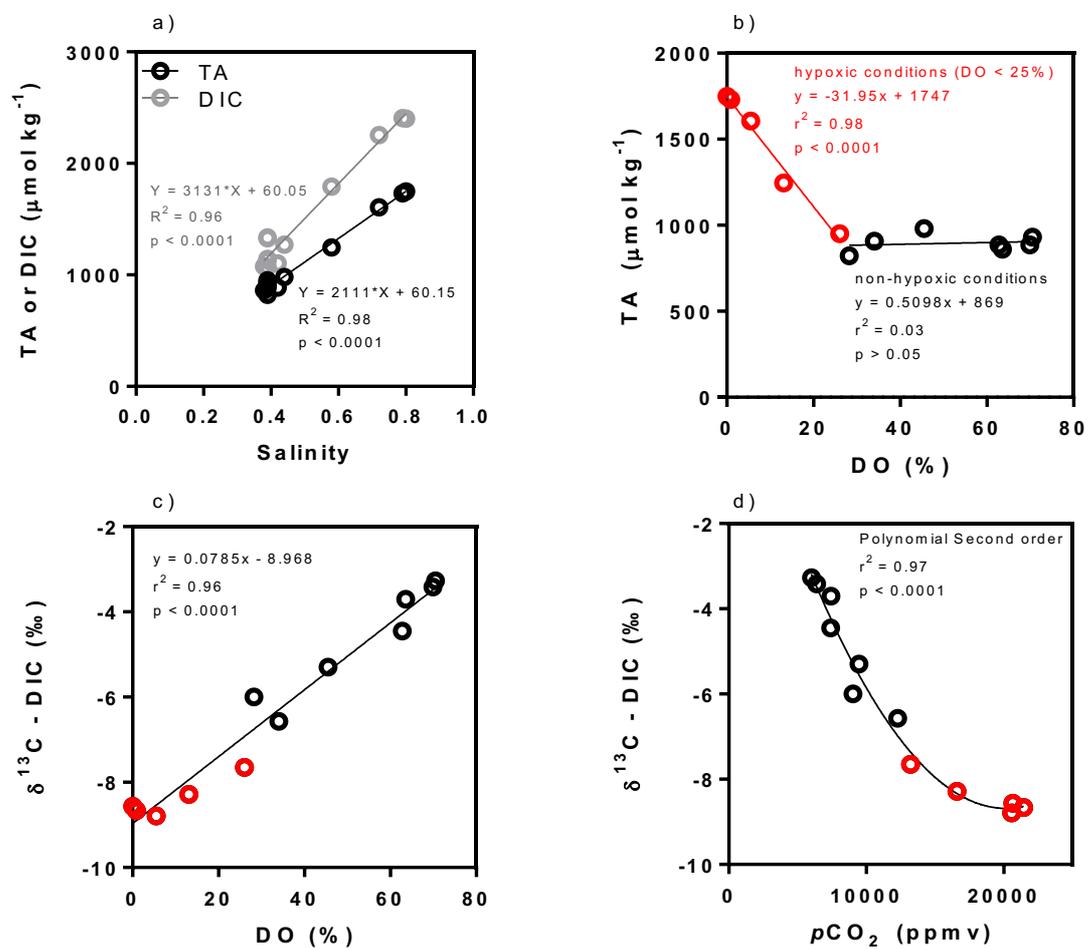


Figure 8

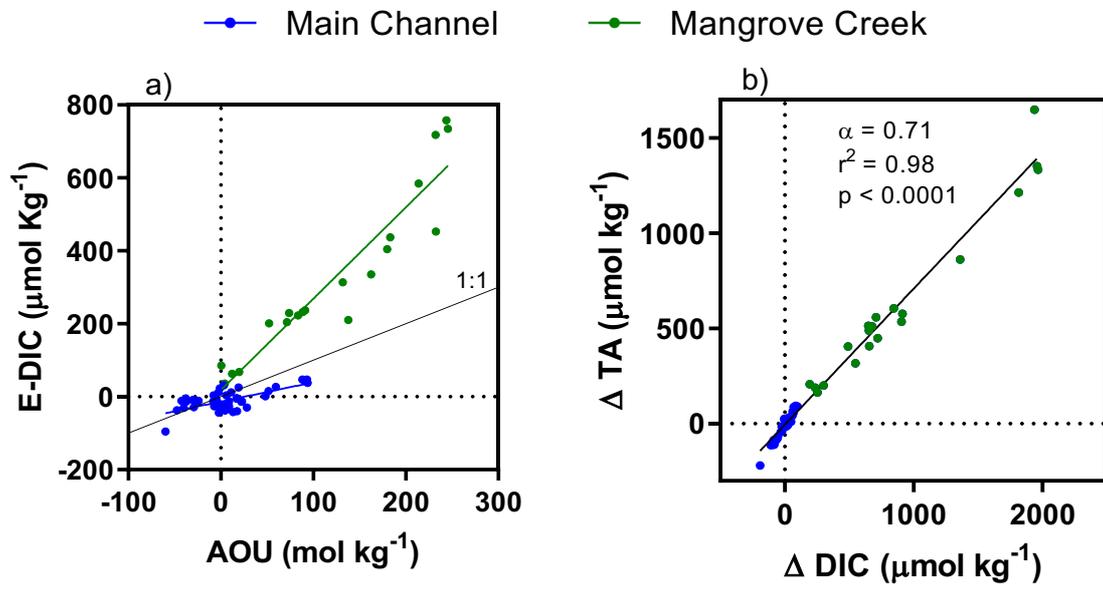


Figure 9

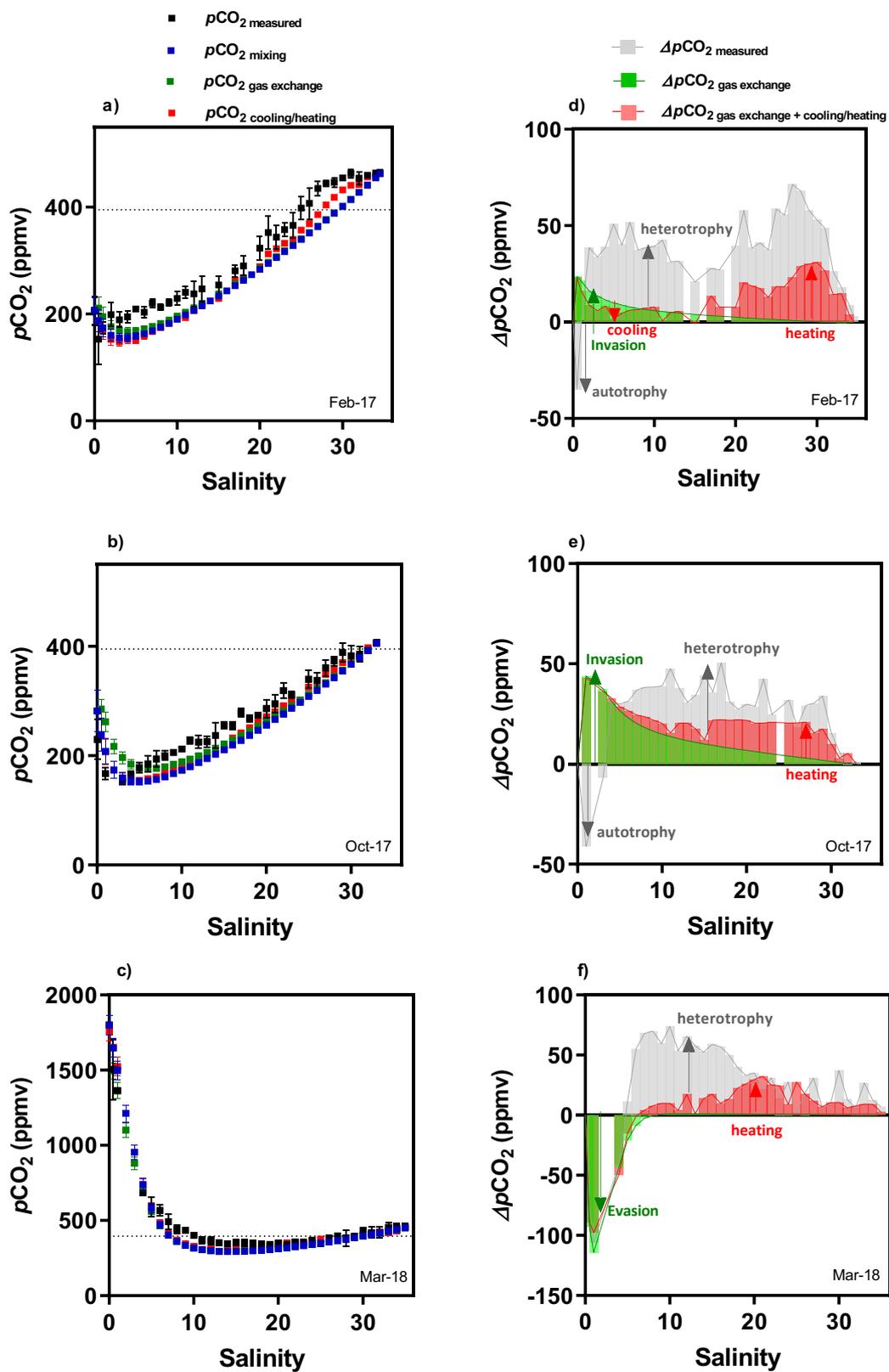


Figure 10

