



HAL
open science

Linking eutrophication to carbon dioxide and methane emissions from exposed mangrove soils along an urban gradient

Glenda C Barroso, Gwenaël Abril, Wilson Machado, Rodrigo C Abuchacra, Roberta B Peixoto, Marcelo Bernardes, Gabriela S Marques, Christian J Sanders, Gabriela B Oliveira, Silvio R Oliveira Filho, et al.

► To cite this version:

Glenda C Barroso, Gwenaël Abril, Wilson Machado, Rodrigo C Abuchacra, Roberta B Peixoto, et al. Linking eutrophication to carbon dioxide and methane emissions from exposed mangrove soils along an urban gradient. *Science of the Total Environment*, 2022, 850, pp.157988. 10.1016/j.scitotenv.2022.157988 . hal-03813858

HAL Id: hal-03813858

<https://cnrs.hal.science/hal-03813858v1>

Submitted on 13 Oct 2022

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 Linking eutrophication to carbon dioxide and methane emissions from exposed
2 mangrove soils along an urban gradient

3 Glenda C. Barroso^{1,2}, Gwenaël Abril^{1,3}, Wilson Machado^{1,2}, Rodrigo C. Abuchacra⁴,
4 Roberta B. Peixoto^{1,2}, Marcelo Bernardes¹, Gabriela S. Marques¹, Christian J. Sanders⁵,
5 Gabriela B. Oliveira², Silvio R. de Oliveira Filho⁶, Leonardo Amora^{2,6}, Humberto
6 Marotta^{1,2,6}

7

8 Science of the Total Environment 850, <https://doi.org/10.1016/j.scitotenv.2022.157988>.

9

10 ¹*Graduate Program in Geosciences (Environmental Geochemistry), Fluminense Federal*
11 *University (UFF). Outeiro São João Baptista, s/n, 24020-007, Niterói, Brazil.*

12 ²*Ecosystems and Global Change Laboratory (LEMG-UFF)/Brazilian Ocean*
13 *Acidification Network (BrOA), Biomass and Water Management Research Center (NAB-*
14 *UFF), Fluminense Federal University (UFF), Av. Edmundo March, s/nº, Niterói, RJ,*
15 *Brazil, 24210-310.*

16 ³*Laboratoire de Biologie des Organismes et Ecosystèmes Aquatiques (BOREA), UMR*
17 *8067, Muséum National d'Histoire Naturelle, CNRS, IRD, SU, UCN, UA, 43 rue Cuvier,*
18 *CP 26, 75231 Paris Cedex 05, France.*

19 ⁴*Department of Geography, Graduate Program in Geography, State University of Rio de*
20 *Janeiro (FFP), Rua Dr. Francisco Portela, 1470 São Gonçalo, 24435-005, Rio de*
21 *Janeiro, Brazil*

22 ⁵ *National Marine Science Centre, Faculty of Science and Engineering, Southern Cross*
23 *University, Coffs Harbour, NSW 2540, Australia*

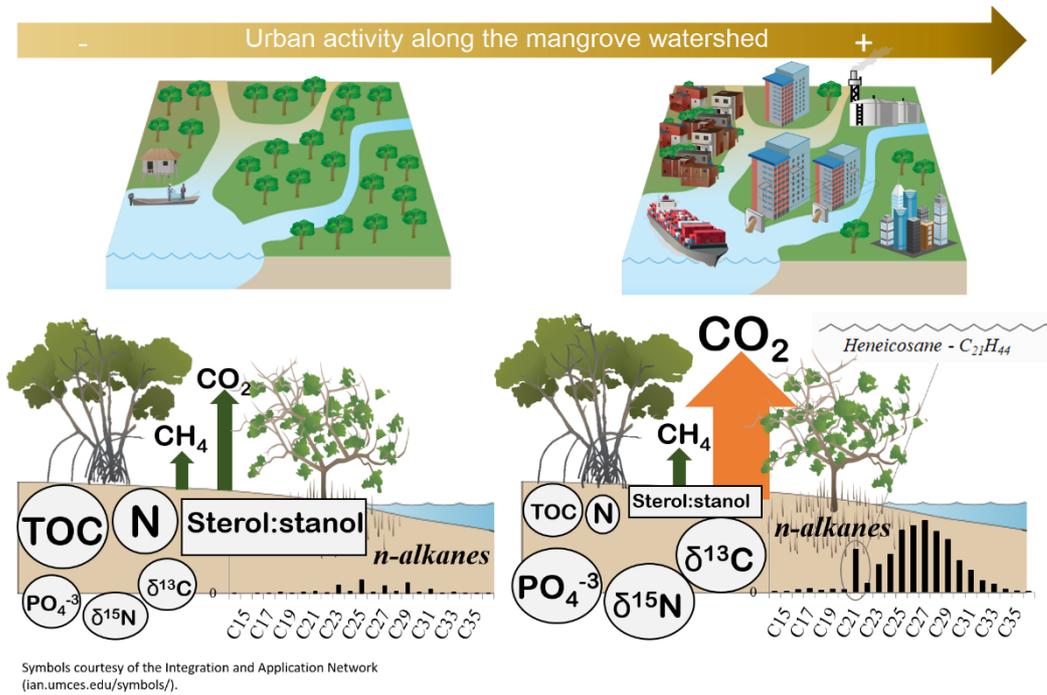
24 ⁶*Physical Geography Laboratory (LAGEF-UFF), Department of Geography, Graduate*
25 *Program in Geography, Fluminense Federal University (UFF), Av. Gal. Milton Tavares*

26 *de Souza, s/nº, Niterói, RJ, Brazil, 24210-346*

27 *corresponding author: humbertomarotta@id.uff.br

28

29 Graphical Abstract



30

31 HIGHLIGHTS

- 32 • Elementary, isotopic, and molecular proxies indicated mangrove organic matter
33 lability;
- 34 • Organic matter lability increased with urban growth and untreated sewage
35 discharges;
- 36 • Carbon dioxide emissions from exposed mangrove soils increased with
37 eutrophication;
- 38 • Methane emissions were 3 orders of magnitude lower than dioxide carbon
39 emissions;
- 40 • n -alkanes and sterol biomarkers suggest enhanced biomass degradation with
41 pollution.

42

43 **Abstract**

44 Mangroves are one of the most important but threatened blue carbon ecosystems globally.
45 Rapid urban growth has resulted in nutrient inputs and subsequent coastal eutrophication,
46 associated with an enrichment in organic matter (OM) from algal and sewage sources and
47 substantial changes in greenhouse gas (GHG) emissions. However, the effects of nitrogen
48 (N) and phosphorus (P) enrichment on mangrove soil OM composition and GHG
49 emissions, such as methane (CH₄) and carbon dioxide (CO₂), are still poorly understood.
50 Here, we aim to evaluate the relationships between CO₂ and CH₄ efflux with OM
51 composition in exposed soils from three mangrove areas along watersheds with different
52 urbanization levels (Rio de Janeiro State, Brazil). To assess spatial (lower vs. upper
53 intertidal zones) and seasonal (summer vs. winter) variability, we measured soil-air CO₂
54 and CH₄ fluxes at low spring tide, analyzing elementary (C, N, and P), isotopic ($\delta^{13}\text{C}$ and
55 $\delta^{15}\text{N}$), and the molecular (n-alkanes and sterols) composition of surface soil OM. A
56 general trend of OM composition was found with increasing urban influence, with higher
57 $\delta^{15}\text{N}$ (proxy of anthropogenic N enrichment), less negative $\delta^{13}\text{C}$, more short-chain n-
58 alkanes, lower C:N ratio (proxies of algal biomass), and higher epicoprostanol content
59 (proxies of sewage-derived OM). The CO₂ efflux from exposed soils increased greatly in
60 median (25/75% interquartile range) from 4.6 (2.9/8.3) to 24.0 (21.5/32.7) mmol m⁻² h⁻¹
61 from more pristine to more urbanized watersheds, independent of intertidal zone and
62 seasonality. The CO₂ fluxes at the most eutrophicated site were among the highest
63 reported worldwide for mangrove soils. Conversely, CH₄ emissions were relatively low
64 (three orders of magnitude lower than CO₂ fluxes), with high peaks in the lower intertidal
65 zone during the rainy summer. Thus, our findings demonstrate the influence of coastal
66 eutrophication on global warming potentials related to enhanced heterotrophic
67 remineralization of blue carbon within mangrove soils.

68 **Keywords:** CO₂; CH₄; Nutrient; Urban Growth; Organic Matter.

69

70

71 **1. Introduction**

72 Recent scientific evidence indicates that increased organic matter (OM) and
73 nutrient flows to coastal areas are critical components of global change, resulting in the
74 degradation of biodiversity, water quality, and C storage (Breitburg et al., 2018).

75 Eutrophication can be defined as an increased rate of OM supply to an ecosystem, not as
76 a trophic state but as a process (Nixon, 1995). Nutrient and OM inputs from natural
77 sources may be increased due to cultural eutrophication associated with urban sewage
78 loading and enhanced coastal productivity. Eutrophication has become widespread in
79 coastal marine environments around the world (Jiao et al., 2018; Häder et al., 2020).
80 Substantial changes in sources and quality of OM deposited in aquatic sediments have
81 been widely reported following eutrophication (Alongi, 2009; Kristensen et al., 2017).

82 Soils are the main organic carbon (OC) pool in mangrove ecosystems (Hamilton
83 and Friess, 2018). These pools are referred to as blue C, an important component of the
84 marine C cycle. (Jiao et al., 2018). However, the large blue C stocks in these systems may
85 be partially remineralized to greenhouse gases (GHGs) and returned to the atmosphere
86 (Jacotot et al., 2018; Martin et al., 2020). Despite their importance to global climate and
87 biodiversity, mangroves have been heavily threatened by deforestation (Hamilton and
88 Friess, 2018) and cultural eutrophication (Barcellos et al., 2019). Previous studies have
89 indicated contrasting effects of eutrophication on C storage in mangrove soils, such as
90 enhanced OM accumulation (Sanders et al., 2014) and remineralization (Queiroz et al.,
91 2020).

92 The principal GHG released from mangrove soils is CO₂, as this gas may be derived
93 from a wide variety of aerobic and anaerobic diagenetic reactions (Alongi, 2009). In turn,
94 CH₄ production is a strictly anaerobic process and limited in coastal wetlands due to high
95 sulphate concentrations from seawater. High sulphate concentrations favor OM
96 degradation through sulphate reduction rather than methanogenesis (Martens and Berner,
97 1974). However, eutrophication and subsequent enrichment of labile organic substrates
98 may stimulate methanogenesis in these environments (Chen et al., 2011).

99 Although several studies have demonstrated changes in OM composition and C
100 cycling processes in mangroves undergoing eutrophication (Sanders et al., 2014;
101 Keuskamp et al., 2015; Pérez et al., 2020), a better understanding of the mechanistic links
102 between GHG emissions and the quality of natural and anthropogenic OM is still needed.
103 Highly variable CO₂ and CH₄ emissions from mangrove soils are also commonly
104 attributed to the effects of biogenic structures (e.g., crab burrows and pneumatophores)
105 that promote oxygenation and gas diffusion (Ouyang et al., 2016). As a result, differences
106 in subaerial exposure time observed between the lower and upper intertidal zones are also
107 a critical control of redox conditions to biogeochemical processes in mangrove soils
108 (Kristensen et al., 2017). In addition to spatial variation from lower to upper intertidal
109 zone, the physical, chemical, and biological drivers of GHG emissions may vary
110 temporally over the seasonal cycles, especially due to variation in temperature and/or
111 rainfall (Kristensen et al., 2008a; Jacotot et al., 2019).

112 Diverse spatial and seasonal responses of highly dynamic GHGs to eutrophication
113 remain poorly understood for a wide intra- (Chen et al., 2012) and inter- (Kristensen et
114 al., 2017) variation of mangrove soils. This study aims to assess the relationship between
115 OM composition (elementary, isotopic, and molecular proxies), biological structures
116 (crab burrow and pneumatophore densities), and GHG emissions (CO₂ and CH₄) from
117 three mangrove soils, with different urbanization levels along specific watersheds within
118 the Rio de Janeiro State, Southeastern Brazil. Our hypothesis was that higher CO₂ and
119 CH₄ emissions would be associated with increasing cultural eutrophication indicated by
120 OM elementary, isotopic, and molecular composition in mangrove soils, independent of
121 intertidal zone and seasonality. To address these assumptions, soil-atmosphere C
122 exchange rates were compared during low spring tides, taking into account differing
123 spatial scales among mangroves and their intertidal zones (lower vs. upper intertidal
124 zones), as well as seasonal variability (summer vs. winter).

125

126 **2. Methods**

127 *2.1. Sampling area and possible eutrophication sources within catchments*

128 This study was conducted in three mangroves along the inner parts of semi-enclosed
129 bays within a relatively close distance of ~160 km along the shoreline of the Rio de
130 Janeiro State (Southeast Brazil). Each study site is shown on Figure 1: Saco de Mamanguá
131 (M1), Guapimirim (M2) and Guaratiba (M3). For each mangrove area, two sites were
132 established considering differences in the topographic profile and dominant vegetation
133 composition: the lower and upper intertidal zones situated at fringe and basin forests,
134 respectively (Fig 1). This classification assumes that fringe forests have higher frequency
135 of tidal inundation than basin forest in the innermost zone, as described by Schaeffer-
136 Novelli et al. (2000). The lower zone here is dominated by *Avicennia schaueriana* in M1
137 and M3 and *Laguncularia racemosa* in M2, while in the upper zone of these mangroves
138 *Rhizophora mangle* is most prevalent (Table S1).

139 The climate of the region according to Köppen-Geiger classification is tropical with
140 wet summers and dry winters (Aw). The 12-year (2007-2019) monthly averages of
141 temperature and accumulated rainfall in the three study regions vary from ~21 to ~26°C
142 and ~121 to ~475mm in winter and summer, respectively (data provided by the Brazilian
143 National Institute of Meteorology, stations A602 and A619 located ~4 and ~12 km from
144 M3 and M1, respectively, and by the Brazilian Airspace Control Institute, station 83746
145 located ~24 km from M2). Monthly mean temperature and accumulated rainfall data in
146 each sampling season and region were provided by meteorological stations A602 and
147 A619 (available at <https://portal.inmet.gov.br/>) and 83746 (available at
148 <https://www.redemet.aer.mil.br/>). The micro-tidal regime of M1, M2 and M3 mangroves

149 is predominantly semidiurnal, averaging 0.75, 0.76 and 0.43m, respectively, as estimated
150 using the software PACMARE (Franco, 1997).

151 M1 is a small and well-preserved ecosystem inside an elongated cove with
152 restricted water circulation, which receives oligotrophic waters from pristine inland and
153 marine environments, located within the Cairuçu Environmental Protection Area in the
154 west portion of the Ilha Grande Bay. Also, the watershed of the M1 mangrove is very
155 small, with a low local river freshwater discharge (Brandini et al., 2019). In contrast, M2
156 site is influenced by eutrophic and mesotrophic rivers, even considering that this site is
157 located within the Guapimirim Environmental Protection Area in Guanabara Bay
158 (Carreira et al., 2001). Lastly, the M3 site is located within Sepetiba Bay, also situated at
159 a conservation area (State Biological Reserve of Guaratiba), though highly impacted due
160 to continuous domestic and industrial sewage discharges from a highly urbanized
161 catchment area (Copeland et al., 2003; Marins et al., 2004). Although the entire drainage
162 basin of Guanabara Bay is one of most urbanized in Brazil (Amador, 2013), with an
163 estimated population ~17 million compared to ~1.8 million in of Sepetiba Bay (IBGE,
164 2010), the immediate watershed of the M2 site is much less urbanized than that of M3
165 (Table S1, Fig 1).

166 The urban growth along the Rio de Janeiro coastline occurred with a low level of
167 wastewater treatment (Fistarol et al., 2015), contributing to the eutrophication of
168 Guanabara and Sepetiba Bays, where M2 and M3 mangroves are respectively located
169 (Figure 1). In constrast, the Ilha Grande Bay, including the cove where M1 is situated,
170 remains relatively pristine (Abril et al., 2022). During the sampling period, the increased
171 eutrophication in surface waters around M3, eastern portion of Sepetiba Bay, is confirmed
172 by the highest DO saturation and inorganic nutrient concentrations (Table S2), which are
173 typically associated with eutrophication in coastal waters (Marotta et al., 2012). As an

174 evidence of eutrophication sources in the study area, data from the Rio de Janeiro State
175 Environmental Institute (N = ~4 monthly samples per 3-6 contributing river of each bay
176 portion from 2017 to 2018, available at <http://www.inea.rj.gov.br>) indicate biochemical
177 oxygen demand, total phosphorus (TP) concentrations, and fecal coliform counts above
178 1.5, 2.5, and 3.5 times higher, respectively, in tributaries near M2 than those of M1. The
179 highest eutrophication in tributaries near M3 is represented by these water parameters
180 above 6, 20, and 170 times higher, respectively, compared to those of M1.

181 2.2. Study Design

182 Samples were taken from each mangrove area: most pristine (M1), intermediate
183 (M2) and most urban (M3). Sampling included measurements of soil-air CO₂ and CH₄
184 fluxes associated with OM elementary, isotopic, and molecular compositions and
185 biogenic structures. Sampling sites included the lower (L) and upper (U) intertidal zones
186 and samples were taken in winter (“W”; July-September 2017) and summer (“S”;
187 February-March 2018) at low spring tide.

188 Gas chambers (N=3-5 and 7 for CO₂ and CH₄, respectively) were randomly
189 distributed in the same day between 08:00 and 13:00 local time at both zones for each
190 mangrove. After gas sampling, the aboveground density of pneumatophores of *Avicennia*
191 *schaueriana* and crab burrows were counted. Then, surface soil samples (~2 cm) for OM
192 composition and granulometric analysis were taken from the area under each chamber where
193 CO₂ and CH₄ emissions were measured. For PCA and correlation analysis, each data of
194 biogenic structures, soil composition, and GHG flux was the median for each upper or lower
195 zone, mangrove ecosystem, as well as winter or summer (N = 12). At each upper or lower
196 intertidal zone of mangrove, samples of live leaves, stems, and roots of the dominant
197 species (*Rhizophora mangle*, *Avicennia schaueriana* or *Laguncularia racemosa*) were still
198 collected (N = 3 samples of plant material from each of 3 individuals per species) to

199 determine isotopic composition of these potential endmembers. Lastly, the topography of
200 each ecosystem was measured along transects from the lower and upper intertidal zones
201 to estimate the number of days in which soils are annually exposed or flooded by tides in
202 each sampling site.

203 2.3. Analytical Methods

204 2.3.1. Gas Emissions from the Exposed Soil-Air interface

205 a) Exposed soil-air CO₂ exchange rates

206 Short-term measurements of CO₂ concentration (ppm) were taken inside Plexiglass
207 chambers (volume of 5776 cm³ and area of 268 cm²; N = 3-5 chambers measured 3-7
208 times each one) coupled in a closed system with a previously calibrated infrared gas
209 analyzer (Licor, LI-820). To minimize disturbance of surface roots or other biogenic
210 structures, these chambers were gently inserted ~2 cm into the soil, permitting the
211 quantification of CO₂ exchange rates as a function of the linear increase gas concentration
212 inside the chambers (Rochette and Hutchinson, 2015). After closing the system and
213 reaching atmospheric levels ($\pm 10\%$), the CO₂ concentrations were measured every
214 second during a short incubation period of ~8 min to avoid bias on gas diffusivity by
215 artificial changes, especially in temperature (Kabwe et al., 2002).

216 b) Exposed soil-air CH₄ exchange rates.

217 These fluxes were measured with the static closed chamber method, derived from
218 significant linear slopes ($p < 0.05$) only with a $R^2 > 0.80$ of gas concentration versus time
219 to ensure accurate measurements. We used 3-5 discrete air samples for CH₄
220 concentrations, of which were taken at ~30-45 min intervals over 90-160 min inside
221 chambers. For detection purposes, low rates require longer incubation times. Seven
222 Plexiglass chambers (volume of 5,776cm³ and area of 268cm²) were gently inserted ~2
223 cm into soils and placed randomly around a 10-20m distance in each studied zone, season,

224 and mangrove (Hutchinson and Livingston, 2001). To reach the atmospheric equilibrium
225 before the initial time, chambers were opened for ~20-min through a gas valve (Keller et
226 al., 2000). Air samples were carefully collected after being homogenized inside each
227 chamber, using a 20-mL gas-tight syringe, and transferred to pre-evacuated 12-mL glass
228 vials (Exetainer®, Labco, UK). Then, these vials were kept at room temperature,
229 transported, and analyzed in the laboratory using a previously calibrated Agilent gas
230 chromatograph (model 7890B) equipped with flame ionization detector and nickel
231 catalytic methanizer.

232 c) Calculations of exposed soil-air gas exchange rates

233 CO₂ or CH₄ fluxes across the exposed soil-air interface (F) were calculated from
234 the linear regression of each gas concentrations inside chambers versus time (only values
235 of R²>0.8 were used), following the Eq. (1):

$$236 \quad F_{(\text{CO}_2, \text{CH}_4)} = (d(\text{CO}_2, \text{CH}_4)/dt) \cdot (P \cdot V) / (R \cdot T \cdot S)$$

237 where F is the CO₂ or CH₄ flux from exposed soils to the atmosphere (CO₂: mmol m⁻¹ h⁻¹
238 ¹; CH₄: μmol m⁻² h⁻¹); d (CO₂, CH₄/dt) is the variation in CO₂ or CH₄ concentrations as a
239 function of time (ppm s⁻¹), P is the atmospheric pressure (μatm), V is the total chamber
240 volume (m³); R is the ideal gas constant of 820528 x 10⁻⁰⁵ (atm m³ K⁻¹ mol⁻¹), T is the
241 absolute air temperature (K), and S is the surface area covered by the incubation chamber
242 (m²).

243 2.3.2. Chemical composition of Mangrove Soils and Endmembers

244 Analysis of elementary (C, N, P), isotopic (δ¹³C and δ¹⁵N), and molecular (sterols
245 and n-alkanes) composition of OM, and soil grain-size were performed in ~2 cm depth
246 surface soils inside each of the CO₂ and CH₄ flux chambers, totalizing 84 samples (14
247 samples per mangrove zone and season). Fresh leaves, stems, and roots considered as
248 endmembers representatives were carefully washed with deionized water before freeze-

249 drying. The soil samples and plant material were kept at -20°C before being freeze-dried,
250 grounded to powder, and stored in plastic containers for further analysis. Plant debris
251 were removed when present in the soil samples before freezing.

252 a) Carbon and Nitrogen content and Isotopic composition

253 Prior to OC and $\delta^{13}\text{C}$ analysis, soil samples were acidified (10% HCl) as described
254 by Wendlandt (1986) to eliminate carbonates, while soil for TN, $\delta^{15}\text{N}$ analysis and all
255 plant samples were not acidified. Both acidified and non-acidified dry-powder soil
256 samples were weighted (10-20 and 6-8 mg sealed in silver and tin capsules for soils and
257 plant tissues, respectively), and the analysis were carried out using a Flash Element
258 Analyzer coupled to a Thermo Fisher isotope ratio (Delta V IRMS) mass spectrometer.
259 Analytical precision was as follows: C=0.1%, N=0.1%, $\delta^{13}\text{C}$ =0.1‰, and $\delta^{15}\text{N}$ =0.15‰.

260 b) Phosphorus content

261 Total phosphorus (TP) was determined after calcination at 450°C for 4h, while
262 inorganic phosphorus (IP) in freeze-dried samples. IP was determined in soil samples
263 extracted with 1N-HCl after stirring for 16 hours, using the ascorbic acid/molybdenum
264 blue colometric method at 880nm (Grasshoff et al., 1999). In turn, the organic phosphorus
265 (PO) was calculated as the difference between total and inorganic P fractions. The
266 absorbance was measured using a Shimadzu UV-1601PC spectrophotometer.

267 c) Lipid biomarkers

268 The n-alkane and sterol extractions were performed in dry-powder soil samples
269 (~2g) following EPA (1996) as adapted by Wakeham and Canuel (1988). The extraction
270 was carried out using ultrasonic baths of dichloromethane (DCM), DCM: methanol (1:1),
271 and methanol (2x). After centrifuge the supernatants, complete reduction in roto-
272 evaporate and transfer to a chromatographic column, the n-alkanes were obtained eluting
273 3 ml of n-hexane, while sterols were eluted with 3.5 ml of hexane and ethyl acetate (3:1).

274 Analysis was performed in a GC-FID 7890A HP-Agilent fitted with a DB-5 capillary
275 column (30m, 0.32mm, 0.25 μ m). Derivatization was performed prior to sterols analysis.
276 The n-alkanes and sterols were identified in comparison with commercial standards,
277 Surrogates (C30D64 and androstanol) and internal standards (C24D50 and 5a-
278 cholestane), respectively. Detection limit for alkanes was 0.005 ng g⁻¹ and for sterols 0.01
279 ng g⁻¹. Due to highly variable OC (Table 2), sterol concentrations were normalized to the
280 organic carbon content (μ g gOrgC⁻¹).

281 To distinguish natural matter sources from anthropogenic impacts, the following
282 proxies were used. For sterols: (I) phytosterols (campesterol, stigmasterol and β -
283 sitosterol) were applied for higher plant or phytoplankton, (II) the sum of coprostanol and
284 epicoprostanol for sewage, and (III) cholesterol and cholestanol for plankton (Mannino
285 and Harvey, 1999). In addition, coprostanol is abundant in untreated domestic sewage,
286 while epicoprostanol is typically low in that untreated (Mudge and Lintern, 1999) and
287 increased by the cholesterol reduction during the sewage treatment, being a proxy of
288 treated sewage (McCalley et al., 1981).

289 Then, the 5 β :(5 β +5 α) ratio (coprostanol:(coprostanol+colestanol) was used as a
290 proxy of fecal contamination (Grimalt et al., 1990), while the coprostanol:cholesterol
291 ratio (Cop:Cho; Mudge and Bebianno, 1997) pointed for sewage influence versus
292 microbial degradation process and the diagenetic ratio stanol:stenol (Nishimura and
293 Koyama, 1976; McCaffrey, 1990) indicated the proportion between fresher phytosterols
294 and their degraded forms (campestanol, stigmastanol and β -sitostanol). For n-alkanes we
295 used the indexes: (1) Terrestrial:Aquatic Ratio (TAR; Bourbonniere and Meyers, 1996)
296 assumed here as (C27+C29+C31):(C15+C17+C19) ratio, in which values > 1.0 indicate
297 the predominance of compounds from terrestrial or mangrove higher plants rather than
298 algae; (2) the input of total n-alkanes (Σ C14-40); (3) Carbon Preference Index (CPI; Clark

299 Jr. and Blumer, 1967) represented here as $\sum(C_{\text{odd}}(15-39)):\sum(C_{\text{even}}(14-40))$, in which CPI <
300 1 indicates anthropogenic inputs, while CPI > 1.0 indicates biogenic sources; (4) Low
301 Molecular Weight:High Molecular Weight Ratio (LMW:HMW, Wang et al., 2006)
302 represented here as $\sum(C_{14-23}):\sum(C_{24-40})$ which was used to attribute aquatic over
303 terrestrial input; and (5) Pristane:Phytane ratio (Pr:Ph, Steinhauer and Boehm 1992) was
304 used as a proxy for redox conditions.

305 2.3.3. Grain Size

306 This procedure was carried out in dry soil samples free of carbonates and organic
307 compounds. Carbonates were removed by adding 20mL of HCl 1M for 48 hours followed
308 by washing and centrifugation with deionized water (5min at 3500rpm), while OM was
309 removed by loss on ignition at 400°C overnight (Schumacher, 2002). In addition, the
310 samples were disaggregated with 20mL of 4% sodium hexametaphosphate dispersant and
311 stirred on an orbital shaker for 24 hours, and subsequently sieved with a mesh diameter
312 of 420µm before laser diffraction analysis using a CILAS 1064 (0.04-500µm range). The
313 grain-size distribution was classified according to the Wentworth scale adopted in the
314 GRADISTAT routine, assuming the statistical parameters of Folk and Ward (1957).

315 2.3.4. Topography and Annual Period of Soil Exposure in Mangroves

316 Topographic profiles of mangrove soils from the lower to the upper intertidal zone
317 were measured with a Leica TS06 Total Station at low spring tide (e.g., Moser et al.,
318 2007; Wheaton et al., 2009). The vertical and horizontal distances of a transversal profile
319 were converted into altimetry using the sea level at the lower intertidal zone (*i.e.*, initial
320 seaward edge) with a GPS receiver (planimetric accuracy of ±3m). Then, the transect was
321 adjusted using the azimuth angle (magnetic north) at specific measured coordinates (Lam
322 and Chen, 2001), considering the mean sea-level which was established by the Brazilian
323 Navy as the altimetric reference. At the mangroves M1 and M3 sites, topographic profiles

324 were measured from the lower to the upper intertidal zones. In turn, two topographic
325 profiles were surveyed at the M2 site due to logistical constraints, associated with highly
326 unstable muddy substrate along single transects.

327 Additionally, between January 2017 and December 2018, we modeled 10-min
328 interval tidal heights based on the harmonic method using the PACMARE software
329 (Franco, 1997), which allows to calculate the annual mangrove soil subaerial exposure
330 and flooding in each zone by the difference between the predicted tide height and the
331 measured topography (Verhoeven et al., 2014). The tide gauge data derived from tidal
332 height measurements and harmonic parameters were established by the Brazilian Navy
333 (<https://www.marinha.mil.br/chm/tabuas-de-mare>).

334 2.4. Statistical analysis

335 The data in this study did not show significant homoscedasticity (Bartlett, $p > 0.05$)
336 and normal distribution (Kolmogorov-Smirnov, $p < 0.05$) even after different
337 transformations (Zar, 1996). For this, the Mann-Whitney test (significance level $p < 0.05$)
338 was used to compare two categories (e.g., upper and lower intertidal zones or summer
339 and winter), while the Kruskal-Wallis test (significance level $p < 0.05$) three or more (e.g.,
340 M1, M2, and M3 or intertidal zones in each mangrove and/or season). As post-test,
341 differences were assessed with False Discovery Rate (FDR; significance level $p < 0.05$),
342 considering p-values from Mann-Whitney tests and the two-stage step-up method
343 described by Benjamini et al. (2006). FDR is also more appropriate for environmental
344 data that involved many multiple comparisons and small samples (García, 2004).

345 In addition, spearman correlation matrix (significance level $p < 0.05$) and principal
346 component analysis (PCA) were applied to find out the major controls on CO₂ and CH₄
347 emissions from mangrove soils (N = 12 including 2 intertidal zones, 2 seasons and 3
348 mangroves for each variable). The PCA was used to assess the magnitude and direction of

349 correlations between both dependent (soil-air CO₂ and CH₄ fluxes) and other independent
350 variables. All statistical tests were performed using GraphPad Prism (version 7.0), except
351 the PCA in Statistica software (version 10).

352

353 **3. Results**

354 The three studied mangroves showed significant heterogeneity in soil OM
355 composition and urban growth along watersheds (Table 1), indicating a higher spatial
356 (among mangroves and intertidal zones) than seasonal (summer vs. winter) variability as
357 detailed below.

358

359 *3.1. Elementary and Isotopic Composition of Soils*

360 The surface soil of the studied mangroves was predominantly composed of silt (71-
361 93%) and clay (4-17%; Table 1). Comparing the three systems, M1 showed ~2 times
362 higher OC concentration than M2 and M3 (FDR, p<0.05; Fig 2). TN, OP, OC:TN and
363 OC:TP ratio were ~2-4 times higher in M1 than in M2 and M3 (FDR, p<0.05; Fig 2;
364 Table 1). δ¹⁵N was ~ 5 times higher in M3 than in M1 and δ¹³C was ~20% higher in M3
365 than in M1 and M2 (FDR, p<0.05; Fig 2). In addition to being the highest in median, the
366 δ¹³C data showed the highest variation in M3 (25/75% interquartile) when compared to
367 M1 and M2 (from -28 to -11‰, from -31 to -24‰, and from -32 to -26‰, respectively;
368 FDR, p<0.05; Fig 2; Table 1). Median IP concentration was similar between M2 and M3,
369 being ~70% higher than M1 (FDR, p<0.05; Fig 2). M2 showed the highest median
370 (25/75% inter-quartil) values of TP concentration, since M1 = 1010 (908/1180), M2=
371 1202 (1054/1338), and M3= 1072 (1001/1150) µg g⁻¹ (FDR p<0.05; Fig 2). Only in M1
372 site, the OP was the predominant P form (Fig 2).

373 In relation to intertidal spatial variability of element composition, OC, TN, TP, $\delta^{13}\text{C}$,
374 $\delta^{15}\text{N}$, C:N, C:P, and OP were from ~10 to 40% higher in the upper than in the lower zone,
375 except IP that decreased ~10% (Mann-Whitney, significance level $p < 0.05$; Fig S1). The
376 seasonal variability between winter and summer was not significantly different for values
377 of OC, TN, TP, $\delta^{15}\text{N}$, C:N, and C:P ratio (Mann-Whitney, $p > 0.05$; Fig S2). However,
378 $\delta^{13}\text{C}$ and IP were significantly higher and OP lower in winter compared to summer
379 (Mann-Whitney, $p < 0.05$; Fig S2). Moreover, the highest soil OC concentrations were
380 found in the upper intertidal zone of M1 in both summer and winter seasons, contrasting
381 with the lowest values in the lower zone of M3 in winter (FDR, $p < 0.05$; Fig S3).

382 In the studied soils, 10 sterol compounds were identified (Table S3 and Table S4),
383 and the total concentrations ranged from not detectable to $57.4 \mu\text{g g}^{-1}$. β -sitosterol and
384 stigmasterol showed a greater participation in the sterol pool in M1, and coprostanol (5 β -
385 cholestan-3 β -ol) in M3. Highest concentrations of epicoprostanol (5 β -cholestan-3 α -ol)
386 were found in M3, and often below the detection limit in M1 and M2. In contrast, the
387 intermediate compounds of the diagenetic degradation of sterols, *i.e.* cholesterol (cholest-
388 5-in-3 β -ol) and cholestanol (5 α -cholestan-3 β -ol), varied among mangrove sites. These
389 results indicate the highest cholesterol values in M2, variability of cholestanol in M3, and
390 diagenetic ratio (stanol:sterol) in M3 (Table S3). Finally, a greater contribution of higher
391 plants and algae sources in M1 and M2 (~60% to 79% of campesterol, stigmasterol, and
392 β -sitosterol) contrasted with the highest influence of sewage in M3 (~3% to 11% of
393 coprostanol and epicoprostanol; Fig. 4).

394 The total n-alkanes ($\sum\text{C}_{\text{N}14-40}$) ranged from 186.3 in M1 to $4,021.1 \mu\text{g gOrgC}^{-1}$ in
395 M2, with an overall predominance of odd long chains ($\text{C}_{\text{N}25-29}$). The dominant compounds
396 were $\text{C}_{\text{N}25}$ in M1, while $\text{C}_{\text{N}25}$, $\text{C}_{\text{N}29}$ and $\text{C}_{\text{N}31}$ in M2 and M3 being $\text{C}_{\text{N}21}$ more abundant in
397 M3 (Table S5). In turn, all studied zones showed LMW:HMW ratio lower than 1, with

398 maximum and minimum values of CPI in M1 and M3, respectively. The TAR values in
399 the upper zone of M3 were from 2 to 10 times lower than in other mangroves. Although
400 maximum values of pristane and phytane were ~3 and 5 times higher in M3, the Pr:Ph
401 ratio was less variable and ranged from 0.2 to 0.6 among mangroves (Table S3).

402

403 3.2. Isotopic composition of mangrove plant tissues

404 No significant difference in median of $\delta^{13}\text{C}$ values from leaves; stems and roots
405 were observed among M1, M2, and M3 in upper and lower zones (Kruskal-Wallis,
406 $p>0.05$; Table 2; Fig. S4). However, $\delta^{15}\text{N}$ from mangroves tree stem and roots were up to
407 72% higher in the lower intertidal zone of the most impacted mangrove (M3) than in all
408 sites of the most pristine ecosystem (M1) (FDR, $p<0.05$; Figs. 3 and S4). Similarly, $\delta^{15}\text{N}$
409 from mangroves tree leaves was up to 70% higher in the upper zone of M3 than in all
410 sites of M1 (FDR, $p<0.05$; Figs. 3 and S4).

411

412 3.3. GHG efflux from exposed soils to the atmosphere

413 Soil-air CO_2 efflux varied from 0.7 to 86.7 $\text{mmol m}^{-2} \text{h}^{-1}$ (Table 1), with higher
414 values in the mangrove with the greatest urban growth along the watershed (M3), which
415 were from near 60 and 30% higher on average than M1 and M2, respectively (FDR,
416 $p<0.05$; Fig 5). Moreover, no significant spatial differences within intertidal zones (upper
417 vs lower) and seasonal difference (summer vs winter) in CO_2 fluxes were observed
418 (Mann-Whitney, $p>0.05$; Fig 5).

419 CH_4 emissions were relatively low but showed a single peak of 1.69 of mmol m^{-2}
420 h^{-1} in the lower intertidal zone of M2 in summer (Table 1). Despite no significant
421 difference among the mangroves M1, M2, and M3 (Kruskall-Wallis, $p>0.05$), soil-air

422 CH4 fluxes were ~70% greater in lower compared to upper intertidal zones and summer
423 to winter seasons (FDR, $p < 0.05$; Fig. 5).

424

425 3.4. Topography, annual subaerial exposure time, and biological structures along
426 mangrove soils

427 All topographic profiles here indicated a very subtle morphological change, with
428 the soil elevation varying from 0.81 to 1.19, 1.12 to 1.18, and 0.88 to 1.32 m in relation
429 to the Mean Sea Level (MSL) between the lower and upper zones of M1, M2 and M3,
430 respectively (Fig. S6). Our estimates calculated from topographic profiles and tide gauge
431 data indicate that soils are exposed during 201 versus 333, 304 versus 320, and 303 versus
432 360 days annually at the lower and upper mangrove zones in M1, M2 and M3,
433 respectively. As a result, the annual subaerial exposure time was ~66, 5, and 19% higher
434 in the upper than lower zones of M1, M2 and M3, respectively. Regarding biological
435 structures, crab burrow density showed an increasing trend from M1 and M2 to M3 soils,
436 in median, 0 and 40 to 150 m^{-2} , respectively, while pneumatopheres did not follow any
437 pattern, reaching 370, 70, and 240 m^{-2} , respectively.

438

439 3.5. Relationships between soil variables

440 Overall, OC was positively related to TN and OP, and negatively related to $\delta^{15}N$,
441 $\delta^{13}C$ and IP ($r_s = 0.90, 0.94, -0.87, -0.59$ and -0.88 , respectively, $p < 0.05$; Table S6 and
442 Fig. 3). TN was positively related to OP, and negatively related to $\delta^{15}N$, $\delta^{13}C$, IP and crab
443 burrow ($r_s = 0.93, -0.95, -0.60, -0.87$ and -0.69 , respectively, $p < 0.05$; Table S6 and Fig.
444 3). $\delta^{15}N$ was positively related to IP and crab burrow, and negatively related to OP ($r_s =$
445 $0.94, 0.73$, and -0.94 , respectively, $p < 0.05$; Table S6 and Fig. 3). $\delta^{13}C$ was positively
446 related to crab burrow, and negatively related to OP ($r_s = 0.82$ and -0.62 , respectively,

447 $p < 0.05$; Table S6 and Fig. 3). IP was positively related to crab burrow, and negatively
448 related to OP, while OP was negatively related to crab burrow ($r_s = 0.65, -0.91$ and -0.70 ,
449 respectively, $p < 0.05$; Table S6 and Fig. 3).

450 In turn, soil-air CO_2 fluxes were positively correlated to Σn -alkanes, $\delta^{15}\text{N}$, $\delta^{13}\text{C}$, IP
451 and crab burrow ($r_s = 0.74, 0.61, 0.70$ and -0.65 , respectively, $p < 0.05$; Table S6 and Fig.
452 3), while CH_4 fluxes was positively related to Σn -alkanes and sandy ($r_s = 0.60$ and 0.88 ,
453 respectively, $p < 0.05$; Table S6 and Fig. 3). The sewage (coprostanol+epicoprostanol) was
454 positively correlated with $5\beta:(5\beta+5\alpha)$ ratio (coprostanol:(coprostanol+cholestanol), $\delta^{15}\text{N}$,
455 and IP as well as negatively with TN ($r_s = 0.82, 0.64, 0.60$ and -0.64 , respectively, $p < 0.05$;
456 Table S6 and Fig. 3). Finally, diagenetic ratio was positively correlated to crab burrow
457 ($r_s = 0.74$, $p < 0.05$; Table S6 and Fig. 3).

458 Considering data from all mangrove soils, CO_2 emissions were positively correlated
459 with the aboveground density of crab burrows ($r_s = 0.65$; $p < 0.05$, Table S7), but no
460 significant relationships were observed with that of pneumatophore ($p > 0.05$). Moreover,
461 CH_4 emissions were not significantly related with aboveground density of
462 pneumatophores and crab burrow.

463 The PCA showed that Factor 1 and Factor 2 together explained $\sim 68\%$ of the total
464 data variance. Factor 1 (CO_2 fluxes) explained $\sim 51\%$ of the total variance with positive
465 loadings for $\delta^{15}\text{N}$, IP, crab burrows, $\delta^{13}\text{C}$, sewage, Σn -alkanes, diagenetic ratio,
466 $5\beta:(5\beta+5\alpha)$, pneumatophores, OP and CH_4 fluxes versus negative loadings for TN, sandy
467 and OC. Factor 2 (CH_4 fluxes) explained $\sim 17\%$ of total variance with negative loading
468 for diagenetic ratio, $\delta^{13}\text{C}$, crab burrows, sewage, $5\beta:(5\beta+5\alpha)$, OC, TN, $\delta^{15}\text{N}$ and CO_2
469 fluxes versus positive loadings for Σn -alkanes, pneumatophores, OP, IP, sandy, and CH_4
470 fluxes (Fig 6, Table S8). Accordingly, the M1 mangrove was grouped at a negative
471 direction of Factor 1 similarly to OP, OC, and TN. The M3 mangrove was grouped at a

472 right direction of Factor 1 and positive direction of Factor 2 such as sewage (coprostanol
473 and epicoprostanol), $5\beta:(5\beta+5\alpha)$ ratio (colestanol and coprostanol), diagenetic ratio
474 (stanol:sterol), IP, $\delta^{15}\text{N}$, and $\delta^{13}\text{C}$. The M2 mangrove displayed an intermediate position
475 with an exception in the lower zone in summer, which difference was likely driven by
476 CH_4 emissions and the percentage of sand in surface soils (Fig. 6; Table S8).

477 **4. Discussion**

478 4.1. Anthropogenic variations in sources, composition, and diagenesis of OM in
479 mangrove soils

480 The trend of eutrophication with urban growth along the watersheds here was
481 apparent by substantial differences in mangrove soil IP and OM. Mainly caused by
482 nutrient inputs and defined as an increase in the rate of supply of OM to an ecosystem
483 (Nixon, 1995), eutrophication has widely been indicated by proxies related to increased
484 algal biomass in benthic coastal marine environments (Dell'Anno et al., 2002; Lemley et
485 al., 2015). As found from M1 to M2 and M3, increased IP content (Wolters et al., 2016;
486 Barcellos et al., 2019), $\delta^{15}\text{N}$ and $\delta^{13}\text{C}$ values (Sanders et al., 2014), and OM lability
487 biomarkers (Kumar et al., 2019) have been largely attributed to increased algal and
488 sewage inputs associated with more intense diagenesis of OM.

489 Previous evidence based on pelagic chlorophyll-*a* satellite data confirms the
490 presence of dense algal blooms as a proxy of water eutrophication in Sepetiba Bay (site
491 M3) and Guanabara Bay (site M2), but not in Ilha Grande Bay where the M1 mangrove
492 is located (Abril et al., 2022). Hence, the present study gives a more detailed assessment
493 of the contribution of natural (*i.e.*, mangrove trees vs algae) and anthropogenic (*i.e.*,
494 sewage) sources of OM, as well as identifying recent diagenesis processes through the
495 proportion of fresh compounds and their degraded forms (stanol/stenol) in mangrove soils
496 with urban growth along their watersheds.

497 The bulk composition of soil OM was consistent with an additional dual source of
498 anthropogenic OM that mixes with material from mangrove trees in the study sites
499 impacted by urban discharges. The increasing $\delta^{15}\text{N}$ trend between mangrove soils (M1 <
500 M2 < M3) was consistent with what was found in the plant material, specifically
501 significantly higher values in tree leaves from M3 compared to M1. The $\delta^{15}\text{N}$ proxy has
502 shown to be a robust indicator of eutrophication as it traces N cycling from untreated
503 sewage to mangrove areas (Gritcan et al., 2016). The range of these soil variables in M3
504 have often been associated with the influence of algal blooms in coastal aquatic sediments
505 under nutrient-enriched conditions (Zhang et al., 2015), and was also observed in urban
506 mangroves receiving untreated wastewaters (Machiwa, 2000). Accordingly, only M3
507 soils presented both $\delta^{15}\text{N}$ and $\delta^{13}\text{C}$ values within the previously observed range of sewage
508 (Barros et al., 2010). In contrast, more negative $\delta^{13}\text{C}$ and higher C:N ratio in soils of the
509 upper intertidal zone of the most pristine mangrove (M1) suggests greater dominance of
510 OM from woody plants (Meyers, 1994; Lamb et al., 2006). This confirms the potential
511 role of tree biomass to fuel the net heterotrophy that was previously reported in its
512 surrounding bay waters (Brandini et al., 2019).

513 In addition, molecular analysis supported potential differences in soil OM quality
514 and source with increasing the urban activity along the watershed. As many sterols may
515 be from natural biomass, the total sterol concentrations in the most pristine mangrove
516 (M1) were much higher than previously reported in estuarine sediments undergone
517 sewage contamination (dos Reis Souza et al., 2020). For instance, the contributions of
518 stigmasterol and β -sitosterol were predominant in pristine M1 soil, consistent with
519 natural source from higher plants (mangrove trees leaves and roots; Nes, 1974). In turn,
520 the coprostanol concentration below $0.5 \mu\text{g g}^{-1}$ in sediments of all sampling sites did not
521 indicate sewage contamination (González-Oreja and Saiz-Salinas, 1998; Carreira et al.,

522 2009). Even the mangrove soils with greater urban pressure along the watershed (M3)
523 showed coprostanol concentrations similar to estuarine sediments not impacted (Muniz
524 et al., 2006) or moderately impacted (Carreira et al., 2009) by sewage, as well as lower
525 than those impacted (dos Reis Souza et al., 2020).

526 Conversely, sterol biomarker distributions indicate a higher contamination of
527 mangrove soils with sewage OM in M3 than M2, compared to non-detectable levels in
528 the most pristine M1. The highest epicoprostanol concentrations found in the M3 soils
529 are typical of sewage contamination, as reported in many coastal bottom sediments in
530 South America (Mudge and Seguel, 1999), Australia (Pratt et al., 2008), and Asia (Isobe
531 et al., 2002; Jeng, 2006). The predominance of epicoprostanol in relation to coprostanol
532 in M2 and M3 soils, independent of sampling site or season, also indicates intense
533 biological degradation likely fueled by OM derived from sewage (Santos et al., 2008).
534 Accordingly, higher values of the sum of epicoprostanol and coprostanol in M3, as a
535 proxy of sewage (McCalley et al., 1981), explains the positive relationships in the
536 correlation matrix and PCA analysis to other indicators of eutrophication in mangrove
537 soils here, including $5\beta:(5\beta + 5\alpha)$, IP, and $\delta^{15}\text{N}$. The sewage contamination in M3 was
538 further indicated by the coprostanol:cholesterol ratios (chop:cho) higher than 1.0 (Mudge
539 and Bebianno, 1997) and coprostanol:cholestanol $5\beta:(5\beta + 5\alpha)$ higher than 0.5 (Santos et
540 al., 2008), as reported in tropical coastal aquatic sediments receiving high sewage
541 discharges (Frena et al., 2016; dos Reis Souza et al., 2020). This limit of $5\beta:(5\beta + 5\alpha)$
542 ratio of 0.5 for sewage pollution is assumed lower at tropical than non-tropical latitudes
543 due to higher microbial activity with increasing temperature (Araujo et al., 2011).

544 Concerning n-alkanes, the CPI index higher than 1.0 in all studied mangrove soils,
545 confirmed a large contribution of biogenic sources rather than petrogenic sources (Kumar
546 et al., 2019). In particular, LMW:HMW ratio lower than 1.0 and TAR values above 1 at

547 all sampling sites confirm a dominance of high molecular OM weight from mangrove
548 trees (Gearing et al., 1976; Wang et al., 2006), as previously reported in mangroves
549 globally (Alongi et al., 1999; Kristensen et al., 2008a). Another proxy of OM sources
550 here was the overall predominance of long and odd chain of n-alkanes (C_{n25-31}), still
551 indicating a large contribution from mangrove tree leaves (Eglinton et al., 1962;
552 Nishigima et al., 2001). In addition, exposed soil conditions might have favored oxidative
553 decarboxylation of fatty acids, also contributing to the predominance of odd-numbered
554 hydrocarbon chain (Guoying et al., 1980), except for the lower zone M2 during summer
555 and the lower intertidal zone of M3 during winter, likely due to petrogenic sources and
556 biological remineralization of OM (Thomazelli, 2010). Petrogenic sources of OM are
557 reasonable in M2 and M3 due to the high influence of industrial plants and ship traffic in
558 Guanabara Bay (Fistarol et al., 2015) and Sepetiba Bay (Molisani et al., 2006),
559 respectively.

560 The CPI index still above but closer to 1.0 in M3 soils typically indicate greater
561 abundance of low molecular weight n-alkanes than M1 and M2, which may be derived
562 from phytoplankton, bacteria, fungi and/or contamination by petroleum products (Boehm
563 and Requejo, 1986; Wang et al., 2003). In these mangrove soils of which was most
564 influenced by urban watershed, a greater abundance of short-chain n-alkanes C_{n15-21}
565 indicates an additional contribution of phytoplankton and bacteria (Clark Jr. and Blumer,
566 1967; Canuel et al., 1997), a common effect of intense metabolic processes under coastal
567 eutrophication (Breitburg et al., 2018). Indeed, the lowest values of TAR observed in the
568 upper zone of M3 confirmed a lower relative contribution of vascular plants in the
569 mangrove to the n-alkane pool in the soil at this impacted site (Carreira et al., 2009). The
570 highly reducing anaerobic conditions of organic mangrove soils were still supported by
571 the values of Pr:Ph ratio below 1.0 in all sampling sites. Both n-alkane and sterols
572 biomarkers thus converge to the idea of a net gradient of increasing contributions not only

573 of sewage derived OM but also algal (phytoplankton and/or microphytobenthos) derived
574 OM from M1 to M2 and M3.

575 Besides differences in OM sources, the organic C and P contents were significantly
576 higher in the most pristine mangrove M1 (particularly along the upper intertidal zone)
577 than in the more impacted mangroves M2 and M3. This trend contributes to the negative
578 relationships between OC with IP, $\delta^{15}\text{N}$ and $\delta^{13}\text{C}$ found in the correlation matrix and PCA
579 analysis. A likely explanation is that local rivers around M2 (Faria and Sanchez, 2001)
580 and M3 (Borges and Nittrouer, 2016) promote a higher discharge of suspended matter
581 (i.e., OM dilution by inorganic sediment loads). This greater discharge of suspended
582 matter is related to deforestation and river straightening along the urban watersheds of
583 M2 and M3. In contrast, the more pristine mangrove (M1) is associated with a lower river
584 flow and more enclosed geomorphology of which could have contributed to the higher
585 OC content at this mangrove.

586 Furthermore, previous experimental evidence has indicated that total C and N
587 stocks may decrease from more pristine to more impacted mangrove soils, as an effect of
588 increased OM remineralization under anthropogenic-derived nutrient enrichment from
589 untreated effluents (Palacios et al., 2021). The higher diagenetic ratio in the most
590 eutrophicated M3 soils is a typical proxy of intense biological degradation of OM (Frena
591 et al., 2016), especially when stanol forms are dominant (i.e., this diagenetic ratio > 1.0 ;
592 Nishimura and Koyama, 1977). In contrast, M1 and M2 soils showed lower than 0.5
593 diagenetic ratios. The phytosterol:OC, C:N and C:P ratios were also higher in M1 and M2
594 soils compared to M3, particularly in the upper intertidal zone soil of M1, indicating that
595 OM is more preserved at these sites.

596 Considering the variability between lower and upper intertidal zones, a higher
597 influence of marine OM was still observed in mangrove soils of the lower than upper

598 zone, a potentially important effect of the increased inputs of marine compounds from
599 higher tidal inundation frequency near the sea (Sanders et al., 2010b). Trees retain woody
600 biomass within their roots, also increasing the nutrient uptake and light attenuation, which
601 could explain the reduced algal composition in soils of the upper intertidal zone (Sanders
602 et al., 2010a, 2014). In addition, more subaerial oxygenation throughout the year could
603 enhance phosphate adsorption by iron oxyhydroxides (FeOOH-PO₄; (Sherman et al.,
604 1998) or the uptake from more dense mangrove vegetation (Servais et al., 2019) could
605 have contributed to decrease IP content in the upper as compared to the lower intertidal
606 zones of the studied mangroves.

607 4.2 Response of GHG fluxes to anthropogenic perturbations and other parameters

608 Overall, our nutrient (N and P), isotopic ($\delta^{13}\text{C}$ and $\delta^{15}\text{N}$), and molecular (sterols and
609 n-alkanes) analysis in the three studied sites allowed us to assess potential controls of OM
610 composition on soil-air CO₂ and CH₄ fluxes. We observed a substantial increase in CO₂
611 emissions among mangrove soils from more pristine to more urban areas, contrasting with
612 similarly low CH₄ fluxes, except a single except peak in the site with more river influence
613 (lower zone of M2). This partially confirm previous evidence on enhanced production of
614 GHGs due to increased biological remineralization of OM with organic pollution in
615 mangrove soils (Sotomayor et al., 1994; Yang et al., 2018). Moreover, the observed
616 positive relationship in the correlation matrix between the abundance of n-alkanes and
617 soil-air CO₂ and CH₄ fluxes suggests the role of organic substrates to enhance biological
618 activity that releases these gases (Guoying et al., 1980).

619 Substantially higher CO₂ emissions from exposed soils, mainly in the most
620 eutrophicated soil (M3), is comparable to highly sewage-impacted mangroves around the
621 world (*e.g.*, Chen et al., 2010; Jacotot et al., 2018). This indicates a potential mechanistic
622 link between the intense urban sprawl (*i.e.*, associated with untreated wastewaters) and

623 increased soil OM remineralization, which have been reported in mangrove soils
624 undergone eutrophication from urban sources (Chen et al., 2010; Martin et al., 2020).
625 Higher soil-air CO₂ fluxes with urban growth along the watersheds here confirm the
626 increased remineralization fueled by higher availability of labile OM from sewage and
627 algae, typically associated with eutrophication (Breitburg et al., 2018). As a result, the
628 highest proportion of fecal sterols and degraded phytosterols associated with less OC
629 content in M3 also corroborates the role of the more labile OM derived from
630 phytoplankton and sewage to produce CO₂ (Drake et al., 2020). Besides the amount of
631 organic substrates to biological remineralization, another explanation for the increased
632 CO₂ release in ecosystems is the priming effect, in which the inputs of labile OM with
633 high energy and nutrients contents lead to additional metabolic breakdown of the more
634 recalcitrant OM pool, contributing to enhanced emissions of this gas (Guenet et al., 2010).
635 Previous studies have reported that heterotrophic responses to more labile OM inputs are
636 potentially a threat to coastal eutrophication and blue carbon preservation (Alongi et al.,
637 1999; Kristensen et al., 2008a). Indeed, experimental research over past decade has
638 indicated increased OM remineralization with CO₂ production by priming effect in a wide
639 variety of coastal marine sediments, such as from estuaries (Gontikaki et al., 2015),
640 seagrass meadows (Liu et al., 2020), as well as other subtidal and intertidal areas (Van
641 Nugteren et al., 2009).

642 In turn, the CH₄ emissions here was within the range often found in pristine to
643 impacted mangroves around the world (Kreuzwieser et al., 2003; Kristensen et al., 2008b;
644 Konnerup et al., 2014). The median CH₄ efflux ~70% is significantly higher and was
645 associated to an increase in temperature of ~6°C and rainfall of ~900% in summer in
646 relation to winter over 30 days before sampling (average between meteorological stations
647 near M1, M2, and M3, as described in the Methods section). This result could be
648 explained by enhanced methanogenesis under warmer conditions (Vizza et al., 2017;

649 Jacotot et al., 2019) and higher freshwater inputs (Rosentreter et al., 2018). Accordingly,
650 the lower intertidal zone closest to the river mouth into the sea (i.e., more susceptible to
651 episodic reductions in salinity) might have contributed to the single peak of CH₄
652 outgassing in the M2 lower intertidal zone in summer, suggesting that transient increases
653 in methanogenesis could be influenced by nutrient enrichment.

654 In general, CH₄ emissions from exposed soils to the atmosphere were three orders of
655 magnitude lower than those of CO₂, confirming earlier findings in mangroves in Southern
656 China (Chen et al., 2010, 2011) and Brazil (Nóbrega et al., 2016). This result is a potential
657 consequence of previous estimates indicating that methanogenesis rates represent only 1-
658 10% of the total carbon mineralization in mangrove soils (Alongi, 2009). Although the
659 positive relationship between eutrophication and CH₄ emissions is commonly reported in
660 coastal aquatic ecosystems (Purvaja and Ramesh, 2001; Konnerup et al., 2014), we found
661 no significant changes along the urban gradient. Methanogenesis is often high in
662 freshwater sediments, while in marine environments the competition with more energetic
663 redox reactions by oxygen (*i.e.*, aerobic respiration) and other electron acceptors present
664 in seawaters (*i.e.*, mainly sulphate; King, 1984) or even the CH₄ oxidation under high
665 oxygenation of exposed soils (Das et al., 2018) is high in coastal wetlands. Oxidation
666 (Kristensen et al., 2008a) and more efficient OM remineralization pathways (Nóbrega et
667 al., 2016) could be especially intense in exposed mangrove soils and explain non-
668 significant changes of CH₄ emissions with eutrophication as found here.

669 Regarding the biogenic structures, pneumatophore and crab burrow densities have
670 presented differing relationships with GHG emissions from the exposed mangrove soils
671 studied. The weak explanation in the PCA and non-significant correlation between
672 pneumatophore density and CO₂ efflux contrasts with previous studies, which have
673 indicated a significant role in the release this gas directly to the atmosphere (Kristensen

674 and Alongi, 2006; Kristensen et al., 2008a; Ouyang et al., 2016). On the other hand, the
675 positive relationship between crab burrow density and CO₂ emissions found in PCA and
676 correlation analyses has been confirmed in a wide variety of mangrove soils (Ouyang et
677 al., 2016; Tomotsune et al., 2020). This result has been attributed to increased aerobic
678 CO₂ production from microbial processes within mangrove soils under more oxygenated
679 conditions driven by crab bioturbation (Kristensen and Alongi, 2006). Here, the
680 increasing trend of crab burrow density in M3 soils contributed to the significant positive
681 relationships of these faunal structures not only with CO₂ emissions, but also with
682 parameters affected by eutrophication (*i.e.*, IP, $\delta^{15}\text{N}$, $\delta^{13}\text{C}$, and diagenetic ratio). Instead,
683 pneumatophere density did not increase in the most impacted mangrove, and as a result
684 significant relationships were not found. In turn, lower CH₄ emissions as compared to
685 CO₂ might have contributed to the weak explanation in the PCA analysis and non-
686 significant correlation with both biogenic structures.

687 In addition to the influence of anthropogenic and natural inputs of OM, the subaerial
688 exposure time is a critical component to determine GHG emissions in mangrove soils
689 during the ebbing period, due to expected variations in metabolic rates with flooding
690 (Alongi et al., 2020). As performed here, previous studies have reported hourly or daily
691 C gas fluxes exclusively under exposed conditions (*e.g.*, Kabwe et al., 2002; Kristensen
692 et al., 2008b; Chen et al., 2010; Nóbrega et al., 2016). On an annual basis, estimates of
693 GHG emissions have assumed that mangrove soils are exposed 50% of the time
694 (Rosentreter et al., 2018). However, this assumption was not valid for any sampling site
695 of M2 or the upper intertidal zones of M1 and M3 (both showing >90 % exposed time),
696 suggesting that more careful consideration on exposure time is needed.

697 Variable subaerial exposure time along the intertidal zone, attributed to local
698 topography and tidal regime, has been rarely considered in estimates of GHG fluxes in

699 mangroves (*e.g.*, Sotomayor et al., 1994). By upscaling the medians of hourly soil-air flux
700 rates only to the annual exposed period, encompassing lower and upper intertidal zones
701 during summer and winter seasons, we can provide first-order estimates of CO₂ versus
702 CH₄ efflux ~507 versus 0.7, 965 versus 0.7, and 1512 versus 0.8 g C m⁻² yr⁻¹ in M1, M2,
703 and M3, respectively. Accordingly, the longer exposure time over the year contributed to
704 still higher GHG emissions from non-flooded soils in the most impacted mangrove (M3)
705 compared to that most pristine (M1).

706

707 **Conclusions**

708 This multi-proxy analysis of OM elementary, isotopic, and molecular compositions
709 confirms increased eutrophication in mangrove soils are associated with greater urban
710 growth along watersheds. Furthermore, the present results indicate a potential link
711 between untreated wastewater inputs and increased CO₂ emissions to the atmosphere,
712 suggesting a potential loss of blue C from algae or plants from mangrove soils. Hence,
713 our hypothesis was confirmed for CO₂, as indicated by an increased presence of sewage
714 (*e.g.*, higher δ¹⁵N, and P, degraded sterols, and coprostanol) and phytoplankton (*e.g.*,
715 lower δ¹³C and C:N), which were associated with higher efflux of this gas, independent
716 of intertidal zone or season. However, CH₄ emissions did not increase in mangrove soils
717 surrounded by more urban areas. Soil-air fluxes of this gas varied significantly between
718 intertidal zones and seasons, likely due to the overall low rates associated with high peaks,
719 which were in turn influenced by a greater contribution of labile algal OM seaward and
720 increased freshwater discharges during the rainy summer. Indeed, annual estimates of
721 GHG emissions from exposed mangrove soils after integrating variable exposure times
722 over the tidal regime here may be more realistic, compared to the common assumption
723 that any sampling site in the intertidal zone is flooded for half of the year. Despite this

724 high complexity of natural and anthropogenic drivers of CO₂ and CH₄ efflux, the greater
725 contribution of OM from algal and sewage sources with coastal eutrophication was
726 generally associated with increased global warming potentials (i.e., carbon emissions to
727 the atmosphere). Our findings support that the control of water pollution and mangrove
728 conservation efforts are critical to climate mitigation for a more sustainable future.

729

730 **Acknowledgment**

731 This work was supported by the Brazilian National Council for Scientific and
732 Technological Development (CNPq no. 314995/2020-0), the Carlos Chagas Filho
733 Foundation for Research Support of the State of Rio de Janeiro (FAPERJ no. E–
734 26/203.304/2017), the Coordination for the Improvement of Higher Education Personnel
735 (CAPES, Finance Code 001 and the internalization program PRINTCAPES/UFF
736 FEEDBACKS no. 99997.310301/2018-00), the French CNRS-INSU LEFE program and
737 the France-Brazil International Research Project VELITROP (Vulnerability of Tropical
738 Littoral Ecosystem facing eutrophication) funded by the CNRS-INEE, France. HM was
739 the recipient of CNPq Research Productivity and FAPERJ Rio de Janeiro State Scientist
740 grants. The authors are also grateful for the support from the Multi-user Facility for Gas,
741 Water, and Sediment Geochemistry at the Fluminense Federal University (GAS-UFF).

742

743 **References**

- 744 Abril, G., Cotovicz Jr, L.C., Nepomuceno, A.M., Erbas, T., Costa, S., Ramos, V.V.,
745 Moser, G., Fernandes, A., Negri, E., Knoppers, B.A., Brandini, N., Machado, W.,
746 Bernardes, M., Vantrepotte, V., 2022. Spreading eutrophication and changing CO₂
747 fluxes in the tropical coastal ocean: a few lessons from Rio de Janeiro. *Arquivos de*
748 *Ciências do Mar* 461–476. <https://doi.org/10.32360/78518>
- 749 Alongi, D., 2009. *The Energetics of Mangrove Forests*, 1st ed. Springer Netherlands,
750 Dordrecht. <https://doi.org/10.1007/978-1-4020-4271-3>
- 751 Alongi, D.M., Tirendi, F., Dixon, P., Trott, L.A., Brunskill, G.J., 1999. Mineralization of
752 Organic Matter in Intertidal Sediments of a Tropical Semi-enclosed Delta. *Estuarine,*
753 *Coastal and Shelf Science* 48, 451–467.

754 <https://doi.org/https://doi.org/10.1006/ecss.1998.0465>

755 Amador, E. da S., 2013. Baía de Guanabara: Ocupação Histórica e Avaliação Ambiental,
756 1st ed. Interciência.

757 APHA, AWWA, WEF, 2012. Standard Methods for examination of water and
758 wastewater, 22nd ed. American Public Health Association, Washington.

759 Araujo, M.P., Costa, T.L.F. da, Carreira, R. da S., 2011. Esteróis como indicadores do
760 acúmulo de esgotos domésticos em sedimentos de um sistema estuarino-lagunar
761 tropical (Mundaú-Manguaba, AL). *Química Nova* 34, 64–70.

762 Barcellos, D., Queiroz, H.M., Nóbrega, G.N., de Oliveira Filho, R.L., Santaella, S.T.,
763 Otero, X.L., Ferreira, T.O., 2019. Phosphorus enriched effluents increase
764 eutrophication risks for mangrove systems in northeastern Brazil. *Marine Pollution*
765 *Bulletin* 142, 58–63. <https://doi.org/10.1016/j.marpolbul.2019.03.031>

766 Barros, G.V., Martinelli, L.A., Oliveira Novais, T.M., Ometto, J.P.H.B., Zuppi, G.M.,
767 2010. Stable isotopes of bulk organic matter to trace carbon and nitrogen dynamics
768 in an estuarine ecosystem in Babitonga Bay (Santa Catarina, Brazil). *Science of the*
769 *Total Environment* 408, 2226–2232. <https://doi.org/10.1016/j.scitotenv.2010.01.060>

770 Boehm, P.D., Requejo, A.G., 1986. Overview of the recent sediment hydrocarbon
771 geochemistry of Atlantic and Gulf Coast outer continental shelf environments.
772 *Estuarine, Coastal and Shelf Science* 23, 29–58.
773 [https://doi.org/https://doi.org/10.1016/0272-7714\(86\)90084-3](https://doi.org/https://doi.org/10.1016/0272-7714(86)90084-3)

774 Borges, H.V., Nittrouer, C.A., 2016. SEDIMENT ACCUMULATION IN SEPETIBA
775 BAY (BRAZIL) DURING THE HOLOCENE: A REFLEX OF THE HUMAN
776 INFLUENCE. *Journal of Sedimentary Environments* 1.
777 <https://doi.org/10.12957/jse.2016.21868>

778 Bourbonniere, R.A., Meyers, P.A., 1996. Sedimentary geolipid records of historical
779 changes in the watersheds and productivities of Lakes Ontario and Erie. *Limnology*
780 *and Oceanography* 41, 352–359.

781 Brandini, F., Michelazzo, L.S., Freitas, G.R., Campos, G., Chuqui, M., Jovane, L., 2019.
782 Carbon Flow for Plankton Metabolism of Saco do Mamanguá Ría, Bay of Ilha
783 Grande, a Subtropical Coastal Environment in the South Brazil Bight. *Front Mar Sci*
784 6. <https://doi.org/10.3389/fmars.2019.00584>

785 Breitburg, D., Levin, L.A., Oschlies, A., Grégoire, M., Chavez, F.P., Conley, D.J.,
786 Garçon, V., Gilbert, D., Gutiérrez, D., Isensee, K., Jacinto, G.S., Limburg, K.E.,
787 Montes, I., Naqvi, S.W.A., Pitcher, G.C., Rabalais, N.N., Roman, M.R., Rose, K.A.,
788 Seibel, B.A., Telszewski, M., Yasuhara, M., Zhang, J., 2018. Declining oxygen in
789 the global ocean and coastal waters. *Science* (1979) 359, eaam7240.
790 <https://doi.org/10.1126/science.aam7240>

791 Canuel, E.A., Freeman, K.H., Wakeham, S.G., 1997. Isotopic compositions of lipid
792 biomarker compounds in estuarine plants and surface sediments. *Limnology and*
793 *Oceanography* 42, 1570–1583. <https://doi.org/10.4319/lo.1997.42.7.1570>

794 Carreira, R., Wagener, A. de L.R., Fileman, T., Readman, J.W., 2001. Distribuição de
795 coprostanol (5beta(H)-colestano-3beta-ol) em sedimentos superficiais da Baía de
796 Guanabara: indicador da poluição recente por esgotos domésticos. *Química Nova*
797 24. <https://doi.org/10.1590/S0100-40422001000100008>

798 Carreira, R.S., Ribeiro, P. v., Silva, C.E.M., Farias, C.O., 2009. Hidrocarbonetos e
799 esteróis como indicadores de fontes e destino de matéria orgânica em sedimentos da
800 Baía de Sepetiba, Rio de Janeiro. *Química Nova* 32. <https://doi.org/10.1590/S0100-40422009000700023>

801

802 Chen, G.C., Tam, N.F.Y., Wong, Y.S., Ye, Y., 2011. Effect of wastewater discharge on
803 greenhouse gas fluxes from mangrove soils. *Atmospheric Environment* 45, 1110–
804 1115. <https://doi.org/10.1016/j.atmosenv.2010.11.034>

805 Chen, G.C., Tam, N.F.Y., Ye, Y., 2010. Summer fluxes of atmospheric greenhouse gases
806 N₂O, CH₄ and CO₂ from mangrove soil in South China. *Science of the Total*
807 *Environment* 408, 2761–2767. <https://doi.org/10.1016/j.scitotenv.2010.03.007>

808 Chen, G.C., Tam, N.F.Y., Ye, Y., 2012. Spatial and seasonal variations of atmospheric
809 N₂O and CO₂ fluxes from a subtropical mangrove swamp and their relationships
810 with soil characteristics. *Soil Biology and Biochemistry* 48, 175–181.
811 <https://doi.org/10.1016/j.soilbio.2012.01.029>

812 Clark Jr., R.C., Blumer, M., 1967. DISTRIBUTION OF n-PARAFFINS IN MARINE
813 ORGANISMS AND SEDIMENT1. *Limnology and Oceanography* 12, 79–87.
814 <https://doi.org/https://doi.org/10.4319/lo.1967.12.1.0079>

815 Copeland, G., Monteiro, T., Couch, S., Borthwick, A., 2003. Water quality in Sepetiba
816 Bay, Brazil. *Marine Environmental Research* 55, 385–408.
817 [https://doi.org/10.1016/S0141-1136\(02\)00289-1](https://doi.org/10.1016/S0141-1136(02)00289-1)

818 Das, S., Ganguly, D., Chakraborty, S., Mukherjee, A., Kumar De, T., 2018. Methane flux
819 dynamics in relation to methanogenic and methanotrophic populations in the soil of
820 Indian Sundarban mangroves. *Marine Ecology* 39, e12493.

821 Dell'Anno, A., Mei, M.L., Pusceddu, A., Danovaro, R., 2002. Assessing the trophic state
822 and eutrophication of coastal marine systems: a new approach based on the
823 biochemical composition of sediment organic matter. *Marine Pollution Bulletin* 44,
824 611–622. [https://doi.org/10.1016/S0025-326X\(01\)00302-2](https://doi.org/10.1016/S0025-326X(01)00302-2)

825 dos Reis Souza, M.R., Santos, E., Suzarte, J.S., do Carmo, L.O., Soares, L.S., Santos,
826 L.G.G.V., Júnior, A.R.V., Krause, L.C., Frena, M., Damasceno, F.C., Huang, Y., da
827 Rosa Alexandre, M., 2020. The impact of anthropogenic activity at the tropical
828 Sergipe-Poxim estuarine system, Northeast Brazil: Fecal indicators. *Marine*
829 *Pollution Bulletin* 154, 111067. <https://doi.org/10.1016/j.marpolbul.2020.111067>

830 Drake, T.W., Podgorski, D.C., Dinga, B., Chanton, J.P., Six, J., Spencer, R.G.M., 2020.
831 Land-use controls on carbon biogeochemistry in lowland streams of the Congo
832 Basin. *Global Change Biology* 26, 1374–1389.
833 <https://doi.org/https://doi.org/10.1111/gcb.14889>

834 Eglinton, G., Gonzalez, A.G., Hamilton, R.J., Raphael, R.A., 1962. Hydrocarbon
835 constituents of the wax coatings of plant leaves: A taxonomic survey.
836 *Phytochemistry* 1, 89–102. [https://doi.org/https://doi.org/10.1016/S0031-](https://doi.org/https://doi.org/10.1016/S0031-9422(00)88006-1)
837 [9422\(00\)88006-1](https://doi.org/https://doi.org/10.1016/S0031-9422(00)88006-1)

838 Faria, M. de M., Sanchez, B.A., 2001. Geochemistry and mineralogy of recent sediments
839 of Guanabara Bay (NE sector) and its major rivers - Rio de Janeiro State - Brazil.
840 *Anais da Academia Brasileira de Ciências* 73, 121–133.
841 <https://doi.org/10.1590/S0001-37652001000100010>

842 Fistarol, G.O., Coutinho, F.H., Moreira, A.P.B., Venas, T., Cánovas, A., de Paula, S.E.M.,
843 Coutinho, R., de Moura, R.L., Valentin, J.L., Tenenbaum, D.R., Paranhos, R., do
844 Valle, R. de A.B., Vicente, A.C.P., Amado Filho, G.M., Pereira, R.C., Kruger, R.,
845 Rezende, C.E., Thompson, C.C., Salomon, P.S., Thompson, F.L., 2015.
846 Environmental and Sanitary Conditions of Guanabara Bay, Rio de Janeiro. *Frontiers*
847 *in Microbiology* 6. <https://doi.org/10.3389/fmicb.2015.01232>

848 Folk, R.L., Ward, W.C., 1957. Brazos River bar [Texas]; a study in the significance of
849 grain size parameters. *Journal of Sedimentary Research* 27, 3–26.
850 <https://doi.org/10.1306/74D70646-2B21-11D7-8648000102C1865D>

851 Franco, A.S., 1997. Marés, Fundamentos, in: Navegação, D. de H. e (Ed.), *Análise e*
852 *Previsão*. Niterói, RJ.

853 Frena, M., Souza, M.R.R., Damasceno, F.C., Madureira, L.A.S., Alexandre, M.R., 2016.
854 Evaluation of anthropogenic contamination using sterol markers in a tropical
855 estuarine system of northeast Brazil. *Marine Pollution Bulletin* 109, 619–623.

856 <https://doi.org/10.1016/j.marpolbul.2016.05.022>

857 García, L. V., 2004. Escaping the Bonferroni iron claw in ecological studies. *Oikos* 105,

858 657–663. <https://doi.org/10.1111/j.0030-1299.2004.13046.x>

859 Gearing, P., Gearing, J.N., Lytle, T.F., Lytle, J.S., 1976. Hydrocarbons in 60 northeast

860 Gulf of Mexico shelf sediments: a preliminary survey. *Geochimica et Cosmochimica*

861 *Acta* 40, 1005–1017. [https://doi.org/10.1016/0016-7037\(76\)90043-0](https://doi.org/10.1016/0016-7037(76)90043-0)

862 Gontikaki, E., Thornton, B., Cornulier, T., Witte, U., 2015. Occurrence of Priming in the

863 Degradation of Lignocellulose in Marine Sediments. *PLOS ONE* 10.

864 <https://doi.org/10.1371/journal.pone.0143917>

865 González-Oreja, J.A., Saiz-Salinas, J.I., 1998. Short-term spatio-temporal changes in

866 urban pollution by means of faecal sterols analysis. *Marine Pollution Bulletin* 36,

867 868–875. [https://doi.org/10.1016/S0025-326X\(98\)00037-X](https://doi.org/10.1016/S0025-326X(98)00037-X)

868 Grasshoff, K., Ehrardt, M., Kremling, K., 1999. *Methods of Seawater Analysis*. Wiley.

869 <https://doi.org/10.1002/9783527613984>

870 Grimalt, J.O., Fernandez, P., Bayona, J.M., Albaiges, J., 1990. Assessment of fecal sterols

871 and ketones as indicators of urban sewage inputs to coastal waters. *Environmental*

872 *Science & Technology* 24, 357–363. <https://doi.org/10.1021/es00073a011>

873 Gritcan, I., Duxbury, M., Leuzinger, S., Alfaro, A.C., 2016. Leaf stable isotope and

874 nutrient status of temperate mangroves as ecological indicators to assess

875 anthropogenic activity and recovery from eutrophication. *Front Plant Sci* 7, 1922.

876 Guenet, B., Neill, C., Bardoux, G., Abbadie, L., 2010. Is there a linear relationship

877 between priming effect intensity and the amount of organic matter input? *Applied*

878 *Soil Ecology* 46, 436–442. <https://doi.org/10.1016/j.apsoil.2010.09.006>

879 Guoying, S., Shanfa, F., Dehan, L., Nengxian, S., Hongming, Z., 1980. The geochemistry

880 of n-alkanes with an even-odd predominance in the Tertiary Shahejie Formation of

881 northern China. *Physics and Chemistry of the Earth* 12, 115–121.

882 [https://doi.org/10.1016/0079-1946\(79\)90093-4](https://doi.org/10.1016/0079-1946(79)90093-4)

883 Häder, D.-P., Banaszak, A.T., Villafaña, V.E., Narvarte, M.A., González, R.A., Helbling,

884 E.W., 2020. Anthropogenic pollution of aquatic ecosystems: Emerging problems

885 with global implications. *Science of The Total Environment* 713.

886 <https://doi.org/10.1016/j.scitotenv.2020.136586>

887 Hamilton, S.E., Friess, D.A., 2018. Global carbon stocks and potential emissions due to

888 mangrove deforestation from 2000 to 2012. *Nature Climate Change* 8, 240–244.

889 <https://doi.org/10.1038/s41558-018-0090-4>

890 Hutchinson, G.L., Livingston, G.P., 2001. Vents and seals in non-steady-state chambers

891 used for measuring gas exchange between soil and the atmosphere. *European Journal*

892 *of Soil Science* 52, 675–682. <https://doi.org/10.1046/j.1365-2389.2001.00415.x>

893 IBGE, 2010. 2010 Census - Brazilian Institute of Geography and Statistics [WWW

894 Document]. URL <https://cidades.ibge.gov.br/brasil/rj/panorama>

895 Isobe, K.O., Tarao, M., Zakaria, M.P., Chiem, N.H., Minh, L.Y., Takada, H., 2002.

896 Quantitative Application of Fecal Sterols Using Gas Chromatography–Mass

897 Spectrometry To Investigate Fecal Pollution in Tropical Waters: Western Malaysia

898 and Mekong Delta, Vietnam. *Environmental Science & Technology* 36, 4497–4507.

899 <https://doi.org/10.1021/es020556h>

900 Jacotot, A., Marchand, C., Allenbach, M., 2018. Tidal variability of CO₂ and CH₄

901 emissions from the water column within a *Rhizophora* mangrove forest (New

902 Caledonia). *Science of the Total Environment* 631–632, 334–340.

903 <https://doi.org/10.1016/j.scitotenv.2018.03.006>

904 Jacotot, A., Marchand, C., Allenbach, M., 2019. Biofilm and temperature controls on

905 greenhouse gas (CO₂ and CH₄) emissions from a *Rhizophora* mangrove soil (New

906 Caledonia). *Science of The Total Environment* 650.

907 <https://doi.org/10.1016/j.scitotenv.2018.09.093>

908 Jeng, W.L., 2006. Higher plant n-alkane average chain length as an indicator of
909 petrogenic hydrocarbon contamination in marine sediments. *Marine Chemistry* 102,
910 242–251. <https://doi.org/10.1016/j.marchem.2006.05.001>

911 Jiao, N., Wang, H., Xu, G., Aricò, S., 2018. Blue carbon on the rise: Challenges and
912 opportunities. *National Science Review* 5, 464–468.

913 Kabwe, L.K., Hendry, M.J., Wilson, G.W., Lawrence, J.R., 2002. Quantifying CO₂
914 fluxes from soil surfaces to the atmosphere. *Journal of Hydrology* 260, 1–14.
915 [https://doi.org/10.1016/S0022-1694\(01\)00601-1](https://doi.org/10.1016/S0022-1694(01)00601-1)

916 Keller, M., Weitz, A.M., Bryan, B., Rivera, M.M., Silver, W.L., 2000. Soil-atmosphere
917 nitrogen oxide fluxes: Effects of root disturbance. *Journal of Geophysical Research:*
918 *Atmospheres* 105, 17693–17698. <https://doi.org/10.1029/2000JD900068>

919 Keuskamp, J.A., Hefting, M.M., Dingemans, B.J.J., Verhoeven, J.T.A., Feller, I.C., 2015.
920 Effects of nutrient enrichment on mangrove leaf litter decomposition. *Science of The*
921 *Total Environment* 508, 402–410. <https://doi.org/10.1016/j.scitotenv.2014.11.092>

922 King, G.M., 1984. Utilization of hydrogen, acetate, and “noncompetitive”; substrates by
923 methanogenic bacteria in marine sediments. *Geomicrobiology Journal* 3, 275–306.

924 Konnerup, D., Betancourt-Portela, J.M., Villamil, C., Parra, J.P., 2014. Nitrous oxide and
925 methane emissions from the restored mangrove ecosystem of the Ciénaga Grande de
926 Santa Marta, Colombia. *Estuarine, Coastal and Shelf Science* 140, 43–51.
927 <https://doi.org/10.1016/j.ecss.2014.01.006>

928 Kreuzwieser, J., Buchholz, J., Rennenberg, H., 2003. Emission of Methane and Nitrous
929 Oxide by Australian Mangrove Ecosystems. *Plant Biology* 5.
930 <https://doi.org/10.1055/s-2003-42712>

931 Kristensen, E., Alongi, D.M., 2006. Control by fiddler crabs (*Uca vocans*) and plant roots
932 (*Avicennia marina*) on carbon, iron, and sulfur biogeochemistry in mangrove
933 sediment. *Limnology and Oceanography* 51.
934 <https://doi.org/10.4319/lo.2006.51.4.1557>

935 Kristensen, E., Bouillon, S., Dittmar, T., Marchand, C., 2008a. Organic carbon dynamics
936 in mangrove ecosystems: A review. *Aquatic Botany* 89, 201–219.
937 <https://doi.org/10.1016/j.aquabot.2007.12.005>

938 Kristensen, E., Connolly, R.M., Otero, X.L., Marchand, C., Ferreira, T.O., Rivera-
939 Monroy, V.H., 2017. Biogeochemical Cycles: Global Approaches and Perspectives,
940 in: *Mangrove Ecosystems: A Global Biogeographic Perspective*. Springer
941 International Publishing, Cham. https://doi.org/10.1007/978-3-319-62206-4_6

942 Kristensen, E., Flindt, M.R., Ulomi, S., Borges, A. v., Abril, G., Bouillon, S., 2008b.
943 Emission of CO₂ and CH₄ to the atmosphere by sediments and open waters in two
944 Tanzanian mangrove forests. *Marine Ecology Progress Series* 370, 53–67.
945 <https://doi.org/10.3354/meps07642>

946 Kumar, M., Boski, T., Lima-Filho, F.P., Bezerra, F.H.R., González -Vila, F.J., Alam
947 Bhuiyan, M.K., González-Pérez, J.A., 2019. Biomarkers as indicators of
948 sedimentary organic matter sources and early diagenetic transformation of
949 pentacyclic triterpenoids in a tropical mangrove ecosystem. *Estuarine, Coastal and*
950 *Shelf Science* 229, 106403. <https://doi.org/10.1016/j.ecss.2019.106403>

951 Lam, S.Y.W., Chen, Y.-Q., 2001. Ground-Based Positioning Techniques, in:
952 *Geographical Data Acquisition*. Springer Vienna, Vienna, pp. 85–97.
953 https://doi.org/10.1007/978-3-7091-6183-8_6

954 Lamb, A.L., Wilson, G.P., Leng, M.J., 2006. A review of coastal palaeoclimate and
955 relative sea-level reconstructions using $\delta^{13}\text{C}$ and C/N ratios in organic material.
956 *Earth-Science Reviews* 75, 29–57.

957 Lemley, D.A., Adams, J.B., Taljaard, S., Strydom, N.A., 2015. Towards the classification

958 of eutrophic condition in estuaries. *Estuarine, Coastal and Shelf Science* 164, 221–
959 232. <https://doi.org/10.1016/j.ecss.2015.07.033>

960 Leng, M.J., Lewis, J.P., 2017. C/N ratios and Carbon Isotope Composition of Organic
961 Matter in Estuarine Environments. pp. 213–237. https://doi.org/10.1007/978-94-024-0990-1_9

962

963 Liu, S., Trevathan-Tackett, S.M., Ewers Lewis, C.J., Huang, X., Macreadie, P.I., 2020.
964 Macroalgal Blooms Trigger the Breakdown of Seagrass Blue Carbon.
965 *Environmental Science & Technology* 54, 14750–14760.
966 <https://doi.org/10.1021/acs.est.0c03720>

967 Machiwa, J.F., 2000. $\delta^{13}\text{C}$ Signatures of Flora, Macrofauna and Sediment of a Mangrove
968 Forest Partly Affected by Sewage Wastes. *Tanzania Journal of Science* 26, 15–28.

969 Mannino, A., Harvey, H.R., 1999. Lipid composition in particulate and dissolved organic
970 matter in the Delaware Estuary: sources and diagenetic patterns. *Geochimica et*
971 *Cosmochimica Acta* 63, 2219–2235. [https://doi.org/https://doi.org/10.1016/S0016-7037\(99\)00128-3](https://doi.org/https://doi.org/10.1016/S0016-7037(99)00128-3)

972

973 Marins, R. V., Machado, W., Paraquetti, H.H.M., Bidone, E.D., Lacerda, L.D., Molisani,
974 M.M., 2004. Environmental changes in Sepetiba Bay, SE Brazil. *Regional*
975 *Environmental Change* 4, 17–27. <https://doi.org/10.1007/s10113-003-0060-9>

976 Marotta, H., Duarte, C.M., Guimarães-Souza, B.A., Enrich-Prast, A., 2012. Synergistic
977 control of CO₂ emissions by fish and nutrients in a humic tropical lake. *Oecologia*
978 168, 839–847. <https://doi.org/10.1007/s00442-011-2131-9>

979 Martens, C.S., Berner, R.A., 1974. Methane Production in the Interstitial Waters of
980 Sulfate-Depleted Marine Sediments. *Science* (1979) 185, 1167–1169.
981 <https://doi.org/10.1126/science.185.4157.1167>

982 Martin, R.M., Wigand, C., Oczkowski, A., Hanson, A., Balogh, S., Branoff, B., Santos,
983 E., Huertas, E., 2020. Greenhouse Gas Fluxes of Mangrove Soils and Adjacent
984 Coastal Waters in an Urban, Subtropical Estuary. *Wetlands* 40.
985 <https://doi.org/10.1007/s13157-020-01300-w>

986 McCaffrey, M.A., 1990. Sedimentary lipids as indicators of depositional conditions in the
987 coastal Peruvian upwelling regime. <https://doi.org/10.1575/1912/5428>

988 McCalley, D. V, Cooke, M., Nickless, G., 1981. Effect of sewage treatment on faecal
989 sterols. *Water Research* 15, 1019–1025.
990 [https://doi.org/https://doi.org/10.1016/0043-1354\(81\)90211-6](https://doi.org/https://doi.org/10.1016/0043-1354(81)90211-6)

991 Meyers, P.A., 1994. Preservation of elemental and isotopic source identification of
992 sedimentary organic matter. *Chemical Geology* 114, 289–302.
993 [https://doi.org/https://doi.org/10.1016/0009-2541\(94\)90059-0](https://doi.org/https://doi.org/10.1016/0009-2541(94)90059-0)

994 Molisani, M.M., Kjerfve, B., Silva, A.P., Lacerda, L.D., 2006. Water discharge and
995 sediment load to Sepetiba Bay from an anthropogenically-altered drainage basin, SE
996 Brazil. *Journal of Hydrology* 331, 425–433.
997 <https://doi.org/10.1016/j.jhydrol.2006.05.038>

998 Moser, K., Ahn, C., Noe, G., 2007. Characterization of microtopography and its influence
999 on vegetation patterns in created wetlands. *Wetlands* 27, 1081–1097.

1000 Mudge, S.M., Bebianno, M.J., 1997. Sewage contamination following an accidental
1001 spillage in the Ria Formosa, Portugal. *Marine Pollution Bulletin* 34, 163–170.
1002 [https://doi.org/https://doi.org/10.1016/S0025-326X\(96\)00082-3](https://doi.org/https://doi.org/10.1016/S0025-326X(96)00082-3)

1003 Mudge, S.M., Lintern, D.G., 1999. Comparison of Sterol Biomarkers for Sewage with
1004 other Measures in Victoria Harbour, B.C., Canada. *Estuarine, Coastal and Shelf*
1005 *Science* 48, 27–38. <https://doi.org/10.1006/ecss.1999.0406>

1006 Mudge, S.M., Seguel, C.G., 1999. Organic Contamination of San Vicente Bay, Chile.
1007 *Marine Pollution Bulletin* 38, 1011–1021.
1008 [https://doi.org/https://doi.org/10.1016/S0025-326X\(99\)00132-0](https://doi.org/https://doi.org/10.1016/S0025-326X(99)00132-0)

- 1009 Muniz, P., Pires-Vanin, A.M.S., Martins, C.C., Montone, R.C., Bicego, M.C., 2006.
1010 Trace metals and organic compounds in the benthic environment of a subtropical
1011 embayment (Ubatuba Bay, Brazil). *Marine Pollution Bulletin* 52, 1098–1105.
1012 <https://doi.org/10.1016/j.marpolbul.2006.05.014>
- 1013 Nes, W.R., 1974. Role of sterols in membranes. *Lipids* 9, 596–612.
1014 <https://doi.org/10.1007/BF02532509>
- 1015 Nishigima, F.N., Weber, R.R., Bicego, M.C., 2001. Aliphatic and aromatic hydrocarbons
1016 in sediments of Santos and Cananéia, SP, Brazil. *Marine Pollution Bulletin* 42,
1017 1064–1072. [https://doi.org/10.1016/S0025-326X\(01\)00072-8](https://doi.org/10.1016/S0025-326X(01)00072-8)
- 1018 Nishimura, M., Koyama, T., 1976. Stenols and stanols in lake sediments and diatoms.
1019 *Chemical Geology* 17, 229–239. [https://doi.org/https://doi.org/10.1016/0009-2541\(76\)90037-1](https://doi.org/https://doi.org/10.1016/0009-2541(76)90037-1)
- 1020
1021 Nishimura, M., Koyama, T., 1977. The occurrence of stanols in various living organisms
1022 and the behavior of sterols in contemporary sediments. *Geochimica et*
1023 *Cosmochimica Acta* 41, 379–385. [https://doi.org/https://doi.org/10.1016/0016-7037\(77\)90265-4](https://doi.org/https://doi.org/10.1016/0016-7037(77)90265-4)
- 1024
1025 Nixon, S.W., 1995. Coastal marine eutrophication: A definition, social causes, and future
1026 concerns. *Ophelia* 41, 199–219. <https://doi.org/10.1080/00785236.1995.10422044>
- 1027 Nóbrega, G.N., Ferreira, T.O., Siqueira Neto, M., Queiroz, H.M., Artur, A.G., Mendonça,
1028 E.D.S., Silva, E.D.O., Otero, X.L., 2016. Edaphic factors controlling summer (rainy
1029 season) greenhouse gas emissions (CO₂ and CH₄) from semiarid mangrove soils
1030 (NE-Brazil). *Science of the Total Environment* 542, 685–693.
1031 <https://doi.org/10.1016/j.scitotenv.2015.10.108>
- 1032 Ouyang, X., Lee, S.Y., Connolly, R.M., 2016. Structural equation modelling reveals
1033 factors regulating surface sediment organic carbon content and CO₂ efflux in a
1034 subtropical mangrove. *Science of the Total Environment* 578, 513–522.
1035 <https://doi.org/http://dx.doi.org/10.1016/j.scitotenv.2016.10.218>
- 1036 Palacios, M.M., Trevathan-Tackett, S.M., Malerba, M.E., Macreadie, P.I., 2021. Effects
1037 of a nutrient enrichment pulse on blue carbon ecosystems. *Marine Pollution Bulletin*
1038 165, 112024. <https://doi.org/10.1016/j.marpolbul.2021.112024>
- 1039 Pérez, A., Machado, W., Gutierrez, D., Smoak, J.M., Breithaupt, J.L., Saldarriaga, M.S.,
1040 Sanders, L., Marotta, H., Sanders, C.J., 2020. Carbon and nutrient accumulation in
1041 mangrove sediments affected by multiple environmental changes. *Journal of Soils*
1042 *and Sediments* 20. <https://doi.org/10.1007/s11368-020-02612-4>
- 1043 Pratt, C., Warnken, J., Leeming, R., Arthur, M.J., Grice, D.I., 2008. Degradation and
1044 responses of coprostanol and selected sterol biomarkers in sediments to a simulated
1045 major sewage pollution event: A microcosm experiment under sub-tropical estuarine
1046 conditions. *Organic Geochemistry* 39, 353–369.
1047 <https://doi.org/https://doi.org/10.1016/j.orggeochem.2007.06.009>
- 1048 Purvaja, R., Ramesh, R., 2001. Natural and anthropogenic methane emission from coastal
1049 wetlands of South India. *Environmental Management* 27, 547–557.
- 1050 Queiroz, H.M., Ferreira, T.O., Taniguchi, C.A.K., Barcellos, D., do Nascimento, J.C.,
1051 Nóbrega, G.N., Otero, X.L., Artur, A.G., 2020. Nitrogen mineralization and
1052 eutrophication risks in mangroves receiving shrimp farming effluents.
1053 *Environmental Science and Pollution Research* 27, 34941–34950.
1054 <https://doi.org/10.1007/s11356-020-09720-1>
- 1055 Rochette, P., Hutchinson, G.L., 2015. Measurement of Soil Respiration in situ: Chamber
1056 Techniques. pp. 247–286. <https://doi.org/10.2134/agronmonogr47.c12>
- 1057 Rosentreter, Judith A., Maher, D.T., Erler, D. V., Murray, R.H., Eyre, B.D., 2018. Methane
1058 emissions partially offset “blue carbon” burial in mangroves. *Sci Adv* 4, eaao4985.
- 1059 Rosentreter, Judith A., Maher, D.T., Erler, D. v., Murray, R.H., Eyre, B.D., 2018.

1060 Methane emissions partially offset “blue carbon” burial in mangroves. *Science*
1061 *Advances* 4. <https://doi.org/10.1126/sciadv.aao4985>

1062 Sanders, C.J., Eyre, B.D., Santos, I.R., Machado, W., Luiz-Silva, W., Smoak, J.M.,
1063 Breithaupt, J.L., Ketterer, M.E., Sanders, L., Marotta, H., Silva-Filho, E., 2014.
1064 Elevated rates of organic carbon, nitrogen, and phosphorus accumulation in a highly
1065 impacted mangrove wetland. *Geophysical Research Letters* 41.
1066 <https://doi.org/10.1002/2014GL059789>

1067 Sanders, C.J., Smoak, J.M., Naidu, A.S., Araripe, D.R., Sanders, L.M., Patchineelam,
1068 S.R., 2010a. Mangrove forest sedimentation and its reference to sea level rise,
1069 Cananea, Brazil. *Environmental Earth Sciences* 60, 1291–1301.

1070 Sanders, C.J., Smoak, J.M., Naidu, A.S., Sanders, L.M., Patchineelam, S.R., 2010b.
1071 Organic carbon burial in a mangrove forest, margin and intertidal mud flat.
1072 *Estuarine, Coastal and Shelf Science* 90, 168–172.

1073 Santos, E.S., Carreira, R. da S., Knoppers, B.A., 2008. Sedimentary sterols as indicators
1074 of environmental conditions in Southeastern Guanabara Bay, Brazil. *Brazilian*
1075 *Journal of Oceanography* 56, 97–113.

1076 Schaeffer-Novelli, Y., Cintrón-Molero, G., Soares, M.L.G., De-Rosa, T., 2000. Brazilian
1077 mangroves. *Aquatic Ecosystem Health & Management* 3, 561–570.
1078 <https://doi.org/10.1080/14634980008650693>

1079 Schumacher, B.A., 2002. METHODS FOR THE DETERMINATION OF TOTAL
1080 ORGANIC CARBON (TOC) IN SOILS AND SEDIMENTS. Las Vegas.

1081 Servais, S., Kominoski, J.S., Davis, S.E., Gaiser, E.E., Pachón, J., Troxler, T.G., 2019.
1082 Effects of Nutrient-Limitation on Disturbance Recovery in Experimental Mangrove
1083 Wetlands. *Wetlands* 39, 337–347. <https://doi.org/10.1007/s13157-018-1100-z>

1084 Sherman, R.E., Fahey, T.J., Howarth, R.W., 1998. Soil-plant interactions in a neotropical
1085 mangrove forest: iron, phosphorus and sulfur dynamics. *Oecologia* 115, 553–563.

1086 Sotomayor, D., Corredor, J.E., Morell, J.M., 1994. Methane Flux from Mangrove
1087 Sediments along the Southwestern Coast of Puerto Rico. *Estuaries* 17.
1088 <https://doi.org/10.2307/1352563>

1089 Steinhauer, M.S., Boehm, P.D., 1992. The composition and distribution of saturated and
1090 aromatic hydrocarbons in nearshore sediments, river sediments, and coastal peat of
1091 the Alaskan Beaufort Sea: Implications for detecting anthropogenic hydrocarbon
1092 inputs. *Marine Environmental Research* 33, 223–253. [https://doi.org/10.1016/0141-1136\(92\)90140-H](https://doi.org/10.1016/0141-1136(92)90140-H)

1094 Thomazelli, F.F., 2010. Composição da matéria orgânica no gradiente estuarino da Baía
1095 de Sepetiba/RJ. Universidade Federal Fluminense.

1096 Tomotsune, M., Arai, H., Yoshitake, S., Kida, M., Fujitake, N., Kinjo, K., Ohtsuka, T.,
1097 2020. Effect of Crab Burrows on CO₂ Flux from the Sediment Surface to the
1098 Atmosphere in a Subtropical Mangrove Forest on Ishigaki Island, Southwestern
1099 Japan. *Estuaries and Coasts* 43, 102–110.

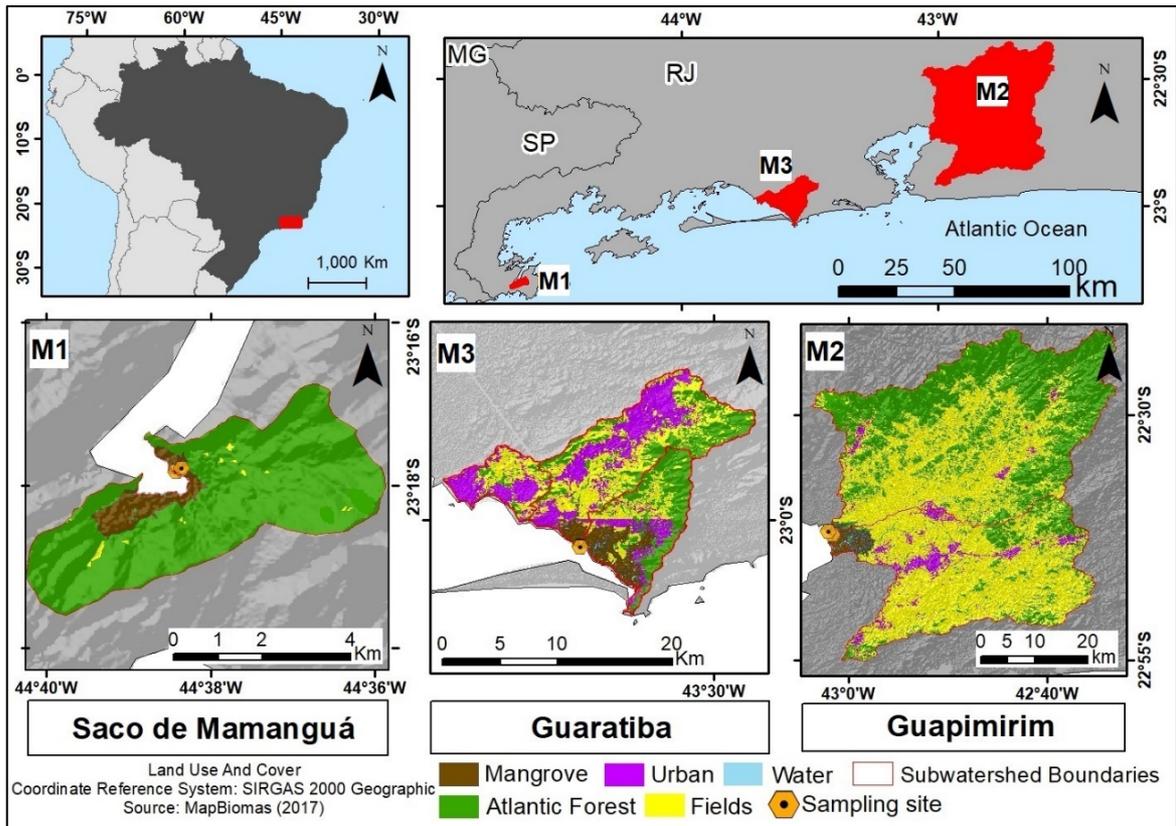
1100 van Nugteren, P., Moodley, L., Brummer, G.-J., Heip, C.H.R., Herman, P.M.J.,
1101 Middelburg, J.J., 2009. Seafloor ecosystem functioning: the importance of organic
1102 matter priming. *Marine Biology* 156, 2277–2287. <https://doi.org/10.1007/s00227-009-1255-5>

1104 Verhoeven, J.T.A., Laanbroek, H.J., Rains, M.C., Whigham, D.F., 2014. Effects of
1105 increased summer flooding on nitrogen dynamics in impounded mangroves. *Journal*
1106 *of Environmental Management* 139, 217–226.
1107 <https://doi.org/10.1016/j.jenvman.2014.02.035>

1108 Vizza, C., West, W.E., Jones, S.E., Hart, J.A., Lamberti, G.A., 2017. Regulators of coastal
1109 wetland methane production and responses to simulated global change.
1110 *Biogeosciences* 14, 431–446.

- 1111 Wakeham, S.G., Canuel, E.A., 1988. Organic geochemistry of particulate matter in the
1112 eastern tropical North Pacific Ocean: Implications for particle dynamics. *Journal of*
1113 *Marine Research* 46, 183–213. <https://doi.org/10.1357/002224088785113748>
- 1114 Wang, X.-C., Chen, R.F., Berry, A., 2003. Sources and preservation of organic matter in
1115 Plum Island salt marsh sediments (MA, USA): long-chain n-alkanes and stable
1116 carbon isotope compositions. *Estuarine, Coastal and Shelf Science* 58, 917–928.
1117 <https://doi.org/https://doi.org/10.1016/j.ecss.2003.07.006>
- 1118 Wang, X.C., Sun, S., Ma, H.Q., Liu, Y., 2006. Sources and distribution of aliphatic and
1119 polyaromatic hydrocarbons in sediments of Jiaozhou Bay, Qingdao, China. *Marine*
1120 *Pollution Bulletin* 52, 129–138. <https://doi.org/10.1016/j.marpolbul.2005.08.010>
- 1121 Wendlandt, W.W.M., 1986. *Thermal Analysis*. John Wiley, New York.
- 1122 Wheaton, J.M., Brasington, J., Darby, S.E., Sear, D.A., 2009. Accounting for uncertainty
1123 in DEMs from repeat topographic surveys: improved sediment budgets. *Earth*
1124 *Surface Processes and Landforms* n/a-n/a. <https://doi.org/10.1002/esp.1886>
- 1125 Wolters, J.-W., Gillis, L.G., Bouma, T.J., van Katwijk, M.M., Ziegler, A.D., 2016. Land
1126 Use Effects on Mangrove Nutrient Status in Phang Nga Bay, Thailand. *Land*
1127 *Degradation & Development* 27, 68–76.
1128 <https://doi.org/https://doi.org/10.1002/ldr.2430>
- 1129 Yang, Z., Song, W., Zhao, Y., Zhou, J., Wang, Z., Luo, Y., Li, Y., Lin, G., 2018.
1130 Differential responses of litter decomposition to regional excessive nitrogen input
1131 and global warming between two mangrove species. *Estuarine, Coastal and Shelf*
1132 *Science* 214, 141–148. <https://doi.org/10.1016/j.ecss.2018.09.018>
- 1133 Zar, J.H., 1996. *Biostatistical analysis*, 3rd ed. Prentice Hall., New Jersey.
- 1134 Zhang, Y., Lu, X., Liu, H., Liu, Q., Yu, D., 2015. Identifying the sources of organic matter
1135 in marine and riverine sediments of Bohai Bay and its catchment using carbon and
1136 nitrogen stable isotopes. *Chinese Journal of Oceanology and Limnology* 33, 204–
1137 209. <https://doi.org/10.1007/s00343-015-4068-z>
- 1138

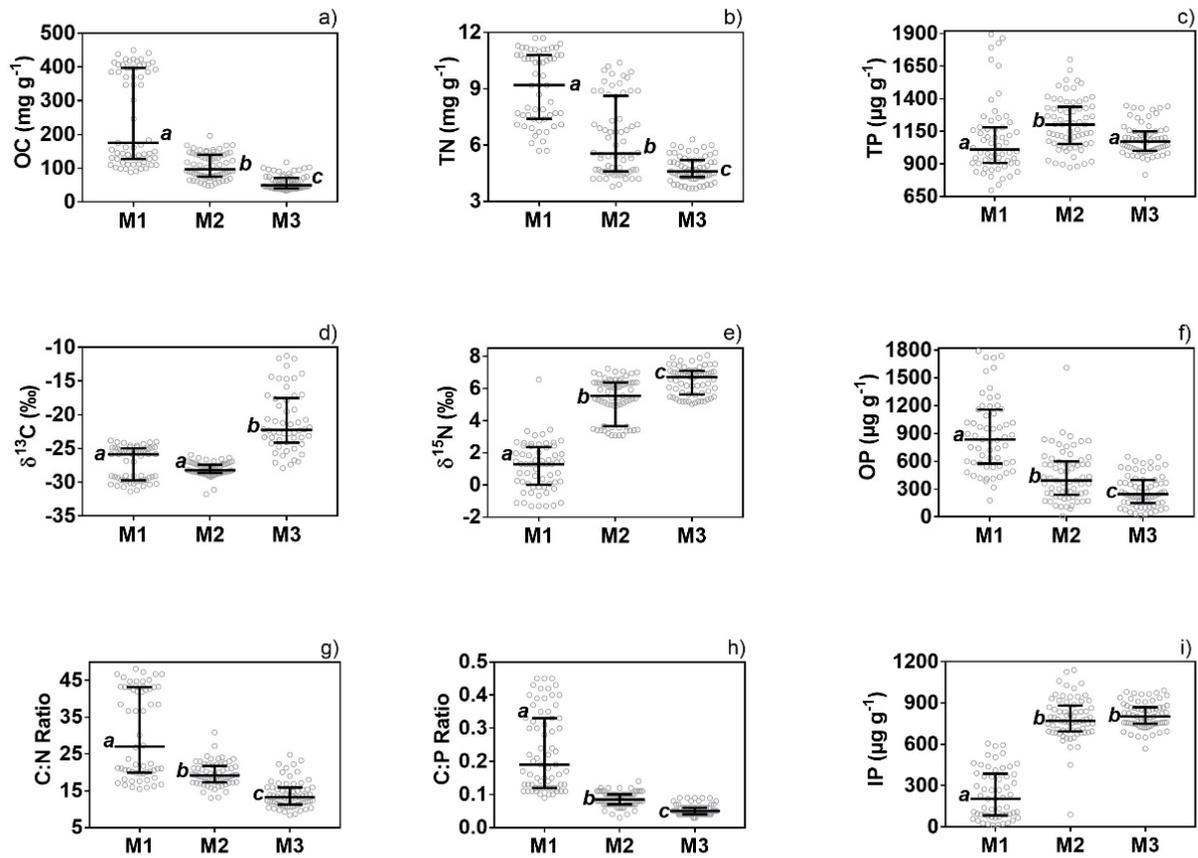
1139 **Figures**



1140

1141 Fig.1. Location of the tree studied mangroves and their respective drainage basins including land
 1142 use characteristics. All sites are located within Rio de Janeiro State, southeastern Brazil. Ilha
 1143 Grande Bay, the Sepetiba Bay and the Guanabara Bay show Saco de Mamanguá (M1), Guaratiba
 1144 (M3) and Guapimirim (M2) mangroves, respectively. Land use and land cover was based on the
 1145 MapBiomias dataset (2017), available at <https://plataforma.mapbiomas.org/map#coverage>.

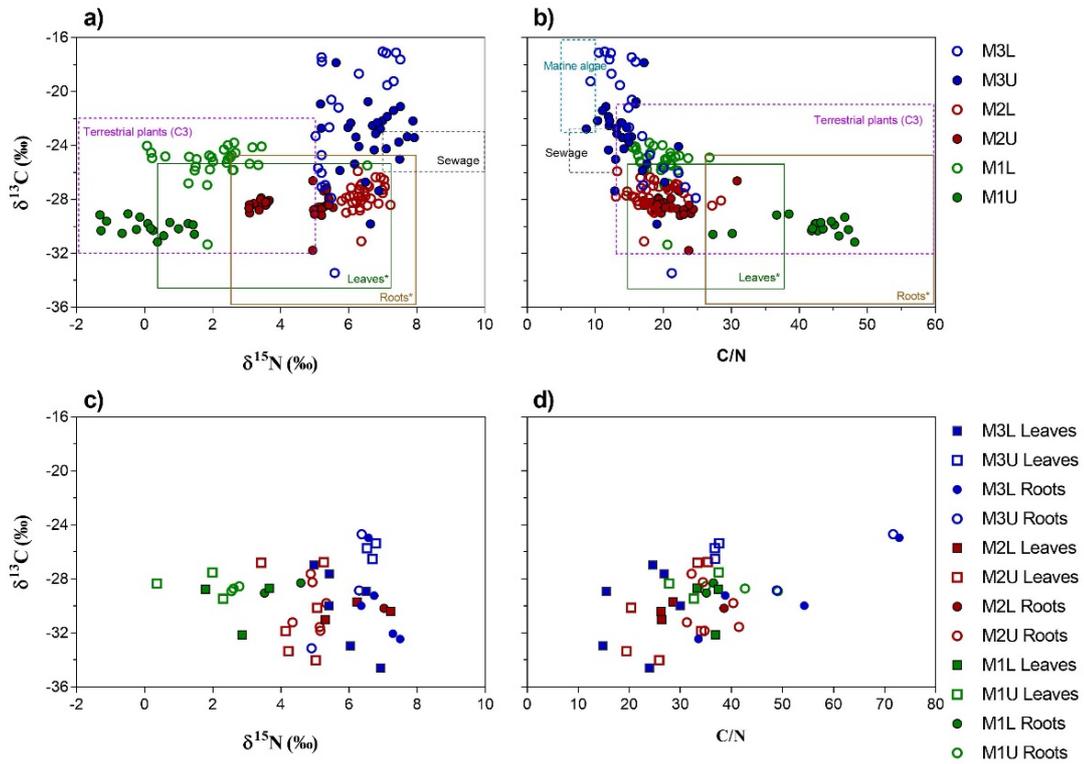
1146



1147

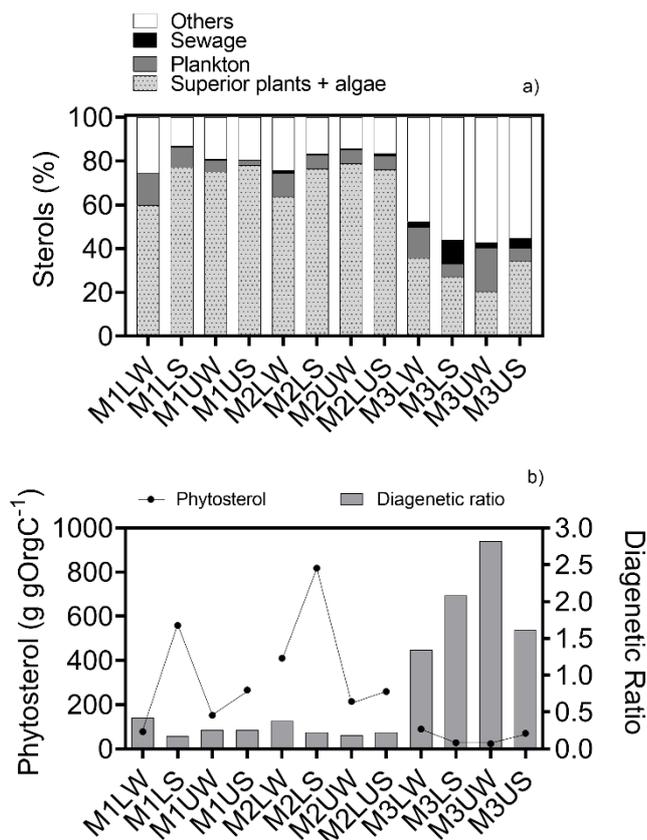
1148 Fig. 2. Spatial comparison of the elementary composition among Mamanguá (M1), Guapimirim
 1149 (M2) and Guaratiba (M3) mangroves soils (Kruskal Wallis, $p < 0,05$), in which a) total organic
 1150 carbon (OC, mg g^{-1}), b) total nitrogen (TN, mg g^{-1}), c) total phosphorus (TP, $\mu\text{g g}^{-1}$), d) isotopic
 1151 ratios of ^{13}C ($\delta^{13}\text{C}$, ‰), e) isotopic ratios of ^{15}N ($\delta^{15}\text{N}$, ‰), f) organic phosphorus (OP, $\mu\text{g g}^{-1}$), g)
 1152 OC to TN ratio (C:N), h) OC to TP ratio (C:P), and i) inorganic phosphorus concentration (IP, $\mu\text{g g}^{-1}$).
 1153 Horizontal line represent median, bars represent interquartile range, and different letters
 1154 represent statistically significant difference.

1155



1156
 1157 Fig. 3. Relationships between (a) $\delta^{15}\text{N}$ and $\delta^{13}\text{C}$ in soils, (b) C:N and $\delta^{13}\text{C}$ in soils, (c) $\delta^{15}\text{N}$ and
 1158 $\delta^{13}\text{C}$ in leaves and roots, and (d) C:N and $\delta^{13}\text{C}$ in leaves and roots of Mamanguá (M1), Guapimirim
 1159 (M2), and Guaratiba (M3) mangroves, including upper and lower zones. The ranges of terrestrial
 1160 plants, marine algae and freshwater algae are those reported in (Leng and Lewis, 2017). Sewage
 1161 range data reported in Barros et al. (2010).

1162
 1163
 1164
 1165
 1166



1167

1168 Fig.4. a) Relative contribution of different sources of sterols in soils of upper (U) and lower (L)

1169 zone in Mamanguá (M1), Guapimirim (M2) and Guaratiba (M3) mangroves during winter (W)

1170 and summer (S) periods. Sewage origin identified by the presence of 5β-cholestan-3β-ol

1171 (coprostanol) and 5β-cholestan-3α-ol (epicoprostanol), plankton origin identified by cholest-5-em-

1172 3β-ol (cholesterol) and 5α-cholestan-3β-ol (cholestanol), and higher plant and algae identified by

1173 24-methylcholesta-5-en-3β-ol(campesterol), 24-ethylcholesta-5,22-dien-3β-ol (stigmasterol) and

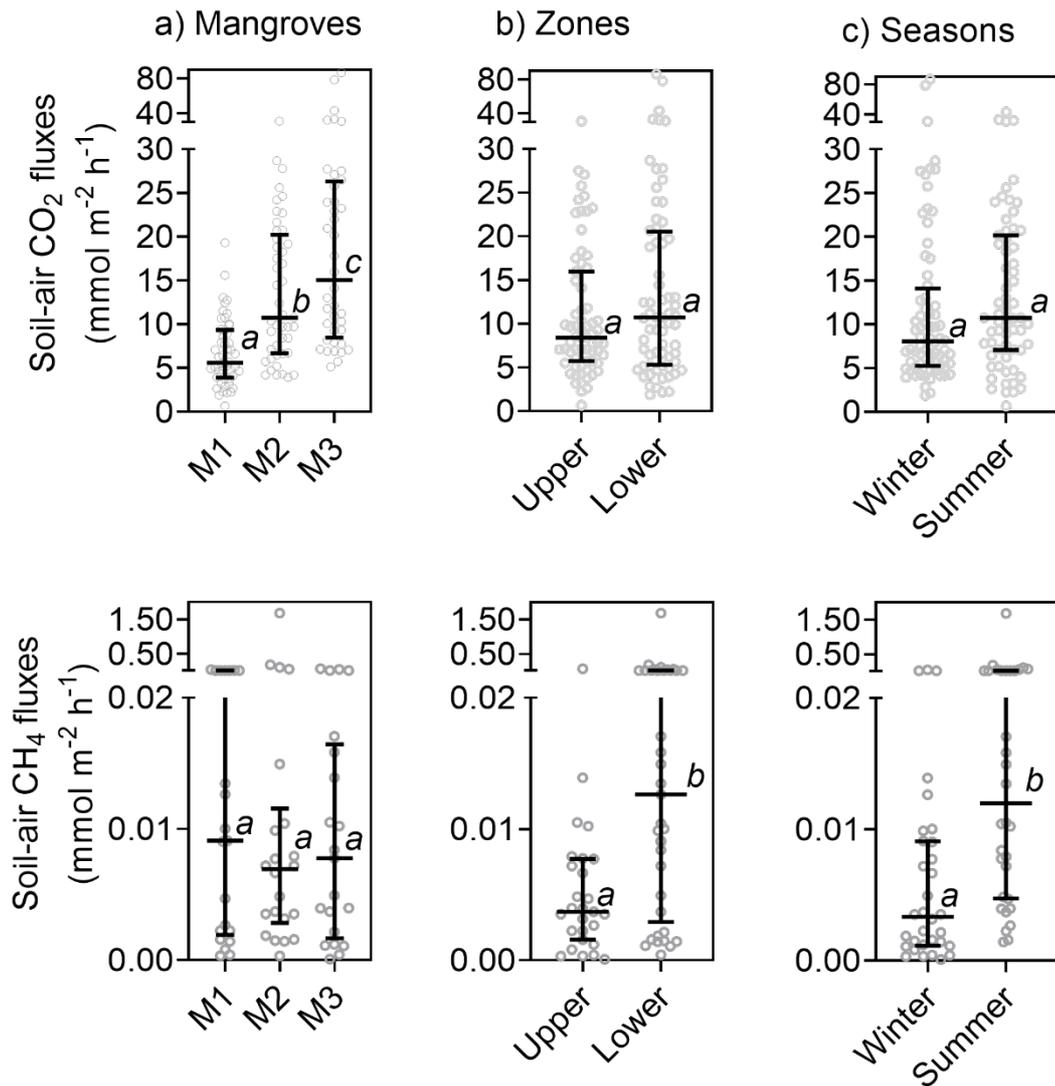
1174 24- ethylcholesta-5-en-3β-ol (β-sitosterol). b) Comparison between diagenetic ratio (bars) and

1175 phytosterols concentration (µg gOrgC⁻¹ black dots and lines) in upper (U) and lower (L) zone of

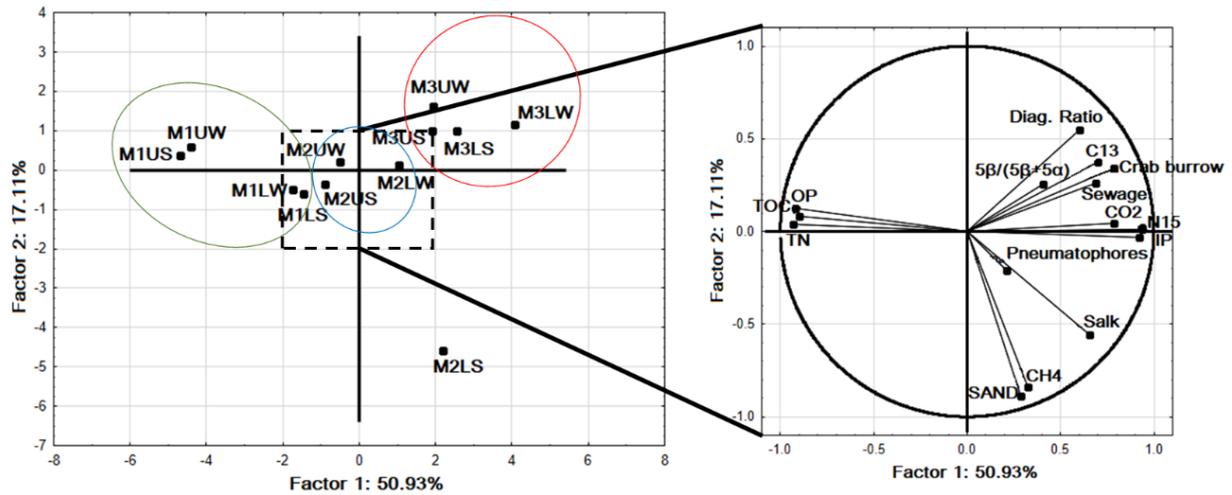
1176 Mamanguá (M1), Guapimirim (M2) and Guaratiba (M3) mangroves during summer (S) and winter

1177 periods (W).

1178



1179
 1180 Fig. 5. CO₂ and CH₄ (mmol m⁻² h⁻¹) fluxes from surface soil to the atmosphere in the upper and
 1181 lower zones of Mamanguá (M1) Guapimirim (M2) and Guaratiba (M3) mangroves during summer
 1182 and winter periods. Horizontal line represent median, bars represent interquartile range, and
 1183 different letters represent statistically significant difference among ecosystems (Kruskal Wallis
 1184 Test, p<0,05), intertidal zones and year seasons (Mann-Whitney Test, p<0.05). Clear circles
 1185 represent chambers measurements (n=3-5 chambers per zone: season, which were measured 3-7
 1186 times consecutively).



1188

1189 Fig. 6. Principal component analysis showing the magnitude and the direction of correlations
 1190 between the different dependent variables: CO₂ and CH₄ fluxes and independent variables: total
 1191 organic carbon (OC), total nitrogen (NT), carbon 13 ($\delta^{13}\text{C}$), nitrogen 15 ($\delta^{15}\text{N}$), diagenetic ratio,
 1192 sewage contamination ratio $5\beta:(5\beta+5\alpha)$, sewage presence (coprostanol + epicoprostanol),
 1193 inorganic phosphorus (IP), organic phosphorus (OP), sand, and total alkanes (ΣNAlk) in the
 1194 mangroves of Mamanguá (M1), Guapimirim (M2), and Guaratiba (M3) according to the two first
 1195 axes. The green, blue, and red circles indicate sampling sites from M1, M2, and M3, respectively.

1196 **Tables**

1197 Table 1. Median (25-75% interquartile range) values of CO₂ (mmol m⁻² h⁻¹) and CH₄ (μmol m⁻² h⁻¹) fluxes in the soil-air interface, elementary
 1198 composition (C, N, P in mg g⁻¹) of surface soil, and number of days of exposed soil conditions in a year in the Mamanguá (M1), Guapimirim
 1199 (M2), and Guaratiba (M3) mangroves at upper and lower zone during summer and winter period for spring tide.

	Mamanguá (M1)				Guapimirim (M2)				Guaratiba (M3)			
	Upper		Lower		Upper		Lower		Upper		Lower	
	Winter	Summer	Winter	Summer	Winter	Summer	Winter	Summer	Winter	Summer	Winter	Summer
CO ₂	5.52 (4.5-7.5)	4.59 (2.9-8.4)	5.0 (3.1-11.2)	8.5 (4.8-10.4)	9.7 (6.1-10.4)	19.5 (16.5-23.9)	6.6 (4.5-23.1)	19.18 (11.6-31.2)	14.8 (6.8-26.1)	8.6 (7.3-13.16)	12.1 (10.5-53.1)	24.0 (21.5-43.1)
CH ₄	1 (1-2)	2 (2.5-3)	9 (13-21)	10 (21-23)	3 (4-7)	2 (4-7)	1 (1-7)	8 (39.5-131.5)	1 (2-4)	4 (9-27.5)	1 (2-5)	8 (17-25)
OC	391.8 (370-407)	414.1 (395.9-433.3)	130.9 (110.1-141.1)	115.5 (101.7-162.3)	127.7 (111.9-140)	150.6 (142-160)	79.1 (71-88.3)	67.2 (57.4-82.1)	58.8 (52.2-75.2)	44.7 (38.7-47)	40 (39.3-43.1)	75 (59.4-97.4)
TN	10.6 (10.5-11.1)	11.1 (10.7-11.3)	7.4 (6.9-7.7)	7.9 (6.9-9.2)	6.7 (6.2-7.1)	9.3 (8.9-9.8)	4.7 (4.3-5.1)	4.5 (4.2-5.4)	4.8 (4.2-5.4)	4.1 (3.8-4.3)	4.5 (4.3-4.7)	5.2 (4.7-5.6)
TP	1.23 (1.00-1.8)	1.18 (1.05-1.29)	0.977 (0.92-1.15)	0.86 (0.81-0.92)	1.26 (1.21-1.32)	1.39 (1.35-1.53)	1.14 (1.06-1.19)	1.03 (0.96-1.13)	0.99 (0.96-1.03)	1.13 (1.09-1.16)	1.02 (0.99-1.04)	1.29 (1.21-1.33)
IP	0.09 (0.07-0.13)	0.05 (0.02-0.09)	0.41 (0.28-0.48)	0.32 (0.22-0.46)	0.74 (0.65-0.92)	0.71 (0.69-0.77)	0.84 (0.72-0.99)	0.80 (0.77-0.90)	0.78 (0.74-0.85)	0.77 (0.75-0.84)	0.94 (0.87-0.97)	0.73 (0.67-0.76)

OP	1.21 (0.88-1.72)	1.16 (1.01-1.22)	0.66 (0.49-0.79)	0.54 (0.42-0.59)	0.43 (0.27-0.54)	0.67 (0.59-0.82)	0.31 (0.20-0.38)	0.19 (0.11-0.29)	0.21 (0.15-0.26)	0.33 (0.24-0.37)	0.10 (0.05-0.15)	0.53 (0.42-0.59)
C:N	43.2 (38.5-44.7)	42.6 (41.8-45.6)	20.6 (18.3-21.5)	17.6 (16.7-20.4)	22.3 (21.1-23.8)	18.9 (18.2-19.5)	19.0 (16.9-22.1)	17.1 (15.5-18.2)	14.8 (13.5-16.5)	12.4 (11.1-13.5)	10.6 (9.9-11.7)	16.4 (14.9-21.0)
C:P	301 (221-396)	323 (287-396)	115 (107-143)	139 (121-176)	102 (100-111)	105 (102-111)	73 (68-77)	65 (56-74)	59 (53-76)	40 (37-42)	39 (38-42)	56 (50-78)
$\delta^{15}\text{N}$	-0.3 (-1.2-0.9)	0.5 (0-1.4)	2.4 (0.9-3.1)	1.9 (1.7-2.5)	5.2 (5-5.5.4)	3.4 (3-3.5)	6.6 (6.4-7.0)	6.2 (6-6.4)	6.6 (6-7.4)	6.9 (6.5-7.1)	7.0 (6.8-7.4)	5.3 (5.2-5.5)
$\delta^{13}\text{C}$	-29.2 (-29.6--29.1)	-30.3 (-30.6--29.9)	-24.8 (-25--24.1)	-25.8 (-25.9--25.2)	-28.5 (-28.9--27.7)	-28.4 (-28.6--28.2)	-27.0 (-27.6--26.8)	-28.1 (-28.8--27.8)	-22.9 (-23.7--22.2)	-22.8 (-24.3--21.8)	-14.7 (-17.4--13.3)	-25.7 (-27.1--22.6)
SAND%	0.1 (0-0.3)	0 (0-52.8)	0	0.1 (0-0.1)	0 (0-0.4)	0 (0-0.3)	5.1 (4.3-36.2)	24.9 (0.2-33.4)	0.2 (0-0.6)	0.1 (0-0.4)	0 (0-0.1)	0.9 (0.4-2.6)
SILT%	86.2 (85.2-88.0)	67.7 (41-69.1)	75.4 (74.9-76.9)	78.8 (77.3-80.1)	87.5 (86.5-89.3)	86.4 (84.6-87.3)	87.4 (57.9-87.9)	66.5 (58.5-86.3)	75.9 (72.2-79.8)	71.1 (63.8-72.6)	81.3 (79.1-82.5)	85.2 (81.1-86.3)
CLAY%	6.7 (5.9-8.3)	15.4 (3.3-16.9)	11.9 (11.5-12.5)	10.5 (10.1-11.4)	7 (5.6-7.6)	7 (6.5-7.9)	4.3 (3.3-4.7)	4.6 (4.2-7.1)	14.2 (11.6-16.2)	17.2 (16.3-21.0)	11.4 (10.4-12.4)	8.2 (6.4-10.9)
OM %	64.8 (63.2-67.0)	73.1 (68.9-73.3)	33.8 (32.2-34.7)	29.7 (28.6-35.2)	32.7 (30.9-34.8)	34.44 (33.82-36.0)	23.2 (21.8-24.5)	18.4 (16.9-21.7)	22.8 (21.3-26.5)	18.7 (17.4-20.2)	19.7 (18.8-20.9)	24.7 (23.5-25.7)

1200

1201

1202 Table 2. Average (\pm SD) values of $\delta^{13}\text{C}$ (‰), $\delta^{15}\text{N}$ (‰) and C:N of leaves, stems and roots for the different species in the three studied
 1203 mangroves.

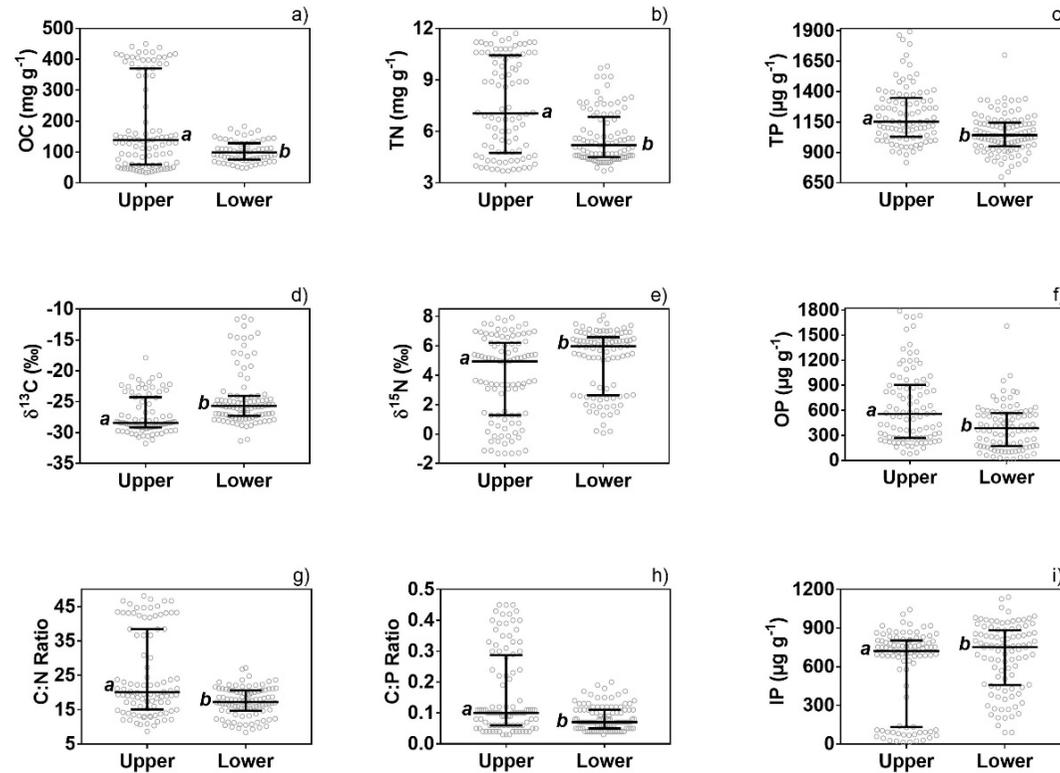
Mangroves	Species	$\delta^{13}\text{C}$			$\delta^{15}\text{N}$			C:N		
		Leaves	Stems	Roots	Leaves	Stems	Roots	Leaves	Stems	Roots
Mamanguá (M1)	<i>Rhizophora</i> **	-28.4 \pm 0.9	-29.2 \pm 1.3	-28.7 \pm 0.2	1.5 \pm 1.0	1.6 \pm 0.4	2.6 \pm 0.1	32,7 \pm 4,8	50,9 \pm 1,3	42,2 \pm 7,1
	<i>Avicennia</i> *	-29.9 \pm 1.9	-31.5 \pm 3.9	-31.2 \pm 4.3	2.8 \pm 0.9	3.8 \pm 2.3	4.2 \pm 0.6	35,9 \pm 2,3	106,5 \pm 66,1	39,6 \pm 6,7
Guapimirim (M2)	<i>Rhizophora</i> **	-28.5 \pm 2.9	-28.4 \pm 0.7	-30.1 \pm 2.2	4.3 \pm 0.9	3.8 \pm 0.7	4.8 \pm 0.4	34,3 \pm 1,1	41,8 \pm 9,0	35,0 \pm 5,6
	<i>Avicennia</i> *	-32.5 \pm 2.1	-29.4 \pm 1.9	-29.9 \pm 1.8	4.8 \pm 0.4	4.8 \pm 0.1	5.1 \pm 0.2	21,9 \pm 3,5	37,6 \pm 8,6	36,5 \pm 3,3
Guaratiba (M3)	<i>Laguncularia</i> *	-30.4 \pm 0.7	-30.2 \pm 0.2	-34.6 \pm 3.9	6.2 \pm 0.9	5.5 \pm 0.7	6.4 \pm 0.5	27,0 \pm 1,3	49,2 \pm 8,8	77,7 \pm 78,8
	<i>Rhizophora</i> **	-28.2 \pm 1.6	-27.1 \pm 1.9	-28.1 \pm 2.7	6.7 \pm 0.1	6.2 \pm 0.2	6.5 \pm 0.2	32,1 \pm 5,7	60,1 \pm 18,5	69,8 \pm 33,5
	<i>Avicennia</i> *	-32.2 \pm 2.9	-31.2 \pm 0.9	-33.6 \pm 2.5	6.5 \pm 0.4	6.4 \pm 0.4	7.6 \pm 0.3	18,1 \pm 5,1	23,5 \pm 5,2	119,5 \pm 76,3

1204 * Lower Intertidal Zone (Fringe Forest) and **Upper Intertidal Zone (Basin Forest). Mangrove Species: *Avicennia shaueriana*, *Rhizophora*

1205 *mangle* and *Laguncularia racemosa*.

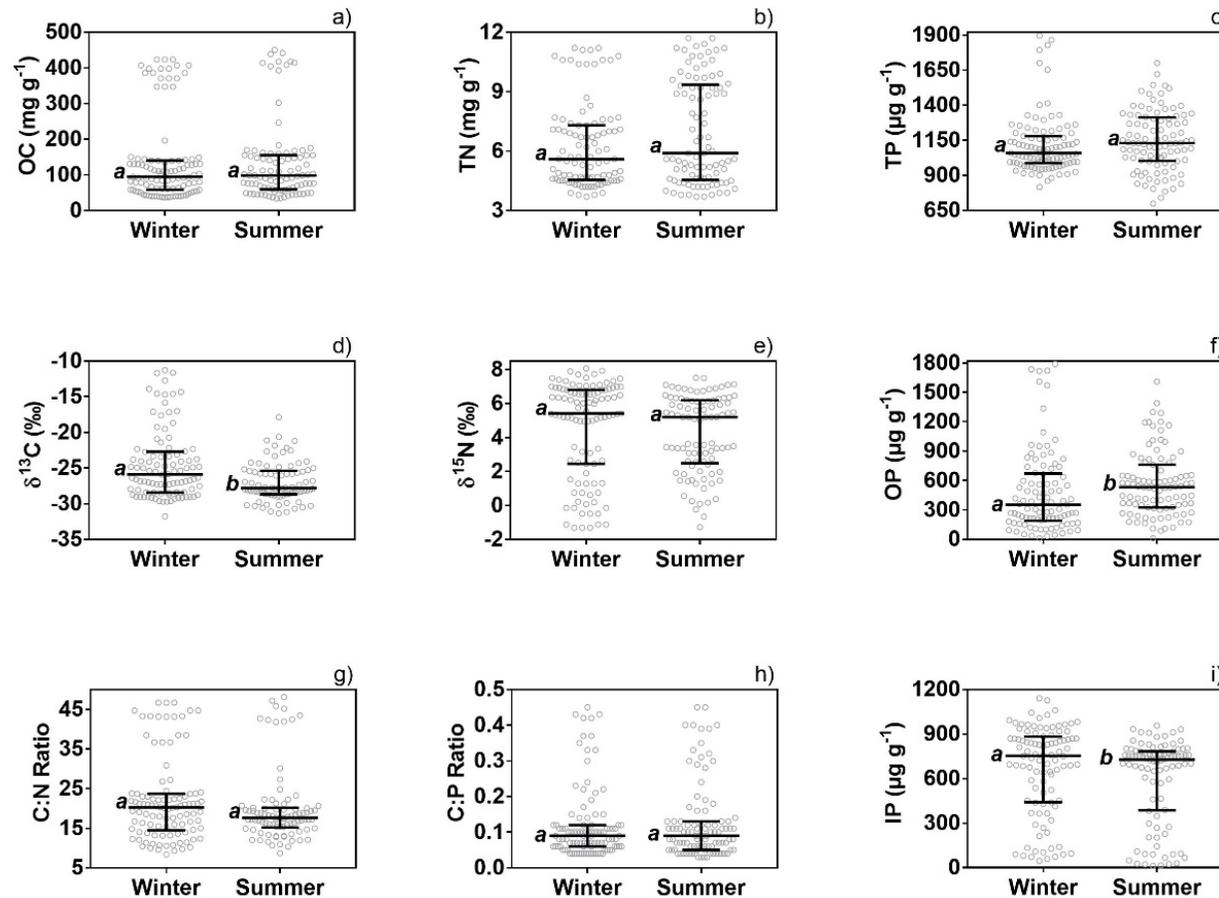
1206

1207 **Supplementary Figures**



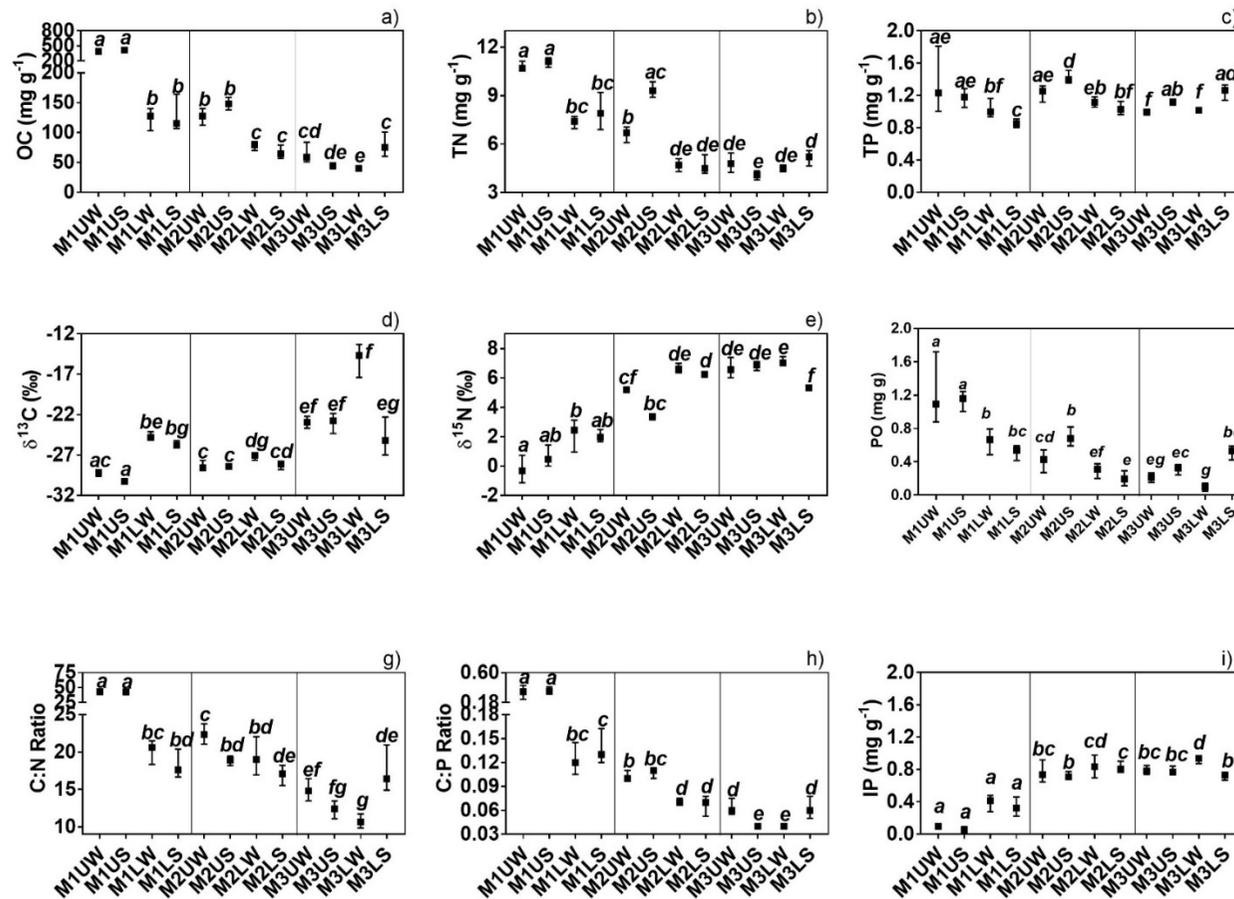
1208

1209 Fig. S1: Intertidal comparison of the elementary composition between upper and lower zones of the studied mangroves soils (Mann-Whitney,
 1210 $p < 0,05$), being a) total organic carbon (OC, mg g^{-1}), b) total nitrogen (TN, mg g^{-1}), c) total phosphorus (TP, $\mu\text{g g}^{-1}$), d) isotopic ratios of ^{13}C ($\delta^{13}\text{C}$,
 1211 ‰), e) isotopic ratios of ^{15}N ($\delta^{15}\text{N}$, ‰), f) organic phosphorus (OP, $\mu\text{g g}^{-1}$), g) OC to TN ratio (C:N), h) OC to TP ratio (C:P), and i) inorganic
 1212 phosphorus concentration (IP, $\mu\text{g g}^{-1}$). Horizontal line represent median, bars represent interquartile range, and different letters represent statistically
 1213 significant difference.



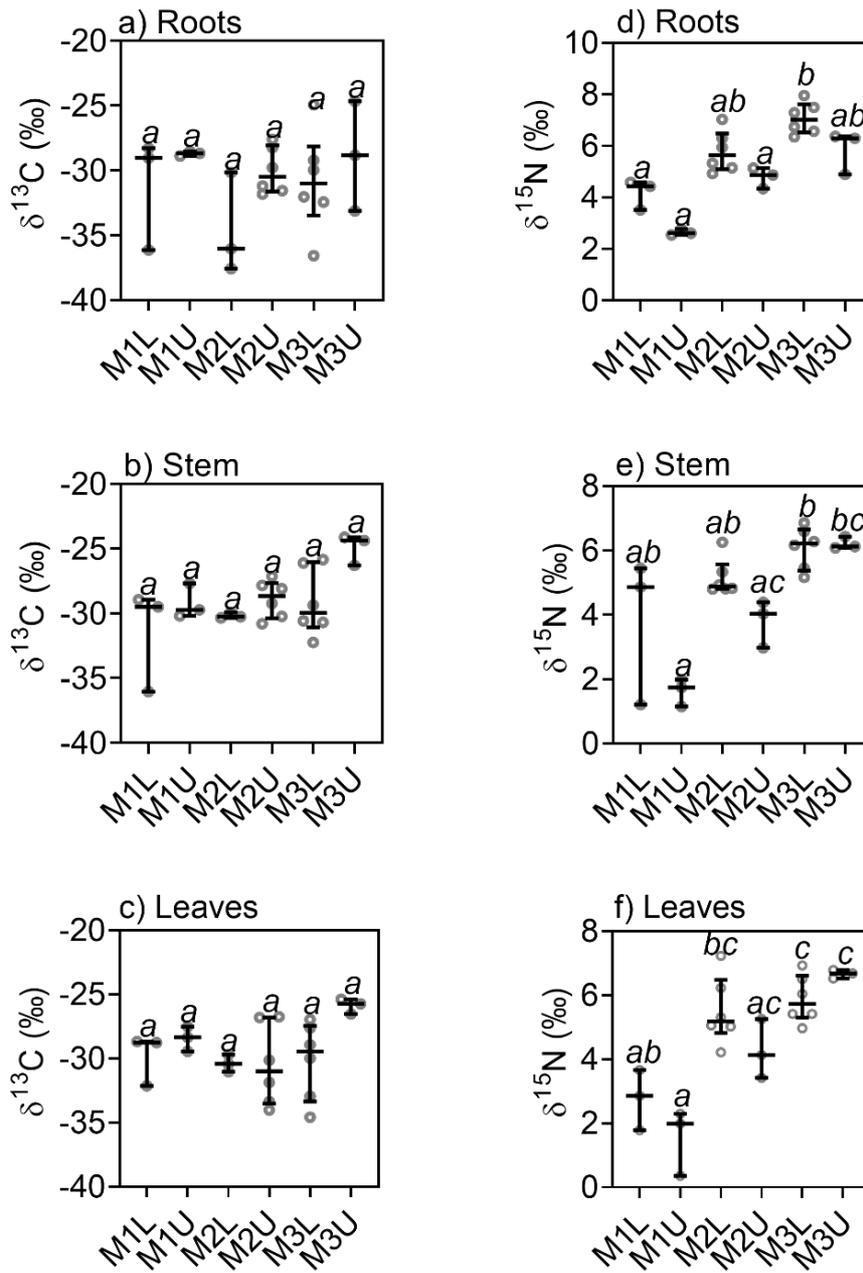
1214

1215 Fig. S2: Seasonal comparison (summer vs. winter) of the elementary composition among the studied mangroves soils (Mann-Whitney, $p < 0,05$),
 1216 being a) total organic carbon (OC, mg g⁻¹), b) total nitrogen (TN, mg g⁻¹), c) total phosphorus (TP, μg g⁻¹), d) isotopic ratios of ¹³C (δ¹³C, ‰), e)
 1217 isotopic ratios of ¹⁵N (δ¹⁵N, ‰), f) organic phosphorus (OP, μg g⁻¹), g) OC to TN ratio (C:N), h) OC to TP ratio (C:P), and i) inorganic phosphorus
 1218 concentration (IP, μg g⁻¹). Horizontal line represent median, bars represent interquartile range, and different letters represent statistically significant
 1219 difference.



1220

1221 Fig. S3: Spatio-temporal variability among mangroves, zones and seasons for the elementary composition of studied soils, being a) total organic
 1222 carbon (OC, mg g⁻¹), b) total nitrogen (TN, mg g⁻¹), c) total phosphorus (TP, mg g⁻¹), d) isotopic ratios of ¹³C (δ¹³C, ‰), e) isotopic ratios of ¹⁵N
 1223 (δ¹⁵N, ‰), f) organic phosphorus (OP, mg g⁻¹), g) total organic carbon and total nitrogen ratio (C:N), h) total organic carbon and total phosphorus
 1224 ratio (C:P), and i) inorganic phosphorus concentration (IP, mg g⁻¹). Horizontal line represent median, bars represent interquartile range, and different
 1225 letters represent statistically significant difference in the Kruskal-Wallis comparison followed by FDR Test (p<0.05).

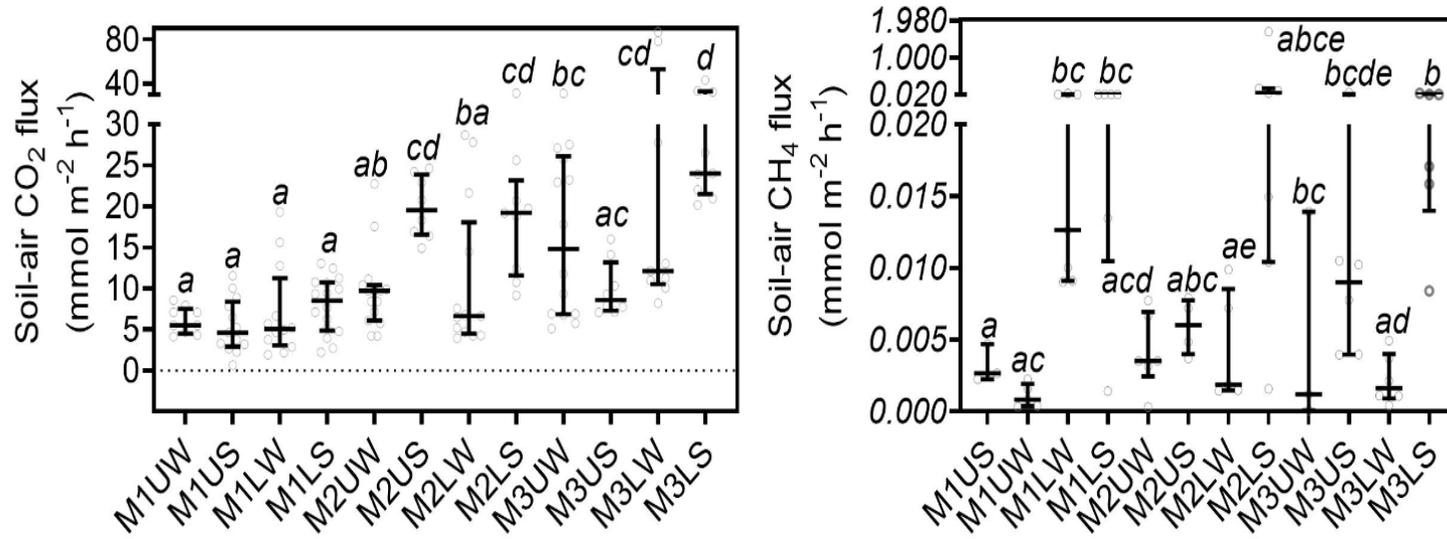


1226

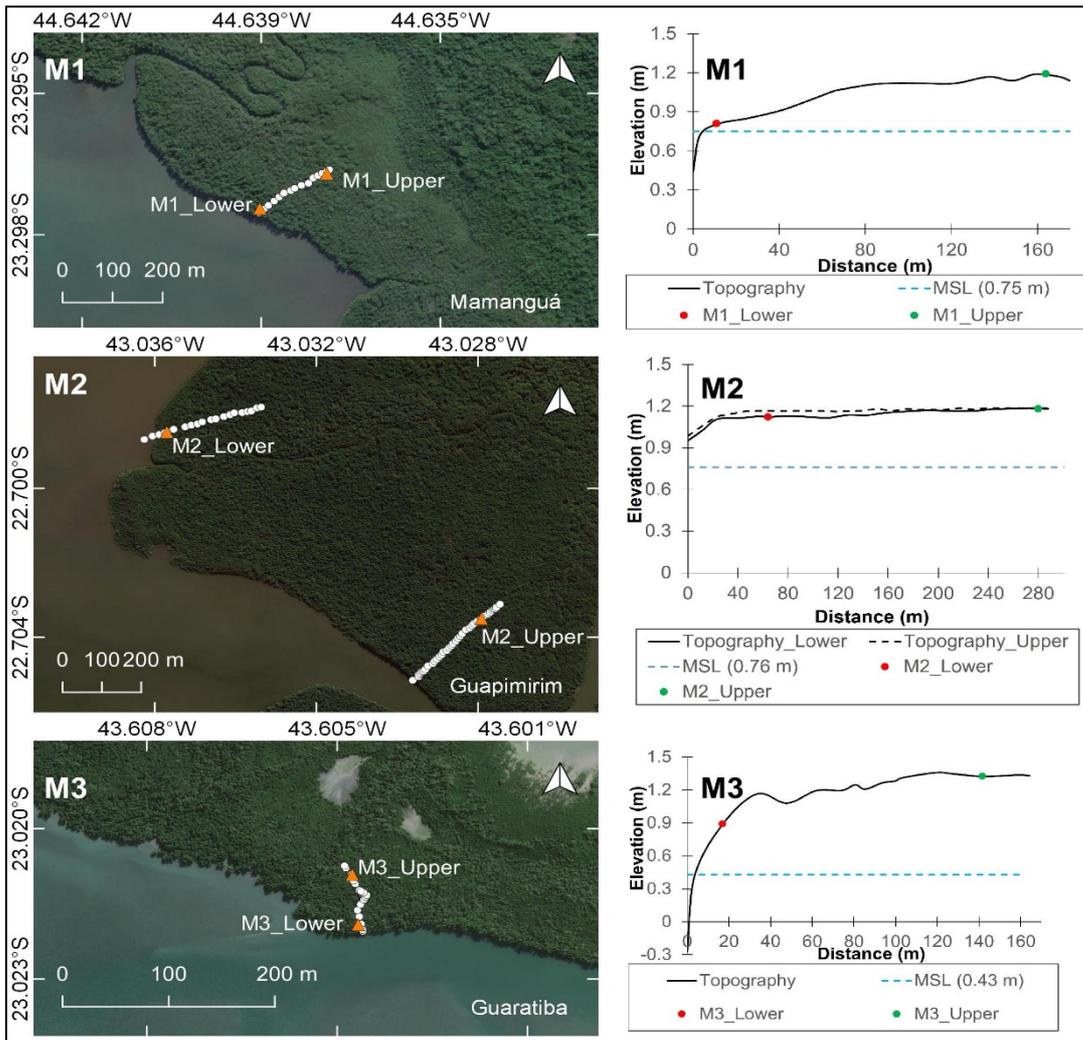
1227 Fig. S4. Comparison of $\delta^{15}\text{N}$ and $\delta^{13}\text{C}$ from roots, stems, and leaves among upper and
 1228 lower zones of Mamanguá (M1), Guapimirim (M2) and Guaratiba (M3) mangroves.
 1229 Horizontal line represent median, bars represent interquartile range, and different letters
 1230 represent statistically significant difference (Kruskal Wallis followed by FDR post-test;
 1231 $p < 0.05$).

1232

1233



1235 Fig S5: Spatio-temporal variability among mangroves, zones and seasons for the a) CO₂ and b) CH₄ fluxes in the soil-air interface. Horizontal line
 1236 represent median, bars represent interquartile range, and different letters represent statistically significant difference in the Analysis of Kruskal-
 1237 Wallis followed by FDR test ($p < 0.05$). Clear circles represent chambers measurements for CO₂ ($n = 3-5$ chambers per zone: season, which were
 1238 measured 3-7 times consecutively) and CH₄ ($n = 3-7$ chambers per zone: season)



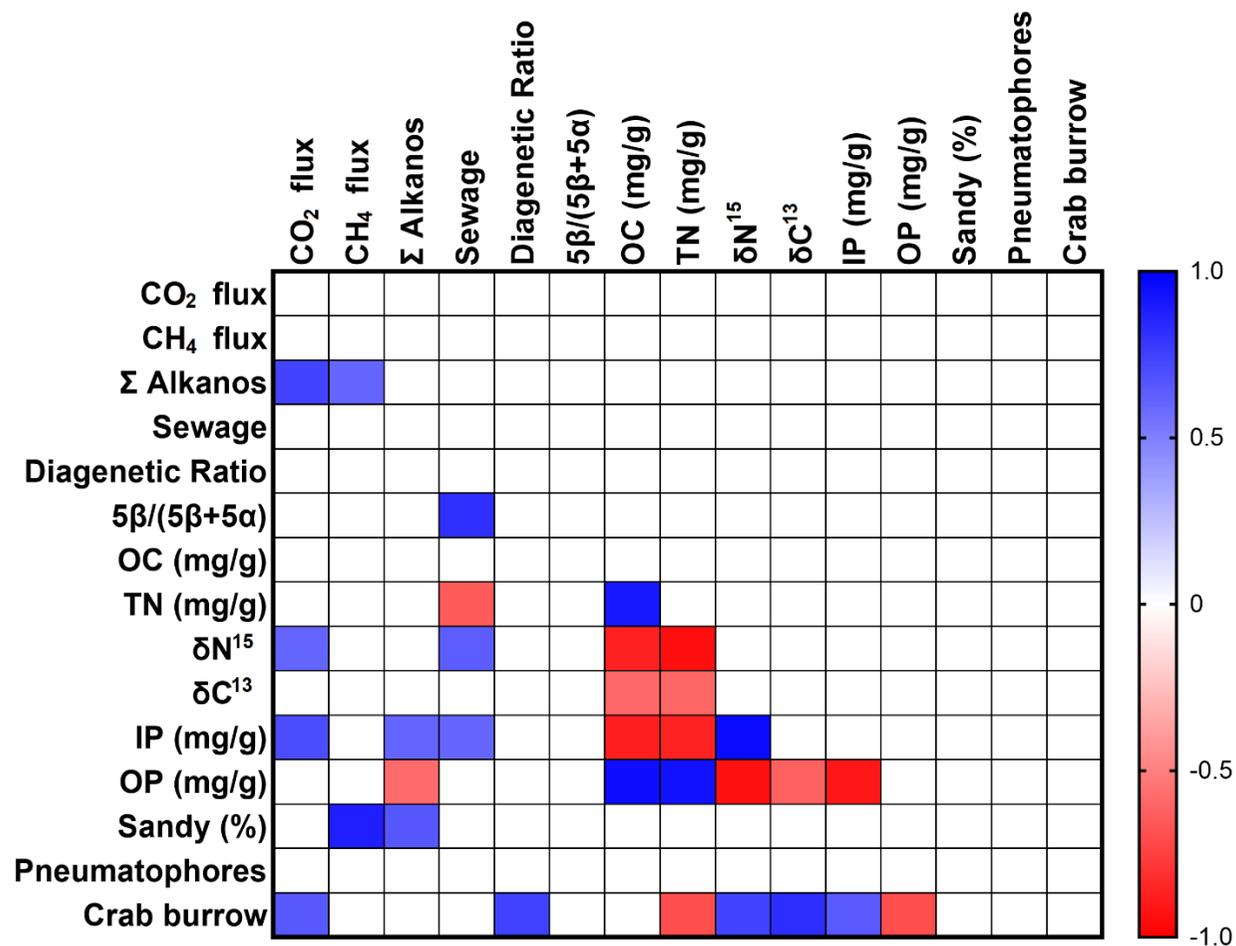
1239

1240 Fig. S6. Topographic profile (white circles) in the study mangroves M1, M2 and M3,
 1241 including the sampling points (red triangles) in lower and upper zone. Data calculated
 1242 based on the altimetry (Elevation) corrected for the MSL (Mean Sea-Level).

1243

1244

1245



1246
 1247 Figure S7: Spearman correlation among soil-air CO₂ and CH₄ flux, Σn-alkanes, Σsterols, diagenetic ratio, 5β:(5β+5α), OC, TN, δ¹³C, δ¹⁵N, IP, OP,
 1248 sand, pneumatophores and crab burrow. Red squares show significant negative relationships between parameters and blue square show significant
 1249 positive relationships between parameters (p<0.05). Open squares represent show non-significant relationships (p>0.05). Each data is the median
 1250 for each upper or lower zone, mangrove ecosystem, as well as winter or summer (N = 12).

1251 **Supplementar Tables**

1252 Table S1. Characteristics of the watershed from the studied mangroves areas.

Mangroves	Mamanguá (M1)	Guapimirim (M2)	Guaratiba (M3)
Location	Ilha Grande Bay	Guanabara Bay	Sepetiba Bay
Sampling sites ^a	23°17'48.12"S, 44°38'15.79"O* 23°17'50.80"S;44°38'20.50"O**	22°41'54.55"S,43°2'8.53"O* 22°42'12.60"S.43°1'40.50"O**	23°01'18.99"S,43°36'16.19"O* 23°01'15.28"S;43°36'17.03"O**
Watershead area (Km ²) ^b	17.9	2,078.8	200.8
Approximate Population in the watershed ^c	2,825	445,610	1,617,538
Population density of the municipality (Hab/Km ²) ^c	158	215	8,056
Dominant land use ^d (%)			
Urban	0.0	3.8	27.8
Fields	0.7	54.4	33.9
Upward Forest	91.8	40.4	30.8
Mangroves	7.5	1.3	6.0
Water	0.0	0.1	0.1
Others ^c	0.0	0.1	1.3
Level of modification	Relatively pristine	Modified	Extensively modified
Dominant mangroves species	<i>A. shaueriana</i> *, <i>R. mangle</i> **	<i>L. racemosa</i> *, <i>R. mangle</i> **	<i>A. shaueriana</i> *, <i>R. mangle</i> *. **

1253 ^a Mangrove Forest.1254 ^bGuapimirim, Cachoeira de Macacu and Caceribu sub watershed in M2; and Portinho, Piraquê, Cabuçu and Porto sub watershed in M3.1255 ^cData from The Brazilian Institute for Geography and Statistics (IBGE) in 2010 (concerning the approximate population of the districts and villages
1256 which each studied watershed).

1257 ^dLand use and land cover was based on the MapBiomas dataset (2017), available at <https://plataforma.mapbiomas.org/map#coverage>.

1258 ^eOthers represent beaches, non-vegetated areas (hilltop, rocky outcrops).

1259 * Lower intertidal zone

1260 **Upper intertidal zone.

1261

1262

1263

1264

1265

1266

1267

1268

1269

1270

1271 Table S2: Physicochemical characteristics of temperature (°C), salinity, DO saturation (%DO, %), dissolved inorganic nitrogen (DIN, uM), and
 1272 fosfato (PO₄-P, uM) in surface bay waters around Mamanguá (M1), Guapimirim (M2) and Guaratiba (M3) mangroves.

	Mamanguá (M1)		Guapimirim (M2)		Guaratiba (M3)	
	Winter	Summer	Winter	Summer	Winter	Summer
Temperature*	25.7-27.2	30.0-29.0	23.0-22.0	35.3-37.0	24.0-26.0	35.4-30.8
Salinity*	30.4-32.0	31.6-32.6	25.0-22.6	20.0-21.3	29.0-29.0	23.7-27.3
% DO*	78.7-63.7	60.0-69.3	78.7-54.7	58.8-62.0	138.9-57.0	210.0-51.4
DIN**	0.5-0.5	1.1-13.5	14.4-17.6	26.1-37.4	no data	20.6-86.9
PO ₄ -P**	0.9-1.2	1.2-1.4	0.7-0.8	1.6-1.8	no data	1.5-2.7

1273
 1274 * Temperature and %DO were taken using a YSI Pro ODO thermoximeter, while salinity by a WTW Cond 330i conductivimeter.
 1275 ** DIN as the sum of NH₄-N, NO₂-N, and NO₃-N, as well as PO₄-P were determined by standard methods (APHA et al., 2012) using a Hach
 1276 DR/4000 spectrophotometer.
 1277

1278 Table S3: Molecular composition (Total organic carbon (OC, g g⁻¹), sterol (μg gOrgC⁻¹), and Σn-alkanes (μg g⁻¹) concentrations, as well as
 1279 diagnostic ratio in surface soils in the Mamanguá (M1), Guapimirim (M2), and Guaratiba (M3) mangroves at upper and lower zone during summer
 1280 and winter period for spring tide.

	Mamanguá (M1)				Guapimirim (M2)				Guaratiba (M3)			
	Upper		Lower		Upper		Lower		Upper		Lower	
	Winter	Summer	Winter	Summer	Winter	Summer	Winter	Summer	Winter	Summer	Winter	Summer
OC	0.39	0.41	0.13	0.12	0.13	0.15	0.08	0.06	0.06	0.04	0.04	0.08
Coprostanol	0.88	0.29	<DL	1.71	1.57	1.09	4.45	3.22	0.95	1.01	3.55	5.08
Epicoprostanol	0.49	<DL	<DL	0.87	<DL	2.62	4.84	<DL	1.89	8.00	3.00	6.52
Cholesterol	6.65	4.02	14.61	51.78	10.60	13.87	55.24	46.80	2.15	9.17	21.25	3.32
Cholestanol	3.71	3.43	4.69	16.07	6.74	7.79	14.03	22.04	21.75	2.80	13.55	2.81
Campesterol	15.85	26.46	11.11	52.51	23.34	26.99	70.87	89.68	9.53	16.88	29.62	7.67
Campestanol	10.10	14.59	17.30	30.86	11.72	21.36	67.60	56.74	51.68	104.51	94.82	52.66
Stigmasterol	61.15	101.58	38.49	265.04	69.50	86.40	182.87	341.91	7.22	26.46	42.64	12.01
Stigmastanol	13.09	23.62	9.61	35.33	11.22	14.79	54.65	57.36	3.57	5.15	13.85	2.70
β-Sitosterol	75.08	138.57	28.22	240.98	121.54	146.10	156.98	386.47	7.25	27.06	17.48	8.26
β-Sitostanol	15.50	28.45	6.15	29.42	15.49	20.34	34.24	65.78	12.44	3.37	11.19	2.62
Total Sterols	202.50	341.00	130.18	724.56	271.73	341.35	645.75	1,070.00	118.44	204.41	250.94	103.65
Phytosterol	152.08	266.61	77.83	558.52	214.39	259.49	410.72	818.06	24.00	70.39	89.74	27.94
Diagenetic Ratio	0.25	0.25	0.42	0.17	0.18	0.22	0.38	0.22	2.82	1.61	1.34	2.08
5β:(5β+5α)	0.19	0.08	<DL	0.10	0.19	0.12	0.24	0.13	0.04	0.27	0.21	0.64
Cop:Cho	0.13	0.07	<DL	0.03	0.15	0.08	0.08	0.07	0.44	0.11	0.17	1.53
Σn-alkanes	186.30	242.60	444.10	1066.80	743.40	2327.30	1010.50	4021.1	693.10	1129.40	3287.2	1655.80
LMW:HMW	0.28	0.22	0.34	0.25	0.21	0.18	0.18	0.15	0.45	0.51	0.22	0.07
CPI	4.10	2.40	4.0	4.80	2.70	4.00	2.90	1.60	2.20	2.00	1.30	2.90
TAR	31.80	33.30	19.9	19.70	24.60	13.40	39.70	15.10	5.10	3.90	20.3	53.5
Pr:Ph	0.30	0.30	0.40	0.60	0.20	0.40	0.20	0.30	0.40	0.20	0.60	0.40
Odd:Even	4.10	2.40	3.90	4.80	2.70	4.00	2.90	1.60	2.20	2.00	1.30	2.90

1281
 1282 Phytosterol includes campesterol, stigmasterol, and β-sitosterol. Diagenetic ratio calculated as Σn-stanol:Σn-sterol. 5β:(5β+5α) calculated as
 1283 coprostanol:(coprostanol+cholestanol). Cop:Cho calculated as coprostanol:cholesterol. CPI: Carbon preferential index considering C_{n12-38}.
 1284 LMW:HMW calculated as Σshort chain (C₁₄₋₂₃): Σlong chain (C₂₄₋₄₀). TAR (Terrestrial:Aquatic ratio) calculated as Σ (C₂₇; C₂₉; C₃₁) :Σ (C₁₅; C₁₇;
 1285 C₁₉). Pr: Ph = pristano:phytano. All data normalized by OC concentration in the soil (for original data in μg g⁻¹ see Fig. S3).
 1286

1287 Table S4. Total organic carbon (OC g g⁻¹) and sterols concentrations (μg g⁻¹). Σn-alkanos (μg g⁻¹), diagenetic ratio. 5β:(5β+5α), and Cop: Cho in
 1288 upper and lower zone of Mamanguá (M1). Guapimirim (M2) and Guaratiba (M3) mangroves during winter and summer periods. Data used to
 1289 calculate standardize values reported in table S3 in μg gCOrg⁻¹.

1290

	Mamanguá (M1)				Guapimirim (M2)				Guaratiba (M3)			
	Upper		Lower		Upper		Lower		Upper		Lower	
	Winter	Summer	Winter	Summer	Winter	Summer	Winter	Summer	Winter	Summer	Winter	Summer
OC	0.39	0.41	0.13	0.12	0.13	0.15	0.08	0.06	0.06	0.04	0.04	0.08
Coprostanol	0.35	0.12	<DL	0.20	0.20	0.16	0.35	0.21	0.06	0.05	0.14	0.38
Epicoprostanol	0.19	<DL	<DL	0.10	<DL	0.39	0.38	<DL	0.11	0.36	0.12	0.49
Cholesterol	2.61	1.67	1.87	5.98	1.35	2.06	4.37	3.02	0.13	0.41	0.86	0.25
Cholestanol	1.45	1.42	0.60	1.86	0.86	1.16	1.11	1.42	1.28	0.13	0.55	0.21
Campesterol	6.21	10.96	1.42	6.06	2.98	4.00	5.61	5.79	0.56	0.75	1.19	0.58
Campestanol	3.96	6.04	2.21	3.56	1.50	3.17	5.35	3.66	3.04	4.67	3.82	3.97
Stigmasterol	23.96	42.06	4.91	30.61	8.88	12.81	14.47	22.07	0.42	1.18	1.72	0.91
Stigmastanol	5.13	9.78	1.23	4.08	1.43	2.19	4.32	3.70	0.21	0.23	0.56	0.2
β-Sitosterol	29.42	57.38	3.60	27.83	15.52	21.67	12.42	24.95	0.43	1.21	0.7	0.62
β-Sitostanol	6.07	11.78	0.79	3.40	1.98	3.02	2.71	4.25	0.73	0.15	0.45	0.2
Total Sterols	79.34	141.21	16.61	83.69	34.70	50.62	51.08	69.07	6.96	9.14	10.11	7.81
Phytosterol	59.58	110.40	9.93	64.51	27.38	38.48	32.49	52.81	1.41	3.15	3.62	2.11
Diagenetic Ratio	0.42	0.17	0.25	0.25	0.38	0.22	0.18	0.22	1.34	2.08	2.82	1.61
5β:(5β+5α)	0.20	0.10	<DL	0.10	0.20	0.10	0.20	0.10	0.60	<DL	0.10	0.2
Cop:Cho	0.10	0.10	<DL	<DL	0.10	0.10	0.10	0.10	1.50	0.40	0.10	0.2
Σn-alkanes	73.9	101.60	58.50	125.50	96.60	350.70	81.20	264.00	43.10	55.20	134.20	125.40
LMW:HMW	0.30	0.20	0.40	0.30	0.20	0.20	0.20	0.20	0.50	0.70	0.20	0.10
CPI	4.10	2.40	3.90	4.80	2.70	4.00	2.90	1.60	2.20	2.00	1.30	2.90
RTA	31.80	33.30	19.90	19.70	24.6	13.40	39.70	15.10	5.10	3.90	20.30	53.50
Pr:Ph	0.30	0.30	0.40	0.60	0.20	0.40	0.20	0.30	0.40	0.20	0.60	0.40
Odd:Even	4.10	2.40	3.90	4.80	2.70	4.00	2.90	1.60	2.20	2.00	1.30	2.90

1291 Legenda: Phytosterol includes campesterol. stigmasterol. and β -sitosterol. Diagenetic ratio calculated as $\sum n\text{-stanol}:\sum n\text{-sterol}$. $5\beta:(5\beta+5\alpha)$
1292 calculated as coprostanol:(coprostanol+cholestanol). Cop:Cho calculated as coprostanol: cholesterol. CPI: Carbon preferential index considering
1293 $C_{n_{12-38}}$. LMH:HMW calculated as \sum short chain (C_{14-23}): \sum long chain (C_{24-40}). TAR (Terrestrial:Aquatic ratio) calculated as $\sum (C_{27}; C_{29}; C_{31}) : \sum$
1294 ($C_{15}; C_{17}; C_{19}$). Pr:Ph = pristano:phytano.

1295

1296

1297

1298

1299

1300

1301

1302

1303

1304 Table S5. Concentration of n-alkanes from C-14 to C-40 chain ($\mu\text{g g}^{-1}$) in surface soil of lower (L) and upper(U) zone from Mamanguá (M1).
 1305 Guapimirim (M2) and Guaratiba (M3) mangroves during winter (W) and summer (S) periods.

	Mamanguá (M1)				Guapimirim (M2)				Guaratiba (M3)			
	Upper		Lower		Upper		Lower		Upper		Lower	
	Winter	Summer	Winter	Summer	Winter	Summer	Winter	Summer	Winter	Summer	Winter	Summer
C14	0.12	0.19	0.10	0.47	0.13	4.20	0.09	1.55	0.19	0.49	0.16	0.51
C15	0.12	0.16	<LD	0.58	0.16	7.02	0.11	3.86	0.64	1.23	0.19	0.54
C16	0.12	0.13	0.39	1.28	0.34	4.98	0.19	3.60	0.78	1.42	0.69	0.67
C17	0.22	0.25	0.51	1.25	0.55	3.94	0.24	1.85	1.01	1.58	0.88	0.33
C18	0.95	0.48	1.10	1.73	0.38	1.57	0.85	1.25	0.74	1.86	0.48	0.19
C19	0.54	0.64	0.55	0.94	0.76	2.51	0.58	0.89	0.72	0.82	0.76	0.14
C20	1.11	0.92	1.33	0.99	0.85	2.35	0.89	1.56	0.91	1.69	0.70	0.22
C21	2.52	2.70	2.07	3.24	2.52	5.74	2.59	3.36	2.98	3.08	10.87	2.33
C22	0.65	1.77	0.83	1.72	1.56	2.66	1.13	3.36	0.90	0.95	2.27	<LD
C23	9.41	10.81	7.39	12.19	8.96	18.80	5.71	13.40	3.80	3.88	7.04	3.05
C24	3.99	7.96	1.96	3.30	5.14	11.89	3.05	17.76	1.66	1.57	9.53	1.28
C25	17.33	19.87	12.28	24.53	18.41	45.24	10.62	33.29	5.04	7.18	15.67	7.05
C26	2.65	6.84	1.43	2.37	6.21	6.49	4.13	26.67	1.00	2.56	16.72	1.80
C27	11.29	14.97	7.18	18.54	15.13	54.71	12.20	43.39	4.45	4.72	18.10	8.76
C28	3.06	6.66	2.00	4.59	5.92	16.54	5.24	25.55	3.07	2.99	15.41	3.75
C29	14.58	16.58	9.77	24.60	15.26	83.98	19.95	45.40	5.11	5.57	13.31	19.11
C30	1.40	3.15	1.39	3.09	3.48	13.61	3.25	12.37	2.40	2.12	8.05	7.99
C31	2.05	3.24	4.15	11.31	5.89	41.84	4.40	10.68	2.58	3.72	5.56	26.69
C32	0.27	0.93	0.36	1.38	0.95	3.47	1.03	4.26	0.61	0.81	2.98	5.51
C33	0.43	0.97	1.29	4.24	1.49	11.23	2.41	3.36	1.20	1.47	2.01	15.73
C34	0.09	0.19	0.11	0.48	0.25	0.85	0.43	0.79	0.34	0.31	0.71	4.79
C35	0.11	0.29	0.22	0.40	0.24	1.39	0.26	0.84	0.31	0.30	0.28	9.22
C36	<LD	0.77	0.25	<LD	0.34	0.15	0.44	0.26	0.32	0.18	0.11	5.11

C37	<LD	<LD	<LD	<LD	<LD	<LD	0.14	0.26	<LD	<LD	<LD	<LD
C38	<LD	<LD	<LD	<LD	<LD	<LD						
C39	<LD	<LD	<LD	<LD	<LD	<LD						
C40	<LD	<LD	<LD	<LD	<LD	<LD						

1306

1307

1308

1309

1310

1311

1312

1313

1314

1315

1316

1317

1318

1319 Table S6: Values of Spearman correlation coefficient (r_s) for statistically significant relationships ($p < 0.05$) reported in Fig. S5.

	CO ₂ flux	CH ₄ flux	Σ Alkanes	Sewage	Diag. Ratio	5β:(5β+5a)	OC	TN	δN ¹⁵	δC ¹³	IP (mg/g)	OP (mg/g)	Sandy (%)	Pneumatophores	Crab burrow
CO ₂ flux															
CH ₄ flux															
Σ Alkanes	0.74	0.60													
Sewage															
Diag. Ratio															
5β:(5β+5a)				0.82											
OC															
TN				-0.64			0.90								
δN ¹⁵	0.61			0.64			-0.87	-0.95							
δC ¹³							-0.59	-0.60							
IP (mg/g)	0.70		0.60	0.60			-0.88	-0.87	0.96						
OP (mg/g)			-0.59				0.94	0.93	-0.93	-0.63	-0.91				
Sandy (%)		0.88	0.66												
Pneumatophores															
Crab burrow	0.65				0.74			-0.69	0.73	0.82	0.65	-0.70			

1320

1321 Table S7. Eigenvectors. variables contribution based on correlations from principal component analysis (PCA). factors-variables correlations
 1322 (factor loadings) based on correlation between variables. Sewage shows coprostanol + epicoprostanol.

	Eigenvectors		Variable contributions		Factor loadings	
	Factor 1	Factor 2	Factor 1	Factor 2	Factor 1	Factor 2
CO ₂ flux	0.283877	0.026262	0.080586	0.000690	0.784619	0.042072
CH ₄ flux	0.116912	-0.525154	0.013668	0.275787	0.323138	-0.841284
Σ n-Alkanes	0.236693	-0.348214	0.056024	0.121253	0.654206	-0.557831
Sewage	0.248625	0.161782	0.061814	0.026173	0.687184	0.259171
Diagenetic Ratio	0.217566	0.340801	0.047335	0.116145	0.601340	0.545955
5β/(5β+5α)	0.146751	0.158754	0.021536	0.025203	0.405611	0.254320
OC	-0.325280	0.049447	0.105807	0.002445	-0.899055	0.079213
TN	-0.337825	0.024001	0.114126	0.000576	-0.933727	0.038448
δ ¹⁵ N	0.340042	0.007945	0.115629	0.000063	0.939856	0.012728
δ ¹³ C	0.252864	0.234537	0.063940	0.055008	0.698900	0.375722
IP	0.332472	-0.018883	0.110537	0.000357	0.918931	-0.030250
Sand	-0.333885	-0.076817	0.111479	0.005901	-0.922836	0.123060
OP	0.103943	-0.554104	0.010804	0.307031	0.287292	-0.887661
Pneumatophores	0.077257	-0.133223	0.005969	0.017748	0.213533	-0.213421
Crab burrows	0.284157	0.213590	0.080745	0.045620	0.785393	0.342165

1323