

Contrasting organic matter composition in pristine and eutrophicated mangroves revealed by fatty acids and stable isotopes (Rio de Janeiro, Brazil)

Mathias Chynel, Sofia Rockomanovic, Gwenaël Abril, Glenda Barroso, Humberto Marotta, Wilson Machado, Christian Sanders, Najet Thiney, Tarik Meziane

▶ To cite this version:

Mathias Chynel, Sofia Rockomanovic, Gwenaël Abril, Glenda Barroso, Humberto Marotta, et al.. Contrasting organic matter composition in pristine and eutrophicated mangroves revealed by fatty acids and stable isotopes (Rio de Janeiro, Brazil). Estuarine, Coastal and Shelf Science, 2022, 277, pp.108061. 10.1016/j.ecss.2022.108061. hal-03797455

HAL Id: hal-03797455 https://cnrs.hal.science/hal-03797455

Submitted on 4 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 Title

- 2 Contrasting organic matter composition in pristine and eutrophicated mangroves
- 3 revealed by fatty acids and stable isotopes (Rio de Janeiro, Brazil)

4

- 5 **Authors.**
- 6 Mathias Chynel^{1,*}, Sofia Rockomanovic¹, Gwenaël Abril^{1,2}, Glenda Barroso², Humberto
- 7 Marotta^{2,3}, Wilson Machado², Christian J. Sanders⁴, Najet Thiney¹, Tarik Meziane¹

8

9 **Affiliations**

- 10 ¹Muséum National d'Histoire Naturelle, Laboratoire Biologie des Organismes et
- 11 Ecosystème Aquatiques (UMR 8067 BOREA), Sorbonne Université, CNRS, IRD 207,
- 12 Université de Caen Normandie, Université des Antilles, 61 rue Buffon, 75005 Paris,
- 13 France
- 14 ²Programa de Pós-Graduação em Geociências (Geoquímica Ambiental),
- 15 Universidade Federal Fluminense, Niterói, RJ, Brazil
- ³Programa de Pós-Graduação em Geografia, Universidade Federal Fluminense,
- 17 Niterói, RJ, Brazil
- ⁴National Marine Science Centre, Faculty of Science and Engineering, Southern Cross
- 19 University PO Box 4321, Coffs Harbour, 2450 NSW, Australia
- 20 *Corresponding author: mathias.chynel@edu.mnhn.fr

21

Abstract

23

24

25

26

27

28

29

30

31

32

33

34

35

36

37

38

39

40

41

42

43

44

45

46

47

Mangrove sediments have a high capacity of carbon storage, as the result of larger organic matter (OM) inputs from mangrove trees (litter fall and fine roots production) than OM microbial degradation and export to coastal waters. Mangrove sediments also act as traps for suspended matter and particulate OM (POM) from surrounding water masses. Fatty acids (FAs) markers, δ^{13} C and δ^{15} N signatures were used here to characterize the OM composition in three mangroves located in three coastal embayments of the Rio de Janeiro state (Brazil) with increasing urbanization from a pristine mangrove M1 to a moderately impacted mangrove M2 and a highly impacted mangrove M3. In these mangroves, the $\delta^{15}N$ signature of tree leaves and sediments increases with anthropogenic influence, consistent with a large-scale eutrophication gradient along the three regions. At mangrove M1, predominant OM inputs from mangrove trees are highlighted by high proportions of long-chain fatty acids, particularly in the inland station, where high organic carbon concentrations (126±108 mg.g⁻¹) indicate limited sedimentation of mineral particles and high carbon storage capacities. The sedimentary OM of M3 mangrove was more labile as confirmed by the higher proportions of algal fatty acids, enriched δ^{13} C signature and the C/N ratio of 1.6 times lower (p < 0.001) than in the pristine mangrove M1. At the M2 mangrove site, high contribution of bacterial FAs (around 20%) to sedimentary OM and high proportion of poorly biodegradable saturated fatty acids suggest that bacteria degrade algal labile OM in surface sediments but do not mineralize the most refractory fraction of OM. At the eutrophic M3 site, our findings suggest that deposition of labile POM induced an increase of fungal biomass on the sediment, apparently enhancing the microbial loop, and potentially leading to mineralization of refractory OM and carbon losses through a priming effect.

48 **Keywords**

- 49 Blue carbon; Organic matter biodegradability; Cultural eutrophication; Microalgal
- 50 blooms; Fungi; Bacteria.

1. Introduction

51

52

53

54

55

56

57

58

59

60

61

62

63

64

65

66

67

68

69

70

71

72

73

74

75

Mangrove forests are coastal ecosystems characterized by the presence of woody plants tolerant to extreme environmental conditions such as high salinity and sediment anoxia. These forest systems are present in tropical and subtropical areas, and colonize a worldwide surface area between 137 600 km² (Bunting et al., 2018) and 157 000 km² (FAO, 2007). Brazil is the country with the 3rd largest mangrove cover on the globe, which representing 8.5% of the total surface area of mangroves worldwide (Webber, 2016). Mangrove forests have an average net primary production (NPP) between 1360 ± 450 g C m⁻² year⁻¹ (Bouillon et al., 2008a) and 1522 g C m⁻² year⁻¹ (Alongi, 2014), that is, 4 to 7 times higher than the NPP by coastal marine phytoplankton (Cloern et al., 2014). An important fraction of the OM produced by mangrove NPP is transferred to their sediments as litter fall and fine roots production, fuelling microbial respiration and CO₂ and CH₄ emission from the sediments to waters and the atmosphere (Alongi, 2020; Maher et al., 2018). However, anoxic conditions in the sediments slow down the degradation rates of OM and favour its preservation and burial over the long term. In addition, due to tidal inundation, exchange of organic and inorganic C occurs between mangrove sediments and the surrounding coastal waters (David et al., 2018; Maher et al., 2018; Santos et al., 2019). Recent estimates indicate that C accumulation in mangrove sediments may reach 41 Mt annually (Wang et al., 2021), representing a long-term C burial with high impact on global carbon budget and global warming mitigation (Kristensen et al., 2008a). Mangroves account for 15% of the "blue carbon" actually buried among all coastal marine ecosystems (Anand et al., 2020). The composition of mangrove sedimentary organic matter (SOM) is strongly influenced

by local sources of OM (Bouillon et al., 2003). It is generally assumed that litterfall and

roots from mangrove trees are the most abundant sources of SOM (Alongi, 2014), largely predominant in pristine mangroves (Sanders et al., 2014). However, microphytobenthos and phytoplankton as well as their detritus in the particulate organic matter (POM) may be an additional source of SOM produced on the mangrove surface sediment and/or brought from the surrounding coastal waters and deposited by the tide (David et al., 2018). Increasing human densities along coastal zones and the intensification of agricultural activities are increasing runoff of OM and nutrient to the coastal zone (Kitsiou & Karydis, 2011; Sanders et al., 2014). This leads in highly anthropized coastal areas to a proliferation of phytoplankton, microphytobenthos and macroalgae that can enter the mangrove surface sediment (Pérez et al., 2018a). A third source is the direct discharge of untreated sewage which is also common in anthropized watersheds (Kitsiou & Karydis, 2011). At low tide, direct exposure of highly surface sediments to the atmosphere leads to the oxygenation of these sediments contributing to intense microbial remineralization of SOM in surface sediments (Sun et al., 2002). Tides also drive mangrove POM exports to adjacent creeks (Meziane & Tsuchiya, 2002). In mangrove sediments, deeper layers are typically depleted in oxygen and SOM is degraded by anaerobic processes (e.g. reductions of nitrate, manganese, iron or sulfides, and methanogenesis), which are less efficient than aerobic remineralization (Sun et al., 1993). Bioturbating organisms (e.g. crabs) and the presence of roots contribute to increased sediment oxidation and subsequent remineralization of SOM (Kristensen & Alongi, 2006; Zhu et al., 2018; Sarker et al., 2021). Indeed, mangrove sediments emit to the atmosphere at low tide and export with tidal pumping, significant amounts of CO₂ and CH₄ coming from the mineralisation of SOM (Kristensen et al., 2008b; Poungparn et al., 2009; Nóbrega et al., 2016).

76

77

78

79

80

81

82

83

84

85

86

87

88

89

90

91

92

93

94

95

96

97

98

99

In addition to the quantity of OM deposited, the quality of SOM is a crucial factor that control remineralization or preservation. Labile compounds (e.g. algal or urban domestic OM) are more easily degraded than refractory compounds (e.g. lignin, cellulose from the mangrove forest) (Fontaine et al., 2003; Guenet et al., 2010). Previous evidence has indicated that the production of labile OM by microalgal blooms can also potentially generate an intensification of the refractory OM remineralization (Gontikaki et al., 2015), through a phenomenon called the priming effect (Bianchi, 2011; Gontikaki et al., 2015). Further research is needed to better understand the changes of the OM quality under increasing eutrophic condition over time and particularly the role of microorganisms in sediment OM degradation (Bianchi, 2011; Bouillon et al., 2008a; Lovelock et al., 2017; Queiroz et al., 2020). Fatty acid and stable isotope composition of organic substrates are useful to identify different POM and SOM sources and are also proxies of the eutrophication process in a wide variety of ecosystems (Bergamino et al., 2014). FAs contribute to between 0.1 and 5% in coastal marine SOM (Canuel, 2001), between 10 and 30% in POM (Wakeham et al., 1997) and between 5 and 25% in DOM (Nebbioso & Piccolo, 2013). Some FAs are synthesized by specific groups of organisms and others are synthesized in most organisms and in specific proportions (Dalsgaard et al., 2003; Kaneda, 1991). FAs are intensively produced and degraded by organisms by heterotrophic micro and macrofauna, especially the polyunsaturated FAs (Wakeham et al., 1997; Camacholbar et al., 2003). FAs are also powerful taxonomic indicators (from the species to class) of 1) the living biomass in algal blooms, 2) sewage OM degradability and 3) bacterial and fungal components within sediments and biofilms in the ecosystem (Meziane & Tsuchiya, 2002; Xu & Jaffé, 2007; Kopprio et al., 2018). Consequently, FAs are an efficient tool to trace the more labile part of SOM and POM, especially

101

102

103

104

105

106

107

108

109

110

111

112

113

114

115

116

117

118

119

120

121

122

123

124

when combined with bulk isotope C and N signature. Moreover, FAs can provide semiquantitative information on various sources to the OM pool.

Despite research attesting to coastal eutrophication around the world (Breitburg et al., 2018), little is known on its impact on SOM composition in mangrove sediments. The coast of Rio de Janeiro state (Brazil) shows contrasting conserved and highly eutrophicated areas due to the discharge of untreated urban sewage (Cotovicz et al., 2018; Ribeiro & Kjerfve, 2002). The aim of this study is to characterize the source and fate of OM in three mangroves within the state of Rio de Janeiro (Brazil) along a eutrophication gradient. For these purposes, the present study uses fatty acids (FAs) and the isotopic signatures of carbon and nitrogen (δ^{13} C and δ^{15} N) to assess the origin and transfers of OM in mangrove sediments located along a gradient of urbanization and eutrophication.

2. Materials and Methods

140 2.1 Study sites

The three studied mangroves in the State of Rio de Janeiro (Brazil) (Fig. 1) were chosen because of their different levels of urban influence. Indeed, in the State of Rio de Janeiro the small increase in wastewater treatment combined with the very large increase in population leads to a wastewater discharge proportional to the watershed population (Abril et al., 2022), thus highly polluted rivers discharge organic matter, nitrogen and phosphorus especially in the bays of Guanabara and Sepetiba (Fistarol et al., 2015; Rodrigues et al., 2009). In contrast, the southwestern region of the state is not densely populated and the bay of Ilha Grande remains relatively pristine (Fig. 1A). The most pristine studied mangrove M1 is located at the back end of an 8km-long

elongated embayment called *Saco de Mamangua* with a very small watershed containing a limited population (Table A1), and classified as an environmental reserve. Although the entire drainage basin of Guanabara Bay is one of most urbanized in Brazil, with an estimated population ~17 million compared to ~1.8 million in Sepetiba Bay, the immediate watershed of the M2 mangrove in the region called *Guapi Mirim* is larger but less populated than that of the M3 mangrove in the area called *Guaratiba* (Table A1; Barroso et al. revised). Accordingly to the microtopography data of Barroso et al. (revised), the estimated inundation times of these mangroves were relatively similar. Finally, the δ^{15} N values of sediments and mangrove leaves attest to the differences in eutrophication between the three sites (Table A1). The plant community composition of each site is displayed in table A1.

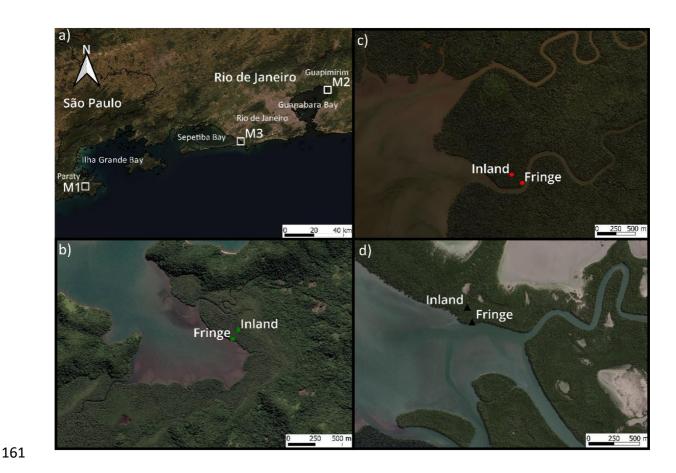


Figure 1: Location of the tree studied mangroves at Rio de Janeiro (a), southeastern Brazil. (b) M1 in Ilha Grande Bay, (c) M2 in Guanabara Bay and M3 (d) in Sepetiba Bay. (2 column)

164 2.2 Sampling

165

166

167

168

169

170

171

172

173

174

175

176

177

178

179

180

181

182

183

185

186

187

Samples from each of the study sites were collected during the rainy season between October 11 and December 7, 2018. At each site, three zones were sampled: water column (adjacent creek or channel), zone F corresponding to the mangrove fringe and zone I corresponding to most inland location of the mangrove forest. The fringe corresponds to the nearest part (about 20m) to the coast and the inland zone corresponds to the part a furthest within the forest (between 100 and 200 meters). Sediment samples were collected at low tide at the three study sites. Four 9cm-long cores were taken at each of the 6 zones. Three sediment depths were sectioned: 0-2 cm (P0), 3-4 cm (P3) and 7-9 cm (P9). In order to characterize potential OM sources, fresh leaves of A. shaueriana, R. mangle et L. racemosa were taken directly from the trees. Samples from the water column were taken as 5 replicates. Water and material collected with a 73 µm mesh plankton net were filtered on GF/F filters (0.7 µm). For M3, because suspended material was very concentrated, the material from the plankton nets was not filtered on GF/F filters but separated by decantation. For M2, the water column samples were taken in two distinct areas: in the proper Guanabara Bay (2B) at about 5km from the mangrove, and in the river channel (2C) during a rising tide. All samples were frozen the day of sampling and were freeze-dried within three days of collection.

2.3. Laboratory analysis

184 2.3.1. Fatty Acids

Prior to extraction, an internal standard (Tricosanoic acid: 23:0) was added in each sample. Lipids were extracted according to the protocol of Bligh and Dyer as modified by Meziane et al. (2007). Samples are extracted by sonication (20 minutes) a first time

in a mixture of chloroform, water and methanol (1:1:2; v:v:v). 1 mL chloroform and 1 mL water are added and the samples are vortexed and centrifuged 5 min at 3000 rpm. The lipids are retained in the chloroform phase, which is collected. 2 mL chloroform is added to the samples before a second extraction with the sonicator (20 min). The samples are centrifuged again, then the chloroform is collected and the total 4 mL is evaporated under nitrogen (N2) flow. Lipids are saponified by adding a methanol:sodium hydroxide (2N) mixture (2:1; v:v). Samples are put at 90°C for 1h30 then 500 µl of chloridric acid (37%) and 1.5 ml of CHCl₃ are added. The tubes are then vortexed and centrifuged (3000 rpm). The chloroform phase is collected and evaporated under nitrogen flow. Samples are methylated to form fatty acid methyl ester (FAME) with 1 mL boron trifluoride and then placed in a dry bath for 10 min at 90°C. 1 mL H20 and 1mL CHCl₃ are added. They are vortexed and centrifuged and then part of the surface water is pipetted and discarded in order to rinse the solution well and purify the final fatty acid extract. 1 mL H20 and 1 mL CHCl₃ are added again and the tubes are vortexed and centrifuged for 5 min (3000 rpm). All the chloroform containing FAME is removed and placed in 2 mL vials. The vials are stored in the freezer at -20°C. FAME are quantified by gas chromatography (Varian 3800-GC) with an ionizing flame detector. The oven temperature is maintained at 60°C for 1 min, then it increases to 150° (40°/min) for 3 min and then to 240° (3°/min) for 25 min. Fatty acids are identified with a mass spectrometer (Varian 220-MS) and the comparison of fatty acid retention times with the retention times of a commercial standard (Supelco® 37). We report the values as % of total FA.

2.3.2. Stable isotopes

188

189

190

191

192

193

194

195

196

197

198

199

200

201

202

203

204

205

206

207

208

209

210

211

212

For δ^{13} C analysis, sediment and filter samples were acidified in order to eliminate carbonates. For sediment samples, 10% HCl was directly added to the samples during

24 hours. Filter samples were fumigated by adding chlorhydric acid (37%). The filters

24 were exposed to the fumes generated by the acid for 6 hours.

Acidification can distort the values of $\delta^{15}N$, therefore the measurements of $\delta^{15}N$ were performed separately for filters and sediments of which the 10% HCl was not applied. About 15 mg of sediments and suspended material scratched from the filters were weighted and stored in tin capsules.

The samples were analyzed at the University of California at the Davis Stable Isotopes Facility (Department of Plant Sciences, University of California, Davis, California) with an Elementar Vario EL Cube or Micro Cube Elemental analyzer (Elementar Analysen systeme GmbH, Hanau, Germany) combined with a PDZ Europa 20-20 isotope ratio mass spectrometer (Sercon Ltd., Cheshire, UK). Stable isotope results are reported in parts per thousand (‰), using the standard delta notation (δ^{13} C and δ^{15} N) relative to international standards: VPDB (Vienna PeeDee Belemnite) for carbon and atmospheric air for nitrogen.

227 2.4. Statistical analysis

Due to the too small number of replicates (4 replicates), statistical analyses were performed using non-parametric tests. ANOSIMs (Clarke, 1993) with Bray-Curtis distance were done to analyze the effect of depth, sampling site and sampling zone within mangrove on fatty acids profiles (significance level p<0.05). To characterize the effect of depth, sampling site and sampling zone within mangrove in individual fatty acid distributions, pairwise Wilcoxon tests (Bauer, 1972) were performed (significance level p<0.05).

- Data were analyzed with R software (version 4.0.5). Wilcoxon-Mann-Whitney comparisons were performed with the "stat" package. ANOSIMs analysis were
- performed with the package "vegan" (Oksanen et al., 2015).

238 **3. Results**

- 3.1. Isotopic composition and C/N ratio
- 240 3.1.1. Leaves
- The δ^{13} C signature of mangrove leaves was relatively similar between the three sites
- 242 (mean \pm SD: 29.9 \pm 1.4%; Fig. 2). Conversely, $\delta^{15}N$ was higher in leaves from M3
- $(7.3\pm0.4\%)$ than in leaves of M2 (5.6±1.4%; p<0.01) and higher in leaves of M2 than
- 244 in those of M1 (1.1 \pm 1.6%; p < 0.001).

247

248

249

250

251

252

253

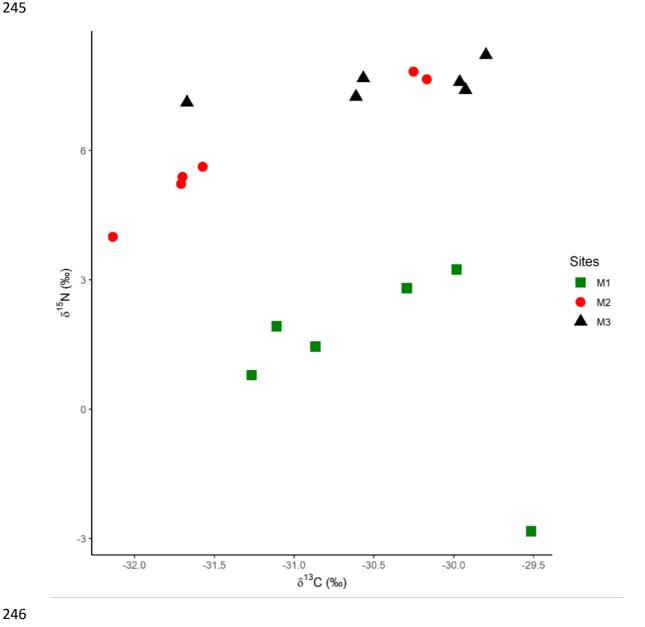


Figure 2: Plot of (a) δ^{13} C vs δ^{15} N values of mangroves leaves in the three mangroves sites: M1 in Ilha Grande Bay, M2 in Guanabara Bay and M3 in Sepetiba Bay. (1 Column)

3.1.2. Particulate organic matter (POM)

The characterization of isotopic signatures and C/N ratio of POM were performed from both plankton nets and GF/F filters for each zone. At the site M2, two areas were sampled: the channel and the bay (Fig. 3).

The δ^{13} C, δ^{15} N signatures and C/N ratios of POM are presented in Figure 3. The δ^{13} C values in M2 reached -28.3±0.2‰. The δ^{13} C values were significantly depleted at M2 channel (-25.5±0.2‰) than in M1 and M3 (-22.7±1.5‰ and -20.9±1.0‰; p < 0.01). The δ^{13} C signature of POM was similar at M1 and M3 (p > 0.05). The δ^{15} N of POM was higher at M1 and M2 (6.1±1.9‰ and 7.2±2.8‰) compared with M3 (0.9±1.3‰; p < 0.01 & p<0.001). The C/N ratio values in the POM was 6.4±1.5 on average and similar between sites.

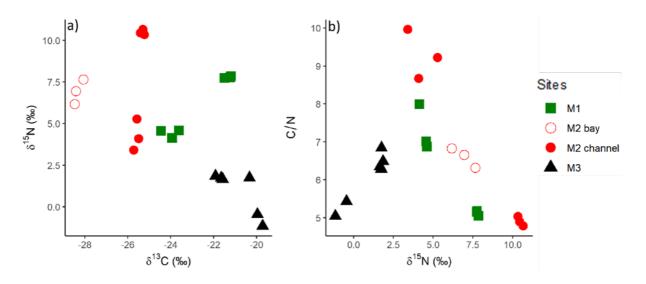


Figure 3: Plot of (a) δ^{13} C vs δ^{15} N and (b) δ^{15} N vs C/N values of particulate organic matter in the three mangroves sites: M1 in Ilha Grande Bay, M2 in Guanabara Bay and M3 in Sepetiba Bay. (2 column)

3.1.3. Sediments

There was no difference (p > 0.05) at M1 in δ^{13} C, δ^{15} N, and C/N values between F and I zone sediments (Fig. 4&5). At M2 I was significantly enriched in δ^{15} N compared to F (I: 6.2±0.4‰; F: 5.3±0.2‰; p < 0.01), while δ^{13} C and C/N were similar (p < 0.05) between the two zones (Fig. 4&5). At M3 the I zone was depleted in δ^{13} C (-25.1±0.1‰; -23.8±0.4‰; p < 0.01), enriched in δ^{15} N (8.1±0.3‰; 7.2±0.5‰; p < 0.01) and had a higher C/N ratio (11.2±0.3; 10.3±0.5; p < 0.01) compared to the F sediments. No

differences in carbon or nitrogen isotopic signature or C/N ratio were observed between surface and subsurface (3 and 9 cm) sediments at all sites.

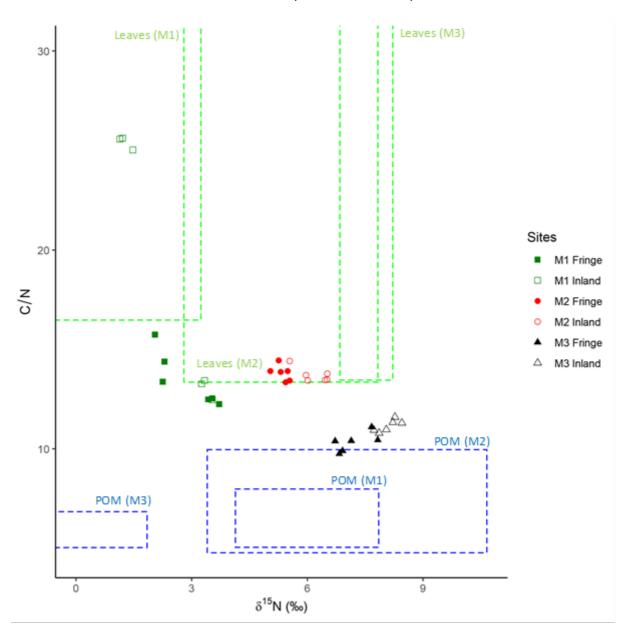


Figure 4: Plot of $\delta^{15}N$ vs C/N in sediments mangroves of the three mangroves sites -: M1 in Ilha Grande Bay, M2 in Guanabara Bay and M3 in Sepetiba Bay. The envelopes of leaves are represented by green boxes and those of particulate organic matter in water are represented by blue boxes. **(1 column)**

Considering surface and subsurface sediments together as a pool, the δ^{13} C was significantly depleted at M2 (-27.1% ± 0.2%) than at the other two sites (M1 : -26.8 ±

0.6‰, p < 0.05; M3 : -24.4‰ \pm 0.7‰, p<0.001). Similarly, δ^{13} C was depleted at M1 (-26.8‰ \pm 0.6‰) compared to M3 (-24.4‰ \pm 0.7‰; p < 0.001). M1 has the lowest δ^{15} N, followed by M2 and then M3 (2.6 \pm 1.0‰ > 5.7 \pm 0.5‰ > 7.6 \pm 0.6 ‰, p < 0.001). The C/N ratio showed no significant difference between M1 and M2, but was significantly higher in subsurface sediments of I site of M1 mangrove (Fig. 4; p < 0.001). The C/N values of surface sediments at the F and the I zones in M1 were comparable to those at M2. M1 and M2 had higher C/N values (16.3 \pm 5.5 and 13.8 \pm 0.4 respectively) than M3 (10.7 \pm 0.6; p < 0.001). M1 and M2 had higher sedimentary organic carbon (Corg) concentrations than M3 (126.6 \pm 108.3 mg.g⁻¹, 54.2 \pm 7.6 mg.g⁻¹ and 36.5 \pm 4.6 mg.g⁻¹; p < 0.001). The high values and standard deviation of OC content in M1 sediments was due to the very high organic carbon concentrations in the subsurface sediment of zone I (Fig. 5).

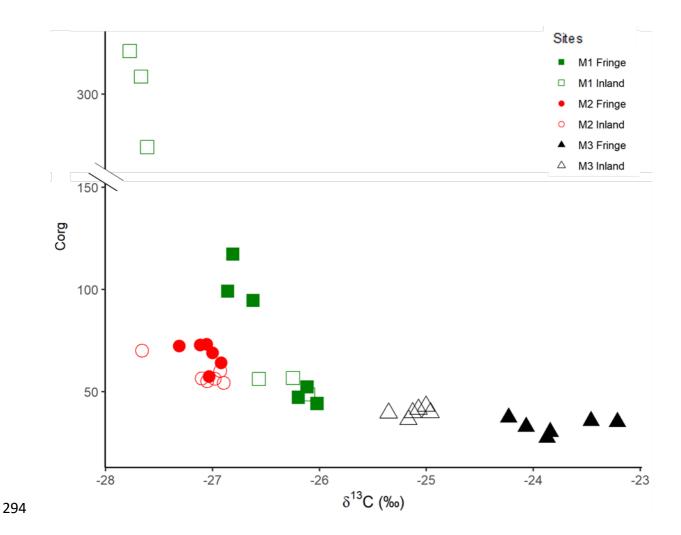


Figure 5: Plot of δ^{13} C vs. organic carbon in sediments mangroves of the three mangroves sites : M1 in Ilha Grande Bay, M2 in Guanabara Bay and M3 in Sepetiba Bay. (1 column)

3.2. Fatty acids composition

3.2.1. Mangrove leaves

Long chain fatty acids (>= 24 carbon) reached an average of 6.6% (Table 1). Among PUFAs, $18:3\omega3$ was the dominant fatty acid followed by $18:2\omega6$. The monounsaturated fatty acids (MUFAs) signature of mangrove leaves was almost entirely caused by the presence of $18:1\omega9$.

Table 1: Mean (± sd) of selected fatty acid composition of leaves in three sampling locations (M1 in Ilha Grande Bay, M2 in Guanabara Bay and M3 in Sepetiba Bay). BD: Below Detection (1 column)

	Site	M1	Site	M2	Site M3			
	Fringe (n = 4)	Inland (n = 4)	Fringe (n = 4)	Inland (n = 4)	Fringe (n = 4)	Inland (n = 4)		
16 :0	23.3 ± 2.5	31.2 ± 2.6	24.6 ± 1.5	22.9 ± 3.6	25.2 ± 6.8	31.9 ± 5.1		
∑LCFAs	2.6 ± 2.8	4.5 ± 2.9	3.1 ± 2.6	2.8 ± 1.5	0.4 ± 0.3	9.0 ± 11.3		
Other SFAs	3.2 ± 0.8	1.7 ± 0.6	6.3 ± 1.5	7.4 ± 2.3	4.4 ± 1.2	2.2 ± 1.0		
∑SFAs	29.3 ± 5.1	41.3 ± 4.5	30.0 ± 1.7	28.8 ± 3.1	29.6 ± 7.6	44.7 ± 7.4		
18:1ω9	13.3 ± 1.1	9.2 ± 0.4	11.3 ± 1.3	12.7 ± 2.0	13.8 ± 2.4	12.9 ± 2.5		
Other MUFAs	6.0 ± 2.6	10.1 ± 3.5	5.4 ± 2.3	5.9 ± 1.5	4.4 ± 0.9	12.8 ± 8.9		
∑MUFAs	16.5 ± 1.1	10.9 ± 0.3	17.6 ± 1.3	20.2 ± 3.5	18.3 ± 3.0	15.1 ± 2.0		
18:2ω6	11.2 ± 1.9	12.0 ± 4.0	13.3 ± 2.0	13.6 ± 3.3	13.5 ± 2.9	15.0 ± 2.8		
18:3ω3	31.7 ± 12.9	34.3 ± 7.6	37.0 ± 1.3	35.7 ± 3.6	30.0 ± 8.4	23.7 ± 6.4		
∑PUFAs	43.0 ± 12.2	46.9 ± 4.6	50.4 ± 1.7	49.3 ± 2.8	43.5 ± 6.8	38.9 ± 9.1		
∑BrFAs	11.3 ± 13.5	1.5 ± 0.2	2.0 ± 0.3	1.6 ± 0.6	8.5 ± 11.1	1.5 ± 0.4		

3.2.2. Particulate organic matter (POM)

The bay of M2 POM had significantly lower MUFA proportion than channel of M2 and M3 (Table 2; p < 0.05). At all sites, $16:1\omega7$ was the dominant fatty acid among MUFAs. PUFAs at M3 and M2 (bay) was significantly lower than at M1 and M2 (channel) (p < 0.05; Table 2; Fig. 6). $20:5\omega3$ and $22:6\omega3$ were the dominant PUFAs at all 4 sites (Table 2). However, we observed a predominance of $20:5\omega3$ over $22:6\omega3$ at M3 (p < 0.001). BrFAs contributed twofold more to the POM fatty acid pool at M3 and M2 than at M1 (Table 2; p < 0.001).

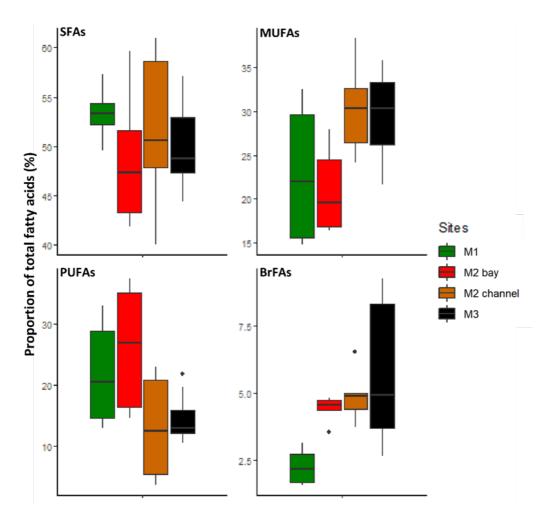


Figure 6: Contribution (% of total fatty acids) of SFAs, MUFAs, PUFAs and BrFAs to the total fatty acid pool in four particulate organic matter sampling locations (Ilha Grande Bay (M1), Guanabara Bay (M2 bay) and channel (M2 channel) and Sepetiba Bay (M3)). Median values (horizontal solid line inside the box), 25th and 75th percentiles (lower and upper ends of the boxes), 95% confidence intervals (whiskers) and outliers (circles) are shown. (1 column)

Table 2: Mean (± sd) proportion (% of total fatty acids) of selected fatty acid composition of particulate organic matter in four sampling locations (M1 in Ilha Grande Bay, M2 in Guanabara Bay and M3 in Sepetiba Bay). BD: Below Detection (1 column)

	Site M1	Site M2 Channel	Site M2 Bay	Site M3
14:0	11.6 ± 1.5	9.8 ± 2.3	5.6 ± 0.7	18.3 ± 6.9
16:0	29.2 ± 1.9	29.0 ± 3.3	27.2 ± 3.2	22.9 ± 2.1
18:0	8.1 ± 1.3	6.7 ± 3.1	14.4 ± 8.6	4.8 ± 3.9
∑Other SFAs	4.2 ± 0.2	3.0 ± 0.5	4.6 ± 1.0	3.8 ± 1.0
∑SFAs	53.0 ± 2.5	48.5 ± 6.9	51.8 ± 8.1	49.9 ± 4.2
16:1ω7	7.2 ± 1.0	12.5 ± 2.8	7.5 ± 2.8	17.9 ± 2.8
18:1ω9	10.4 ± 7.9	3.8 ± 1.9	13.4 ± 6.4	5.7 ± 4.0
∑Other MUFAs	4.2 ± 1.5	4.6 ± 0.6	9.4 ± 3.6	6.9 ± 3.3
∑MUFAs	21.9 ± 8.1	20.9 ± 5.0	30.3 ± 5.2	29.7 ± 4.8
20:5ω3	6.3 ± 3.6	9.1 ± 5.2	3.3 ± 2.7	6.2 ± 3.2
22:6ω3	7.5 ± 4.9	7.9 ± 6.1	3.7 ± 3.0	1.5 ± 1.0
∑Other PUFAs	9.1 ± 0.7	9.1 ± 1.2	6.1 ± 3.1	6.9 ± 1.8
∑PUFAs	23.0 ± 8.1	26.1 ± 10.7	13.1 ± 8.7	14.5 ± 4.1
∑BrFAs	2.1 ± 0.6	4.4 ± 0.5	4.9 ± 0.9	5.8 ± 2.7

326 3.2.3. Sediments

3.2.3.1. Variations with depth at each site

At M1, the percentages of LCFAs that were higher at 3-9 cm sediments of I zone than in F zone (p < 0.01). The fatty acid $16:1\omega7$ was significantly less abundant at the P3 and P9 depths at I zone of M1 than in the F zone and surface sediments at I zone (p < 0.001). The BrFAs group showed the same trend with a lower percentage for P3 and P9 depth at the I zone of the M1 compared to the other samples (p < 0.05). PUFAs were the least abundant group at M1 and showed no significant difference between the different depths of the F and I zones (p > 0.05).

The FA composition of the mangrove I and F zones of M2 were not significantly different (ANOSIM, R = 0.186, p>0.05). Thus, for M2 data from I and F zones were pooled and only tested according to depth. There was a significant difference in term of FA composition between the three depths (R=0.62; p=0.001; Table 3). LCFAs

contributed twice (p<0.05) as much to the fatty acid pool at P9 depth as they did at P0 and P3 depths. The fatty acid $16:1\omega7$ was more abundant at the surface than below. Conversely, $18:1\omega9$ was lower in surface sediments than at subsurface. The group of BrFAs was similar between the three sampled depths. The group of PUFAs tend to decreased from P0, to P9 (no significant difference).

At M3, the FA $16:1\omega7$ was more abundant in surface than in subsurface sediments at both zones F and I (p < 0.05; Table 3). FA $18:1\omega9$ showed the opposite trend (p < 0.05). BrFAs were more abundant in I sediment profiles than in F (p < 0.05). BrFAs were also more abundant in subsurface sediments (P3 and P9 depths) than in surface sediments (p < 0.05). At M3, PUFAs did not differ significantly between I and F but were more abundant at the surface than at depth in the I (p<0.05) and more abundant at P0 and P3 than at P9 in the F (p<0.05).

Table 3: Mean (± sd) proportion (% of total fatty acids) of selected fatty acid composition of sediments of inland and fringe mangrove at 0 cm, 3 cm and 9cmin three sampling locations (M1 in Ilha Grande Bay, M2 in Guanabara Bay and M3 in Sepetiba Bay). BD: Below Detection (2 column)

	Site M1					Site M2						Site M3						
		Fringe			Inland			Fringe			Inland			Fringe			Inland	
Depth	0 cm	3 cm	9 cm	0 cm	3 cm	9 cm	0 cm	3 cm	9 cm	0 cm	3 cm	9 cm	0 cm	3 cm	9 cm	0 cm	3 cm	9 cm
16:0	20.9 ±	22.1 ±	20.1 ±	20.7 ±	23.9 ±	23.1 ±	20.4 ±	22.6 ±	21.2 ±	22.4 ±	22.4 ±	22.4 ±	22.0 ±	21.1 ±	22.1 ±	21.1 ±	21.3 ±	20.8 ±
	1.8	0.2	0.6	1.4	1.8	3.0	0.7	1.5	0.4	0.9	0.6	1.1	0.7	1.5	1.7	8.0	0.4	0.6
ΣLCFAs	5.1 ±	4.5 ±	$3.9 \pm$	3.4 ±	15.0 ±	18.9 ±	4.4 ±	$3.7 \pm$	8.8 ±	2.5 ±	$3.8 \pm$	5.9 ±	2.0 ±	2.9 ±	3.1 ±	2.1 ±	1.8 ±	2.6 ±
	0.9	0.4	1.8	1.5	5.1	3.1	1.9	0.6	1.3	0.7	1.1	1.5	1.2	1.1	0.6	1.0	1.1	0.9
ΣSFAs	47.3 ±	48.0 ±	45.8 ±	47.3 ±	61.8 ±	65.1 ±	44.6 ±	48.9 ±	54.4 ±	45.0 ±	49.3 ±	50.7 ±	42.5 ±	44.5 ±	44.5 ±	39.1 ±	39.4 ±	39.2 ±
	2.3	1.8	1.8	1.2	4.9	1.6	2.2	1.1	1.7	0.6	1.9	1.9	0.1	3.2	2.3	1.4	0.7	0.6
16:1ω7	9.3 ±	7.3 ±	8.4 ±	6.0 ±	2.9 ±	2.1 ±	9.0 ±	5.2 ±	4.0 ±	8.4 ±	6.6 ±	5.7 ±	9.4 ±	4.3 ±	3.2 ±	6.8 ±	4.3 ±	4.3 ±
	0.7	1.6	0.7	1.2	8.0	0.6	1.9	1.2	0.9	0.4	1.1	1.4	1.9	1.5	0.6	2.4	8.0	2.6
16:1ω5	1.3 ±	1.2 ±	1.6 ±	1.2 ±	$0.7 \pm$	$0.6 \pm$	2.0 ±	1.5 ±	1.2 ±	2.0 ±	1.6 ±	1.6 ±	2.2 ±	2.4 ±	2.6 ±	3.8 ±	4.1 ±	3.2 ±
	0.3	0.3	0.1	0.2	0.3	0.2	0.1	0.3	0.3	0.2	0.3	0.2	0.3	0.3	0.9	0.7	1.0	0.2
18:1ω9	5.2 ±	$6.7 \pm$	$6.7 \pm$	8.2 ±	$6.5 \pm$	$6.7 \pm$	5.9 ±	8.9 ±	7.9 ±	7.3 ±	7.5 ±	8.3 ±	7.4 ±	10.3 ±	11.1 ±	8.2 ±	$9.6 \pm$	10.9 ±
	0.3	1.4	0.7	2.4	1.0	1.9	0.2	1.4	1.1	0.3	0.3	1.1	0.3	2.5	0.7	1.4	0.6	8.0
18:1ω7	8.2 ±	7.9 ±	8.1 ±	7.1 ±	$3.5 \pm$	$2.7 \pm$	8.3 ±	4.7 ±	$3.9 \pm$	7.1 ±	5.6 ±	4.8 ±	7.4 ±	4.8 ±	4.4 ±	6.6 ±	5.8 ±	5.1 ±
	1.6	1.3	0.2	0.5	0.4	0.7	0.4	0.7	0.9	0.3	0.5	1.1	0.9	1.3	0.3	0.3	0.7	0.4
19:1ω9	1.5 ±	1.8 ±	1.0 ±	1.0 ±	$2.7 \pm$	2.5 ±	1.8 ±	2.5 ±	2.6 ±	1.7 ±	2.1 ±	$2.3 \pm$	2.2 ±	$4.3 \pm$	5.4 ±	4.8 ±	$6.3 \pm$	$6.7 \pm$
	0.2	0.3	0.1	0.2	0.4	0.4	0.1	0.3	0.5	0.2	0.1	0.2	8.0	1.1	0.6	0.9	0.5	0.6
ΣOther	4.3 ±	2.8 ±	5.1 ±	4.7 ±	$2.5 \pm$	$2.7 \pm$	3.8 ±	2.3 ±	$2.5 \pm$	4.3 ±	2.8 ±	$3.4 \pm$	5.5 ±	4.4 ±	3.8 ±	4.4 ±	3.2 ±	3.1 ±
MUFAs	8.0	0.4	0.9	1.0	0.9	0.4	0.3	0.4	0.3	0.4	1.1	0.5	0.8	1.0	0.6	0.4	0.3	0.4
Σ MUFAs	29.8 ±	27.7 ±	31.0 ±	28.2 ±	18.9 ±	17.3 ±	30.8 ±	25.2 ±	22.2 ±	30.8 ±	26.2 ±	26.1 ±	34.1 ±	$30.5 \pm$	30.6 ±	34.5 ±	33.3 ±	33.3 ±
	2.9	2.1	1.5	1.8	2.8	0.8	1.8	1.0	1.0	0.5	1.3	1.5	0.8	1.5	2.2	1.0	1.5	1.1
18:2ω6	1.3 ±	2.0 ±	1.0 ±	1.7 ±	3.0 ±	2.9 ±	1.2 ±	3.1 ±	2.3 ±	1.3 ±	1.1 ±	1.7 ±	1.6 ±	2.9 ±	3.0 ±	2.4 ±	2.4 ±	3.4 ±
	0.2	1.1	0.2	0.7	0.9	8.0	0.1	1.0	1.3	0.1	0.2	0.8	0.4	0.9	1.0	1.4	0.6	0.6
20:4ω6	1.4 ±	0.6 ±	0.8 ±	0.9 ±	0.4 ±	BD	0.7 ±	0.5 ±	BD	0.7 ±	0.4 ±	0.3 ±	1.7 ±	1.5 ±	1.1 ±	1.8 ±	1.4 ±	1.0 ±
	0.3	0.2	0.2	0.5	0.2		0.1	0.4		0.1	0.1	0.1	1.1	1.5	0.3	0.5	0.4	0.2
20:5ω3	1.6 ±	0.3 ±	0.7 ±	0.7 ±	BD	BD	0.7 ±	BD	BD	0.9 ±	BD	BD	1.5 ±	0.6 ±	BD	1.2 ±	BD	BD
-04	0.7	0.1	0.1	0.3	00.	٥	0.1		00.	0.2		40.	0.4	0.6	44.	0.6	40.	47.
ΣOther	2.0 ±	0.8 ±	1.2 ±	1.5 ±	0.6 ±	0.5 ±	1.4 ±	1.0 ±	0.8 ±	1.6 ±	0.6 ±	1.0 ±	1.9 ±	1.4 ±	1.4 ±	2.2 ±	1.2 ±	1.7 ±
PUFAs	0.5	0.1	0.3	0.4	0.4	0.4	0.3	0.2	0.2	0.3	0.2	0.2	0.5	0.4	0.3	0.3	0.6	0.3
ΣPUFAs	6.3 ±	3.8 ±	3.7 ±	4.8 ±	4.0 ±	3.8 ±	4.0 ±	4.5 ±	3.3 ±	4.4 ±	2.3 ±	2.9 ±	6.8 ±	6.3 ±	5.7 ±	7.6 ±	5.3 ±	6.2 ±
77DEA-	1.3	0.8	0.3	1.8	1.1	0.8	0.4 20.7 ±	0.5	1.4	0.6	0.3	0.9	1.9	1.7	1.4	1.7 18.7 ±	1.2	1.0
ΣBrFAs	16.5 ±	20.6 ±	19.5 ±	19.7 ±	15.4 ±	13.7 ±		21.3 ±	20.1 ±	19.7 ±	22.2 ±	20.3 ±	16.7 ±	18.7 ±	19.3 ±		22.0 ±	21.3 ±
	1.8	0.4	1.1	0.7	2.4	2.3	0.3	0.6	2.6	0.8	0.9	8.0	1.4	1.8	1.7	0.7	1.4	1.6

3.2.3.2. Inter-sites comparison

At surface sediments, there was a significant difference in FA composition between the three mangrove sites (ANOSIM, R = 0.475; p < 0.001). LCFAs showed a higher contribution at M1 compared to M2 (p < 0.01) and at M2 compared to M3 (p < 0.01; Fig. 7). Among MUFAs, $16:1\omega7$ and $18:1\omega9$ had the largest contributions but did not show significant differences in surface sediments of the three sites (p > 0.05; Table 3). BrFAs were significantly more abundant in surface sediment from M2 than from M1 and M3 (p < 0.01; Fig. 7). PUFAs contribute more to the TFA pool in the surface sediments of M1 and M3 than in M2 (p < 0.01, Fig. 7). In the surface sediments of M3 there was a higher contribution of $20:5\omega3$ compared to M2 (p < 0.01; Table 3).

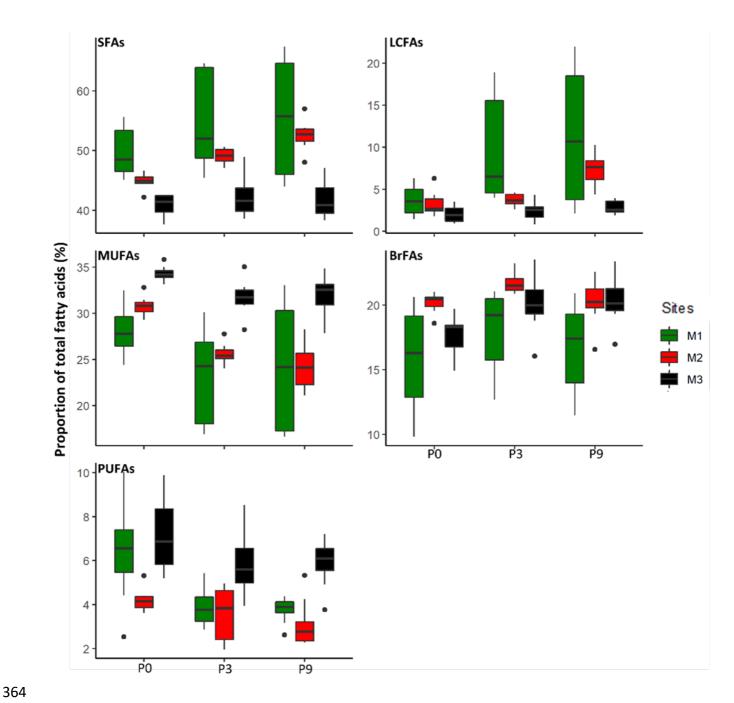


Figure 7: Contribution (% of total fatty acids) of SFAs, LCFAs, MUFAs, BrFAs and PUFAs to the total fatty acid pool in the sediments of the three mangroves (M1 in Ilha Grande Bay, M2 in Guanabara Bay and M3 in Sepetiba Bay.). Median values (horizontal solid line inside the box), 25th and 75th percentiles (lower and upper ends of the boxes), 95% confidence intervals (whiskers) and outliers (circles) are shown. (1 column)

At three centimetres depth (P3), FA composition of the sediment were different between the three sites (ANOSIM, R = 0.476; p<0.001). The LCFAs were higher in M1 than in M2 (p < 0.01) and in M2 than in M3 (p < 0.05; Fig. 7). The most contributing

MUFAs were $16:1\omega 7$, $18:1\omega 9$, and $18:1\omega 7$ (Table 3). BrFAs showed significant difference only between M1 and M2 (p< 0.01; Fig. 7). PUFAs were less abundant in M1 and M2 than in M3 (p < 0.01 and p <0.05 respectively; Fig. 7). Strong standard deviations were observed at M1 (both zones) for P3 sediments in contrast to the other two sites. These large standard deviations were caused by the strong difference in profiles between the I and the F zones of M1 (Fig. 7).

In sediments at P9 depth, the FA profiles were significantly different between the three sites (ANOSIM, R = 0.639, p < 0.001). LFCAs were particularly abundant in P9 sediments at M1 and M2 but not at M3. MUFAs were less abundant in the sediment FA profiles of M1 and M2 compared to M3 (p < 0.05 and < 0.001 respectively; Fig. 7). The $16:1\omega 5$ (p < 0.001) was more abundant at M3 than at M1 and M2. BrFAs were lower at M1 compared to M2 and M3 (Fig. 7). PUFAs were less abundant in the P9 sediments of M1 and M2 than in those of M3 (p < 0.01; Fig. 7). Among PUFAs $18:2\omega 6$ was more abundant in the P9 sediments of M3 than those of M1 and M2 (p < 0.05).

4. Discussion

387

388

389

390

391

392

393

394

395

396

397

398

399

400

401

402

403

404

405

406

407

408

409

410

4.1. Eutrophication gradient in the coast of Rio de Janeiro

Stable isotopes and fatty acids analysed in POM, SOM and mangrove leaves clearly indicate the existence of gradient of eutrophication in the three investigated mangroves in the state of Rio de Janeiro (Brazil). This gradient from M1 to M3 sites is consistent with urban occupation in the region (Table A1), as also analysed in Barroso et al. (in revision). The high proportions of BrFA found at M3 highlight a strong bacterial (Table A2) contribution in the POM. Previous studies have shown that in the presence of wastewater, heterotrophic bacteria generate a strong recycling of nitrogen which leads to the excretion of ammonium with a depleted $\delta^{15}N$ signature in the water column that can be further incorporated in the growth of marine phytoplankton (Ke et al., 2019). The high contribution of microalgal material in M3 mangroves POM is demonstrated by a high ratio of 16:1ω7/16:0 (Mortillaro et al., 2012; Napolitano et al., 1997) together with an enriched δ^{13} C signature (Fig. 3). At site M3, these high microalgal and bacterial contributions in POM, lead to a δ^{15} N signature near 0, therefore disconnected from SOM which is characterized by enriched $\delta^{15}N$ signature of about 8 (sewage characteristic) (Fig. 3 & 4). Isotopic fractionation during nitrogen uptake (Liu et al., 2013) and the preferential use of ¹⁴N-rich ammonium (generated by bacterial recycling) as a nitrogen source by algae (Liu et al., 2013) could explain the δ^{15} N-depleted isotopic signatures of the POM at M3. Our results reveal a greater influence of untreated sewage discharge to the M3 mangrove sediments compared to M1 and M2 consistent with Barroso et al. (in revision) based on the ratio of stanol biomarkers

(coprostanol/(coprostanol+colestanol)). Urban sewage loads, enriched with nutrients,

received by M3 mangroves could also trigger the growth of marine microalgae (Unger et al., 2013) and generate important changes in the algal community (Smith, 2003). In the POM of the water column of M3, the relative abundance of 20:5\omega3 was 3 times higher than that of 22:6ω3 (Table 3 and A2). This suggests that diatoms dominate dinoflagellates within the planktonic biomass unlike in the waters of the M1 and M2 sites where the proportions of these two PUFAs were comparable (Antonio & Richoux, 2016; Bergamino et al., 2014). In general, it is accepted that eutrophication favours dinoflagellates over diatoms (Dale, 2001). However, in eutrophic waters surrounding mangroves, a dominance of diatoms over dinoflagellates was also observed (Choudhury et al., 2015). In particular, high nitrogen concentrations are known to promote planktonic diatom growth in mangroves waters (Hilaluddin et al., 2020). In the waters of the Bay of Sepetiba, Rodrigues et al. (2009) showed a N/P ratio of 20 during the wet season as well as high concentrations of silica. In general, diatoms are favoured over dinoflagellates in coastal waters where nitrogen and silica are not limiting (Svensen et al., 2007). Thus, the nature of eutrophication-related inputs as well as the recycling of nitrogen by heterotrophs bacteria could explain the difference in the phytoplankton derived fatty acids in the M3 mangrove compared to the other two sites. In addition, the $\delta^{15}N$ signatures of sediments and leaves at the studied sites are showing a clear gradient of eutrophication (Fig. 2, Fig. 4). Because mangrove trees incorporate anthropogenic nitrogen present in the sediment porewaters, their $\delta^{15}N$ signatures can be used to identify a gradient of eutrophication locally or at a larger scale (Dugdale & Wilkerson, 1986; Gritcan et al., 2016). Sedimentary δ¹⁵N signatures are also sensitive to anthropogenic nitrogen inputs (Pérez et al., 2020). Accordingly, the mangrove surface sediments at M3 are the most eutrophic, followed by those of mangrove sediments at M2 and with M1 showing the most pristine conditions (Fig. 2

411

412

413

414

415

416

417

418

419

420

421

422

423

424

425

426

427

428

429

430

431

432

433

434

and Fig. 4). Barroso et al. (revised) also found at the same three study sites an increase in sedimentary inorganic phosphorus content from site M1 to M3. Several studies have described eutrophication in waters of Guanabara and Sepetiba Bays, where high concentrations of chlorophyll, inorganic nitrogen and phosphorus are found (Fistarol et al., 2015; Rodrigues et al., 2009). The eutrophication induced by domestic wastewater leads to an accumulation of exchangeable inorganic phosphorus in mangrove sediments (Barcellos et al., 2019). Although Guanabara Bay is more populated (Table A1) and eutrophic than Sepetiba Bay, because of local settings of the sampled mangroves, the M3 mangrove sampled in Sepetiba appeared more impacted by inputs of labile SOM from sewage and phytoplankton than the M2 mangrove in Guanabara Bay.

The C/N values in sediments in the inland of M1 mangrove (mean value: 19.3) are in the range of those reported in mangroves sediments under micro- to meso-tidal influence (i.e. Bouillon et al., 2003). These high values indicate a predominant input of mangrove tree material to the sediments. Indeed, sediments of inland M1 are composed of almost pure litter and R. mangle fine roots. In contrast, the fringe sediments at M1 and sediments of both fringe and inland zones at M2 mangrove have lower C/N ratios, in the range of those documented for mangroves influenced by tidal deposition and river inputs (Bouillon et al., 2003). The C/N values at M3 are even lower, in the range of values described by Leng & Lewis (2017) for riverine POC and by Jennerjahn and Ittekkot (1997) for sediments from another mangrove of the state of Rio de Janeiro influenced by a river (Paraiba do sul). This could be due to a larger influence of sewage inputs or marine phytoplankton in sediments of M3 than in the mangroves of the two other sites. This is also corroborated by the significantly depleted δ^{13} C signatures of superficial sediments in inland mangrove (-25,12±0,14) compared

to the coastal fringe mangrove (-23,78±0,38; more influenced by algal contributions) could be caused by a greater influence of urban wastewater at the inland zone, and/or of marine phytoplankton at the fringe zone.

461

462

463

464

465

466

467

468

469

470

471

472

473

474

475

476

477

478

479

480

481

482

483

484

4.2. Organic matter sources and exchange of OM between waters and mangroves sediments

At the most pristine mangrove location (M1), concentrations of C_{org} at the inland site were 3 times higher in subsurface sediments (3 and 9 cm depths) than at surface sediments (Fig. 5). At that site, we observed the presence of a dense rhizosphere of R.mangle in subsurface, in particular fine roots with very little silt. Root contribution was characterized by more than 3-fold higher proportions of LCFAs and 18:2ω6 (FAs characteristics of mangroves: Meziane et al., 2007; Table A2) and enriched δ^{13} C values in subsurface sediments compared to the surface (-26.3±0.2%>-27.7±0.1%). The presence of *R.mangle* fine roots explains the higher C_{org} concentrations in these sediments at 3 and 9cm depth than in the surface sediments. Concerning the fringe M1 site, the sediment organic carbon concentration was between 3 and 7 times lower and the proportions of LCFAs and 18:206 were 3 to 5-fold lower than at the inland site (both surface and subsurface; Fig. 5). This was apparently due to lower root density of A. shaueriana at the fringe compare to R. mangle at the inland site, as well as a larger contribution of deposited clays and silts at the fringe. This corroborates the study of Xiong et al. (2018) which shows a lower contribution of mangrove vegetation in mangroves near the sea than in those located inland. The sediments of fringe M1 mangrove have δ^{13} C-enriched signature compared to the inland subsurface sediments which reveals a greater influence of marine phytoplankton in the OM. The POM at M1 was characterized by a high relative contribution of 18:1ω9, abundant in mangrove leaf,

and $\delta^{13}C$ values close to those of mangrove leaves. This suggests an effective tidal export of mangrove-derived POM at site M1.

485

486

487

488

489

490

491

492

493

494

495

496

497

498

499

500

501

502

503

504

505

506

507

508

509

Concentrations of C_{org} in subsurface sediments at the inland site of M1 mangrove were 4 to 6 times higher than M2 sediments, and between 7 and 10 times higher than in M3 sediments. These lower Corg concentrations in the two more eutrophic mangroves when compared to the more pristine one can certainly be caused by the watersheds that convey more mineral matter via a higher river flow, which leads to a lower OM contribution to the sediments. In addition, the organic matter in a pristine mangrove in Ilha Grande (about 40 km of our M1 mangrove) was composed almost exclusively of mangrove material, with insignificant inputs of marine-derived organic matter (Sanders et al. 2008) similarly to our M1 site. This is consistent with the high contribution of LCFAs and 18:2w6, the δ^{13} C values in our samples, as well as with lignin and sterol biomarkers which revealed that mangrove's subsurface sediment at M1 and M2 are richer in plant material than at M3 (Barroso et al., revised). In the most eutrophic M3 mangroves, the additional OM supply was due to a contribution of phytoplankton, benthic algae, and urban sources (Pérez et al., 2020; Silva-Filho et al., 2011). Finally, river inputs rich in mineral sediments has a strong influence on Corg concentration by diluting it.

At high tide, as for other estuaries and bays (Bouillon et al., 2008b), the water columns of the three studied bays contain some POM resuspended from the mangrove forest. The presence of $18:2\omega6$ and $18:3\omega3$ FAs (David et al. 2019) in the POM samples in the creeks and channels at all sites indicates an export of mangrove organic carbon to waters (Table 2 and A2). At M2, the higher contribution of OM produced in the mangrove forest and/or of terrestrial origin is also reflected by the signature of δ^{13} C of the water column POM which is more depleted than the two other sites (M1 and M2).

At M1 (fringe) and M2, the δ^{13} C values (respectively 26.7‰ and 27.1‰ on average) are typical of tidal sediments influenced by inputs from mangroves leaves (Kennedy et al., 2004; Pessenda et al., 2012) and therefore emphasize the significant contribution of mangroves carbon to the POM. The difference in δ^{13} C signature between mangrove leaves and sediments at M1 (fringe) and M2 (fringe and inland) mangroves could be the result of a mixing with marine OM but also of diagenesis of litter compounds which leads to the enrichment in 13 C of the sedimentary OM (Kennedy et al., 2004). At M3 site, the low δ^{13} C and C/N values in sediment (Fig. 4 & 5) corroborate the significant contribution of marine phytoplankton and/or microphytobenthic OM sources.

510

511

512

513

514

515

516

517

518

519

520

521

522

523

524

525

526

527

528

529

530

531

532

533

534

4.3. Impact of eutrophication on organic carbon degradation in mangrove sediments

At M1, the sedimentary OM appears relatively refractory with a high proportion of LCFAs and a low proportion of algal FAs, which are respectively the most refractory and the most labile fatty acids (Camacho-Ibar et al., 2003). Conversely, in mangroves of the more eutrophic bays (M2 and M3) the relative contributions of algal FAs as well as the enriched ¹³C signature suggest that SOM is more labile than at M1. Moreover, C/N values of sediments and water at M2 (~13 and 6 respectively) and M3 (~10 and 6 respectively) indicate a higher microbial contribution than at M1 in view of their low values bacteria in (C/N 5; Leng & Lewis (2017)and phytoplankton/microphytobenthos (C/N ~ 6-7; Leng & Lewis (2017)) compared to mangrove leaves (C/N~22; present study). The C/N consistently decreased from site M1 to M2 and M3 and was 1.2 and 1.6 times lower at M2 and M3 respectively than at M1 (Fig. 4) showing that when eutrophication occurs, nitrogen-rich compounds become more abundant in SOM, relative to carbon-rich compounds. Also, along the eutrophication gradient of our three study sites, FAs, ¹³C signatures and C/N ratios

consistently reveal a larger contribution in the SOM of algal and microbial material, which are more degradable, than the part derived from litters and roots in the mangrove ecosystem. Thus, in our study, the C/N decreases with lability which is consistent with the finding of Pérez et al. (2018b) in another mangrove of Guanabara Bay. This is also consistent with Jennerjahn & Ittekkot (1997 and 1999) who show that the C/N ratio is low in fresh planktonic biomass but high in plant material or material that has undergone degradation because N-rich compounds such as amino acids are preferentially degraded. However, the variability of the lability of N-rich compounds showed by Nordhaus et al. (2011 and 2017) on total hydrolysable amino acids (THAA) reveal that low C/N ratio is not necessarily an indicator of higher lability of OM. Indeed, Nordhaus et al. (2017) found that during a litterbag experiments in an Indonesian mangrove, THAA concentration was negatively correlated with the C/N but that the basic THAA (more reactive than other amino acids groups) were preferentially degraded over other amino acids and that their concentration was not correlated with C/N ratio. Nordhaus et al. (2011) also found that crabs of various species feed preferentially on mangrove leaves with high N bioavailability (shown by THAA-N% of N) or high reactivity index (aromatic THAA/non-protein THAA) and that the food preferences of these crabs is not correlated with C/N composition. Various parameters can also influence the lability of SOM in a eutrophic mangrove such as, effluent type (Queiroz et al., 2020), distance from the pollution source (Queiroz et al., 2020), planktonic primary production (Cotovicz et al., 2018; Sanders et al., 2014) or heterotrophic activity (Davis et al., 2003).

535

536

537

538

539

540

541

542

543

544

545

546

547

548

549

550

551

552

553

554

555

556

557

558

559

The M2 mangrove was found to be moderately impacted by eutrophication. However, in both zones of M2 mangrove, SOM exhibits higher bacterial contribution than M1 and M3 as evidenced by the higher proportions of BrFAs (Mfilinge et al., 2003). The

proliferation of these bacteria in the SOM at M2 is enhanced by the presence of labile algal OM in sediments, as indicated by the high 16:1 ω 7/16:0 ratio, acting as a substrate for their growth (Bouillon et al., 2004). These FAs data suggest a higher activity of bacteria at M2 mangrove than at M1 mangrove, consistent with higher CO₂ emissions to the atmosphere reported by Barroso et al. (revised). At the same time, M1 and M2 sediments have comparable contribution of LCFAs which indicate they have a similar contribution of refractory OM. At M2, our data suggest that bacteria degrade algal labile OM in surface sediments but do not mineralize the more refractory fraction of OM. This corroborates studies that have shown that eutrophication enhances OM sedimentation (Sanders et al. 2014) and at the same time enhances OM remineralization (Barroso et al. revised; Chen et al., 2010; Jessen, 2016; Martin et al., 2020). The M3 was the most eutrophised site, particularly because of the sewage effluent inputs. High bacterial biomass in the POM is evidenced by the high proportion of BrFAs at M3 (Table 2), which may be attributed to sewage organic matter degraded by bacteria and fungi (Blaszczyk & Krzysko-Lupicka, 2013; Kaneda, 1991). Relative contributions of fungal markers (16:1005 and 18:1009; Chen et al., 2001; Meziane et al., 2006; Ngosong et al., 2012; Table A2) in the POM were not different at M1, M2 and M3 sites. In contrast, in the surface and subsurface sediments, these fungal FAs where 1.2 to 2 times more abundant at site M3 than at sites M1 and M2 (Table 3). The fact that at M3, high contribution of fungal biomarkers was measured in the SOM, but not in the POM suggests that fungal growth occurred in the sediment. Fungi degrade complex and refractory compounds into more labile OM and thereby make OM bioavailable to bacteria (Chung & Suberkropp, 2008; Ferreira et al., 2006). The higher CO₂ fluxes at M3 than at M1 and M2 (Barroso et al., revised) can therefore be caused by the more efficient degradation of OM through the microbial loop stimulated by the

560

561

562

563

564

565

566

567

568

569

570

571

572

573

574

575

576

577

578

579

580

581

582

583

higher fungal contribution through the inputs of labile organic matter (Fenchel, 2008). In addition, the increase of fungal biomass at subsurface sediments could lead to a stronger degradation of low-quality OM at depth (LCFAs), contribute to increase the CO₂ effluxes. Finally, even though C_{org} concentration is lower at M3 than at M1 and M2 mainly due to the higher inputs of mineral material, the enhanced microbial loop could also to a lesser extent explain this measure. Our result reveal that coastal eutrophication results in a mixing of refractory mangrove derived SOM with labile OM from algal and sewage sources and this mixing enhances the fungal and bacterial growth and CO₂ fluxes, potentially through a priming effect particularly at the M3 site.

5. Conclusion

This study provides combined data of fatty acid markers along with δ^{13} C and δ^{15} N signatures that characterizes the source of OM in three mangroves within the state of Rio de Janeiro. These mangroves are located along a eutrophication gradient as assessed by δ^{15} N, δ^{13} C signatures and C/N ratio in sediments, and particulate organic matter. The organic matter at the more impacted site M3 sediments was found to be supplied with greater algal or microphytobenthic biomasses than in the lesser impacted site, M1 and M2, in which mangrove production is found to be the main organic input. The SOM at M3 was more labile as indicated by the high contribution of PUFAs. Concomitantly to the algal biomass increase, biomasses of fungi were higher within the M3 sediments than at pristine M1 which suggests and enhancement of the microbial loop. In the highly impacted M3 mangrove sediments, refractory LCFAs, were in lower proportion than in the sediments of pristine site. Although the lower concentration of C_{org} at M3 than at M2 and M1 may be preliminary due to a larger input of mineral particles by rivers, it could also be promoted by a priming effect that potentially decomposes the refractory OM from the mangrove vegetation. In view of

the preliminary data presented here, a better understanding of the biogeochemical mechanisms involved in this important global storage of carbon could be gained by implementing experiments under controlled conditions in which known amounts of several OM sources can be added.

Acknowledgments

610

611

612

613

614

615

616

617

618

619

620

621

622

623

624

625

626

627

This work was supported by the French National programs LEFE (CNRS-INSU), the France-Brazil International Research Project VELITROP (Vulnérabilité des Ecosystèmes Littoraux Tropicaux face à l'Eutrophisation) funded by the French National Centre for Scientific Research (CNRS-INEE), the French chair at the University of the State of Rio de Janeiro (UERJ) Multidisciplinary approaches to describe, understand and monitor eutrophication in the tropical coastal ocean, the Brazilian National Council for Scientific and Technological Development (CNPq no. 314995/2020-0), Carlos Chagas Filho Foundation for Research Support of the State of Rio de Janeiro (FAPERJ no. E-26/203.304/2017), the Coordination for the Improvement of Higher Education Personnel (CAPES, Finance Code 001 and the internalization PRINTCAPES/UFF **FEEDBACKS** 772 program 99997.310301/2018-00). M.C. is funded by a Ph.D grant of the TOTAL Fondation

Literature cited

628

Abril, G., C. Cotovicz Jr., L., Nepomuceno, A., Erbas, T., Costa, S., V. Ramos, V., 629 Moser, G., Fernandes, A., Negri, E., A. Knoppers, B., Brandini, N., Machado, 630 631 W., Bernardes, M., Vantrepotte, V., 2022. Spreading eutrophication and changing CO2 fluxes in the tropical coastal ocean: a few lessons from Rio de 632 Janeiro. **ACMAR** 55, 461-476. 633 634 https://doi.org/10.32360/acmar.v55iEspecial.78518 Alongi, D. M. (2014). Carbon Cycling and Storage in Mangrove Forests. *Annual Review* 635 of Marine Science, 6(1), 195-219. https://doi.org/10.1146/annurev-marine-636 010213-135020 637 Alongi, D. M. (2020). Carbon Balance in Salt Marsh and Mangrove Ecosystems: A 638 639 Global Synthesis. Journal of Marine Science and Engineering, 8(10), 767. https://doi.org/10.3390/jmse8100767 640 Anand, A., Pandey, P. C., Petropoulos, G. P., Pavlides, A., Srivastava, P. K., Sharma, 641 J. K., & Malhi, R. K. M. (2020). Use of Hyperion for Mangrove Forest Carbon 642 Stock Assessment in Bhitarkanika Forest Reserve: A Contribution Towards 643 Carbon 644 Blue Initiative. Remote Sensing, 12(4), 597. https://doi.org/10.3390/rs12040597 645 Antonio, E. S., & Richoux, N. B. (2016). Tide-Induced Variations in the Fatty Acid 646 Composition of Estuarine Particulate Organic Matter. Estuaries and Coasts, 647 648 39(4), 1072-1083. https://doi.org/10.1007/s12237-015-0049-x Barcellos, D., Queiroz, H. M., Nóbrega, G. N., de Oliveira Filho, R. L., Santaella, S. T., 649 650 Otero, X. L., & Ferreira, T. O. (2019). Phosphorus enriched effluents increase eutrophication risks for mangrove systems in northeastern Brazil. Marine 651 Pollution Bulletin, 142, 58-63. https://doi.org/10.1016/j.marpolbul.2019.03.031 652

- Barroso, G. C., Abril, G., Machado, W., Abuchacra, R. C., Peixoto R. B., Bernardes,
- M., Marques, G. S., Sanders, C. J., Oliveira, G. B., de Oliveira Filho, S. R.,
- Amora, L., Marotta, H. (Revised). Linking eutrophication to carbon dioxide and
- methane emissions from exposed mangrove soils along an urban gradient.
- Bauer, D. F. (1972). Constructing Confidence Sets Using Rank Statistics. *Journal of*
- the American Statistical Association, 67(339), 687-690.
- https://doi.org/10.1080/01621459.1972.10481279
- Bergamino, L., Dalu, T., & Richoux, N. B. (2014). Evidence of spatial and temporal
- changes in sources of organic matter in estuarine sediments: Stable isotope
- and fatty acid analyses. *Hydrobiologia*, 732(1), 133-145.
- https://doi.org/10.1007/s10750-014-1853-1
- Bianchi, T. S. (2011). The role of terrestrially derived organic carbon in the coastal
- ocean: A changing paradigm and the priming effect. Proceedings of the
- 666 National Academy of Sciences, 108(49), 19473-19481.
- 667 https://doi.org/10.1073/pnas.1017982108
- 668 Błaszczyk, K., & Krzyśko-Łupicka, T. (2013). Microbial diversity of sewage sludge.
- 669 Proceedings of ECOpole, Vol. 7, No. 2.
- 670 https://doi.org/10.2429/proc.2013.7(2)059
- Bouillon, S., Borges, A. V., Castañeda-Moya, E., Diele, K., Dittmar, T., Duke, N. C.,
- Kristensen, E., Lee, S. Y., Marchand, C., Middelburg, J. J., Rivera-Monroy, V.
- H., Smith, T. J., & Twilley, R. R. (2008a). Mangrove production and carbon
- sinks: A revision of global budget estimates. Global Biogeochemical Cycles,
- 675 22(2), Article 2. https://doi.org/10.1029/2007GB003052
- Bouillon, S., Connolly, R. M., & Lee, S. Y. (2008b). Organic matter exchange and
- cycling in mangrove ecosystems: Recent insights from stable isotope studies.

of 678 Journal Sea Research, 59(1), 44-58. https://doi.org/10.1016/j.seares.2007.05.001 679 Bouillon, S., Dahdouh-Guebas, F., Rao, A. V. V. S., Koedam, N., & Dehairs, F. (2003). 680 Sources of organic carbon in mangrove sediments: Variability and possible 681 ecological implications. Hydrobiologia, 495(1), 33-39. 682 https://doi.org/10.1023/A:1025411506526 683 Bouillon, S., Moens, T., Koedam, N., Dahdouh-Guebas, F., Baeyens, W., & Dehairs, 684 685 F. (2004). Variability in the origin of carbon substrates for bacterial communities 686 in mangrove sediments. FEMS Microbiology Ecology, 49(2), 171-179. https://doi.org/10.1016/j.femsec.2004.03.004 687 Breitburg, D., Levin, L. A., Oschlies, A., Grégoire, M., Chavez, F. P., Conley, D. J., 688 689 Garçon, V., Gilbert, D., Gutiérrez, D., Isensee, K., Jacinto, G. S., Limburg, K. E., Montes, I., Nagvi, S. W. A., Pitcher, G. C., Rabalais, N. N., Roman, M. R., 690 Rose, K. A., Seibel, B. A., Zhang, J. (2018). Declining oxygen in the global 691 coastal waters. Science, 359(6371), 692 ocean and eaam7240. 693 https://doi.org/10.1126/science.aam7240 Bunting, P., Rosenqvist, A., Lucas, R. M., Rebelo, L.-M., Hilarides, L., Thomas, N., 694 Hardy, A., Itoh, T., Shimada, M., & Finlayson, C. M. (2018). The Global 695 Mangrove Watch—A New 2010 Global Baseline of Mangrove Extent. Remote 696 697 Sensing, 10(10), 1669. https://doi.org/10.3390/rs10101669 Camacho-Ibar, V. F., Aveytua-Alcázar, L., & Carriquiry, J. D. (2003). Fatty acid 698 reactivities in sediment cores from the northern Gulf of California. Organic 699 Geochemistry, 34(3), 425-439. https://doi.org/10.1016/S0146-6380(02)00211-5 700 Canuel, E. A. (2001). Relations between river flow, primary production and fatty acid 701 702 composition of particulate organic matter in San Francisco and Chesapeake

703	Bays: A multivariate approach. Organic Geochemistry, 32(4), 563-583.
704	https://doi.org/10.1016/S0146-6380(00)00195-9
705	Chen, G. C., Tam, N. F. Y., & Ye, Y. (2010). Summer fluxes of atmospheric greenhouse
706	gases N2O, CH4 and CO2 from mangrove soil in South China. Science of The
707	Total Environment, 408(13), 2761-2767.
708	https://doi.org/10.1016/j.scitotenv.2010.03.007
709	Chen, J., Ferris, H., Scow, K. M., & Graham, K. J. (2001). Fatty acid composition and
710	dynamics of selected fungal-feeding nematodes and fungi. Comparative
711	Biochemistry and Physiology Part B: Biochemistry and Molecular Biology,
712	130(2), 135-144. https://doi.org/10.1016/S1096-4959(01)00414-6
713	Choudhury, A. K., Das, M., Philip, P., & Bhadury, P. (2015). An Assessment of the
714	Implications of Seasonal Precipitation and Anthropogenic Influences on a
715	Mangrove Ecosystem Using Phytoplankton as Proxies. Estuaries and Coasts,
716	38(3), 854-872. https://doi.org/10.1007/s12237-014-9854-x
717	Chung, N., & Suberkropp, K. (2008). Influence of shredder feeding and nutrients on
718	fungal activity and community structure in headwater streams. Fundamental
719	and Applied Limnology 173(1):35-46, 173(1), 35-46.
720	https://doi.org/10.1127/1863-9135/2008/0173-0035
721	Clarke, K. R. (1993). Non-parametric multivariate analyses of changes in community
722	structure. Austral Ecology, 18(1), 117-143. https://doi.org/10.1111/j.1442-
723	9993.1993.tb00438.x
724	Cloern, J.E., Foster, S.Q., Kleckner, A.E., 2014. Phytoplankton primary production in
725	the world's estuarine-coastal ecosystems. Biogeosciences 11, 2477–2501.
726	https://doi.org/10.5194/bg-11-2477-2014

- Cotovicz, L. C., Knoppers, B. A., Brandini, N., Poirier, D., Costa Santos, S. J., Cordeiro,
- 728 R. C., & Abril, G. (2018). Predominance of phytoplankton-derived dissolved and
- particulate organic carbon in a highly eutrophic tropical coastal embayment
- 730 (Guanabara Bay, Rio de Janeiro, Brazil). Biogeochemistry, 137(1), 1-14.
- 731 https://doi.org/10.1007/s10533-017-0405-y
- 732 Dale, B. (2001). Marine dinoflagellate cysts as indicators of eutrophication and
- industrial pollution: A discussion. Science of The Total Environment, 264(3),
- 734 235-240. https://doi.org/10.1016/S0048-9697(00)00719-1
- Dalsgaard, J., St. John, M., Kattner, G., Müller-Navarra, D., & Hagen, W. (2003). Fatty
- acid trophic markers in the pelagic marine environment. In *Advances in Marine*
- 737 Biology (Vol. 46, p. 225-340). Academic Press. https://doi.org/10.1016/S0065-
- 738 2881(03)46005-7
- 739 David, F., Marchand, C., Taillardat, P., Thành-Nho, N., & Meziane, T. (2018).
- Nutritional composition of suspended particulate matter in a tropical mangrove
- creek during a tidal cycle (Can Gio, Vietnam). Estuarine, Coastal and Shelf
- 742 Science, 200, 126-130. https://doi.org/10.1016/j.ecss.2017.10.017
- David, F., Marchand, C., Thiney, N., Nhu-Trang, T.-T., & Meziane, T. (2019). Short-
- term changes in the quality of suspended particulate matter in a human
- impacted and mangrove dominated tropical estuary (Can Gio, Vietnam).
- 746 Continental Shelf Research, 178, 59-67.
- 747 https://doi.org/10.1016/j.csr.2019.03.011
- Davis, S. E., Corronado-Molina, C., Childers, D. L., & Day, J. W. (2003). Temporally
- dependent C, N, and P dynamics associated with the decay of Rhizophora
- mangle L. leaf litter in oligotrophic mangrove wetlands of the Southern

- Everglades. *Aquatic Botany*, 75(3), 199-215. https://doi.org/10.1016/S0304-3770(02)00176-6
 Dugdale, R. C., & Wilkerson, F. P. (1986). The use of 15N to measure nitrogen uptake
- in eutrophic oceans; experimental considerations1,2. *Limnology and*
- 755 Oceanography, 31(4), 673-689. https://doi.org/10.4319/lo.1986.31.4.0673FAO.
- 756 (2007). *The world's mangroves 1980-2005*. Food and Agriculture Organization
- of the United Nations. http://www.fao.org/3/a1427e/a1427e00.htm
- Fenchel, T. (2008). The microbial loop 25 years later. *Journal of Experimental Marine*
- 759 *Biology and Ecology*, 366(1), 99-103.
- 760 https://doi.org/10.1016/j.jembe.2008.07.013
- 761 Ferreira, V., Gulis, V., & Graça, M. A. S. (2006). Whole-stream nitrate addition affects
- litter decomposition and associated fungi but not invertebrates. Oecologia,
- 763 149(4), 718-729. https://doi.org/10.1007/s00442-006-0478-0
- Fistarol, G. O., Coutinho, F. H., Moreira, A. P. B., Venas, T., Cánovas, A., de Paula,
- S. E. M. J., Coutinho, R., de Moura, R. L., Valentin, J. L., Tenenbaum, D. R.,
- Paranhos, R., do Valle, R. de A. B., Vicente, A. C. P., Amado Filho, G. M.,
- Pereira, R. C., Kruger, R., Rezende, C. E., Thompson, C. C., Salomon, P. S., &
- Thompson, F. L. (2015). Environmental and Sanitary Conditions of Guanabara
- Rio de Janeiro. Frontiers in Microbiology, 6.
- 770 https://doi.org/10.3389/fmicb.2015.01232
- 771 Fontaine, S., Mariotti, A., & Abbadie, L. (2003). The priming effect of organic matter:
- A question of microbial competition? Soil Biology and Biochemistry, 35(6),
- 773 837-843. https://doi.org/10.1016/S0038-0717(03)00123-8

774	Gontikaki, E., Thornton, B., Cornulier, T., & Witte, U. (2015). Occurrence of Priming in
775	the Degradation of Lignocellulose in Marine Sediments. PLOS ONE, 10(12),
776	e0143917. https://doi.org/10.1371/journal.pone.0143917
777	Gritcan, I., Duxbury, M., Leuzinger, S., & Alfaro, A. C. (2016). Leaf Stable Isotope and
778	Nutrient Status of Temperate Mangroves As Ecological Indicators to Assess
779	Anthropogenic Activity and Recovery from Eutrophication. Frontiers in Plant
780	Science, 7. https://doi.org/10.3389/fpls.2016.01922
781	Guenet, B., Danger, M., Abbadie, L., & Lacroix, G. (2010). Priming effect: Bridging the
782	gap between terrestrial and aquatic ecology. Ecology, 91(10), 2850-2861.
783	https://doi.org/10.1890/09-1968.1
784	Hilaluddin, F., Yusoff, F. M., Natrah, F. M. I., & Lim, P. T. (2020). Disturbance of
785	mangrove forests causes alterations in estuarine phytoplankton community
786	structure in Malaysian Matang mangrove forests. Marine Environmental
787	Research, 104935.
788	Jennerjahn, T., Ittekkot, V., 1997. Organic matter in sediments in the mangrove areas
789	and adjacent continental margins of Brazil .1. Amino acids and hexosamines.
790	Oceanolica Acta 20, 359–369.
791	Jennerjahn, T.C., Ittekkot, V., 1999. Changes in organic matter from surface waters to
792	continental slope sediments off the São Francisco River, eastern Brazil. Marine
793	Geology 161, 129-140. https://doi.org/10.1016/S0025-3227(99)00045-6
794	Jessen, B. (2016). Ecological Effects of Nutrient Enrichment on a Coastal Fringe
795	Mangrove Forest. Open Access Dissertations. https://doi.org/10.23860/diss-
796	jessen-brita-2016

797 Kaneda, T. (1991). Iso- and anteiso-fatty acids in bacteria: Biosynthesis, function, and 798 taxonomic significance. Microbiology and Molecular Biology Reviews, 55(2), 799 288-302. Ke, Z., Tan, Y., Huang, L., Liu, J., Xiang, C., Zhao, C., & Zhang, J. (2019). Significantly 800 801 depleted 15N in suspended particulate organic matter indicating a strong influence of sewage loading in Daya Bay, China. Science of The Total 802 Environment, 650, 759-768. https://doi.org/10.1016/j.scitotenv.2018.09.076 803 Kennedy, H., Gacia, E., Kennedy, D. P., Papadimitriou, S., & Duarte, C. M. (2004). 804 805 Organic carbon sources to SE Asian coastal sediments. Estuarine, Coastal and 806 Shelf Science, 60(1), 59-68. https://doi.org/10.1016/j.ecss.2003.11.019 Kitsiou, D., & Karydis, M. (2011). Coastal marine eutrophication assessment: A review 807 analysis. Environment 37(4), 778-801. 808 data International, on https://doi.org/10.1016/j.envint.2011.02.004 809 810 Kopprio, G. A., Dutto, M. S., Garzón Cardona, J. E., Gärdes, A., Lara, R. J., & Graeve, M. (2018). Biogeochemical markers across a pollution gradient in a Patagonian 811 812 estuary: A multidimensional approach of fatty acids and stable isotopes. Marine 137, 813 Pollution Bulletin, 617-626. https://doi.org/10.1016/j.marpolbul.2018.10.059 814 Kristensen, E., & Alongi, D. M. (2006). Control by fiddler crabs (Uca vocans) and plant 815 roots (Avicennia marina) on carbon, iron, and sulfur biogeochemistry in 816 mangrove sediment. Limnology and Oceanography, 51(4), 1557-1571. 817 https://doi.org/10.4319/lo.2006.51.4.1557 818 Kristensen, E., Bouillon, S., Dittmar, T., & Marchand, C. (2008a). Organic carbon 819 dynamics in mangrove ecosystems: A review. Aquatic Botany, 89(2), 201-219. 820

https://doi.org/10.1016/j.aguabot.2007.12.005

821

- Kristensen, E., Flindt, M. R., Ulomi, S., Borges, A. V., Abril, G., & Bouillon, S. (2008b).
- Emission of CO2 and CH4 to the atmosphere by sediments and open waters in
- two Tanzanian mangrove forests. *Marine Ecology Progress Series*, 370, 53-67.
- 825 https://doi.org/10.3354/meps07642
- 826 Leng, M. J., & Lewis, J. P. (2017). C/N ratios and Carbon Isotope Composition of
- Organic Matter in Estuarine Environments. In K. Weckström, K. M. Saunders,
- P. A. Gell, & C. G. Skilbeck (Éds.), Applications of Paleoenvironmental
- Techniques in Estuarine Studies (p. 213-237). Springer Netherlands.
- https://doi.org/10.1007/978-94-024-0990-1_9
- 831 Liu, K.-K., Kao, S.-J., Chiang, K.-P., Gong, G.-C., Chang, J., Cheng, J.-S., & Lan, C.-
- Y. (2013). Concentration dependent nitrogen isotope fractionation during
- ammonium uptake by phytoplankton under an algal bloom condition in the
- Danshuei estuary, northern Taiwan. *Marine Chemistry*, 157, 242-252.
- 835 https://doi.org/10.1016/j.marchem.2013.10.005
- 836 Lovelock, C. E., Fourgurean, J. W., & Morris, J. T. (2017). Modeled CO2 Emissions
- from Coastal Wetland Transitions to Other Land Uses: Tidal Marshes,
- 838 Mangrove Forests, and Seagrass Beds. Frontiers in Marine Science, 4.
- https://doi.org/10.3389/fmars.2017.00143
- Maher, D. T., Call, M., Santos, I. R., & Sanders, C. J. (2018). Beyond burial: Lateral
- exchange is a significant atmospheric carbon sink in mangrove forests. *Biology*
- 842 *Letters*, 14(7), Article 7. https://doi.org/10.1098/rsbl.2018.0200
- Martin, R. M., Wigand, C., Oczkowski, A., Hanson, A., Balogh, S., Branoff, B., Santos,
- 844 E., & Huertas, E. (2020). Greenhouse Gas Fluxes of Mangrove Soils and
- Adjacent Coastal Waters in an Urban, Subtropical Estuary. *Wetlands*, 40(5),
- 846 1469-1480. https://doi.org/10.1007/s13157-020-01300-w

Meziane, T., d'Agata, F., & Lee, S. Y. (2006). Fate of mangrove organic matter along 847 848 a subtropical estuary: Small-scale exportation and contribution to the food of 849 communities. Marine Ecology **Progress** 312, crab Series, 15-27. https://doi.org/10.3354/meps312015 850 Meziane, T., Lee, S. Y., Mfilinge, P. L., Shin, P. K. S., Lam, M. H. W., & Tsuchiya, M. 851 (2007). Inter-specific and geographical variations in the fatty acid composition 852 of mangrove leaves: Implications for using fatty acids as a taxonomic tool and 853 1103-1113. 150(6), 854 tracers of organic matter. Marine Biology, 855 https://doi.org/10.1007/s00227-006-0424-z Meziane, T., & Tsuchiya, M. (2002). Organic matter in a subtropical mangrove-estuary 856 subjected to wastewater discharge: Origin and utilisation by two 857 858 macrozoobenthic species. Journal of Sea Research. 47(1), 1-11. https://doi.org/10.1016/S1385-1101(01)00092-2 859 Mfilinge, P. L., Meziane, T., Bachok, Z., & Tsuchiya, M. (2003). Fatty acids in 860 decomposing mangrove leaves: Microbial activity, decay and nutritional quality. 861 Series, 862 Marine Ecology **Progress** 265, 97-105. 863 https://doi.org/10.3354/meps265097 Mortillaro, J.-M., Rigal, F., Rybarczyk, H., Bernardes, M., Abril, G., Meziane, T., 2012. 864 Particulate Organic Matter Distribution along the Lower Amazon River: 865 Addressing Aquatic Ecology Concepts Using Fatty Acids. PLOS ONE 7, 866 867 e46141. https://doi.org/10.1371/journal.pone.0046141 868 Napolitano, G. E., Pollero, R. J., Gayoso, A. M., Macdonald, B. A., & Thompson, R. J. (1997). Fatty acids as trophic markers of phytoplankton blooms in the Bahía 869 870 Blanca estuary (Buenos Aires, Argentina) and in Trinity Bay (Newfoundland,

871	Canada). Biochemical Systematics and Ecology, 25(8), 739-755.
872	https://doi.org/10.1016/S0305-1978(97)00053-7
873	Nebbioso, A., & Piccolo, A. (2013). Molecular characterization of dissolved organic
874	matter (DOM): A critical review. Analytical and Bioanalytical Chemistry, 405(1),
875	109-124. https://doi.org/10.1007/s00216-012-6363-2
876	Ngosong, C., Gabriel, E., & Ruess, L. (2012). Use of the Signature Fatty Acid 16:1ω5
877	as a Tool to Determine the Distribution of Arbuscular Mycorrhizal Fungi in Soil.
878	Journal of Lipids, 2012, e236807. https://doi.org/10.1155/2012/236807
879	Nóbrega, G. N., Ferreira, T. O., Siqueira Neto, M., Queiroz, H. M., Artur, A. G.,
880	Mendonça, E. D. S., Silva, E. D. O., & Otero, X. L. (2016). Edaphic factors
881	controlling summer (rainy season) greenhouse gas emissions (CO2 and CH4)
882	from semiarid mangrove soils (NE-Brazil). Science of The Total Environment,
883	542, 685-693. https://doi.org/10.1016/j.scitotenv.2015.10.108
884	Nordhaus, I., Salewski, T., Jennerjahn, T.C., 2011. Food preferences of mangrove
885	crabs related to leaf nitrogen compounds in the Segara Anakan Lagoon, Java,
886	Indonesia. Journal of Sea Research 65, 414–426.
887	https://doi.org/10.1016/j.seares.2011.03.006
888	Nordhaus, I., Salewski, T., & Jennerjahn, T. C. (2017). Interspecific variations in
889	mangrove leaf litter decomposition are related to labile nitrogenous compounds.
890	Estuarine, Coastal and Shelf Science, 192, 137-148.
891	https://doi.org/10.1016/j.ecss.2017.04.029
892	Oksanen, J., Blanchet, F. G., Kindt, R., Legendre, P., Minchin, P., O'Hara, B., Simpson,
893	G., Solymos, P., Stevens, H., & Wagner, H. (2015). Vegan : Community Ecology
894	Package. R Package Version 2.2-1, 2, 1-2.

- 895 Pérez, A., Libardoni, B. G., & Sanders, C. J. (2018a). Factors influencing organic
- carbon accumulation in mangrove ecosystems. Biology Letters, 14(10),
- 897 20180237. https://doi.org/10.1098/rsbl.2018.0237
- 898 Pérez, A., Machado, W., Gutiérrez, D., Borges, A. C., Patchineelam, S. R., & Sanders,
- 899 C. J. (2018b). Carbon accumulation and storage capacity in mangrove
- 900 sediments three decades after deforestation within a eutrophic bay. Marine
- 901 *Pollution Bulletin*, 126, 275-280.
- 902 https://doi.org/10.1016/j.marpolbul.2017.11.018
- 903 Pérez, A., Machado, W., Gutierrez, D., Smoak, J. M., Breithaupt, J. L., Saldarriaga, M.
- 904 S., Sanders, L., Marotta, H., & Sanders, C. J. (2020). Carbon and nutrient
- 905 accumulation in mangrove sediments affected by multiple environmental
- 906 changes. Journal of Soils and Sediments, 20(5), 2504-2509.
- 907 https://doi.org/10.1007/s11368-020-02612-4
- 908 Pessenda, L. C. R., Vidotto, E., De Oliveira, P. E., Buso, A. A., Cohen, M. C. L.,
- 909 Rossetti, D. de F., Ricardi-Branco, F., & Bendassolli, J. A. (2012). Late
- 910 Quaternary vegetation and coastal environmental changes at Ilha do Cardoso
- 911 mangrove, southeastern Brazil. Palaeogeography, Palaeoclimatology,
- 912 Palaeoecology, 363-364, 57-68. https://doi.org/10.1016/j.palaeo.2012.08.014
- 913 Poungparn, S., Komiyama, A., Tanaka, A., Sangtiean, T., Maknual, C., Kato, S.,
- Tanapermpool, P., & Patanaponpaiboon, P. (2009). Carbon dioxide emission
- 915 through soil respiration in a secondary mangrove forest of eastern Thailand.
- 916 *Journal of Tropical Ecology*, 25(4), 393-400.
- 917 https://doi.org/10.1017/S0266467409006154
- 918 Queiroz, H. M., Ferreira, T. O., Taniguchi, C. A. K., Barcellos, D., do Nascimento, J.
- 919 C., Nóbrega, G. N., Otero, X. L., & Artur, A. G. (2020). Nitrogen mineralization

- and eutrophication risks in mangroves receiving shrimp farming effluents.
- 921 Environmental Science and Pollution Research, 27(28), 34941-34950.
- 922 https://doi.org/10.1007/s11356-020-09720-1
- 923 Ribeiro, C., & Kjerfve, B. (2002). Anthropogenic influence on the water quality in
- Guanabara Bay, Rio de Janeiro, Brazil. Regional Environmental Change, 3,
- 925 13-19. https://doi.org/10.1007/s10113-001-0037-5
- 926 Rodrigues, R. P., Knoppers, B. A., Souza, W. F. L. de, & Santos, E. S. (2009).
- 927 Suspended matter and nutrient gradients of a small-scale river plume in
- 928 Sepetiba Bay, SE-Brazil. Brazilian Archives of Biology and Technology, 52,
- 929 503-512. https://doi.org/10.1590/S1516-89132009000200030
- 930 Sanders, C. J., Eyre, B. D., Santos, I. R., Machado, W., Luiz-Silva, W., Smoak, J. M.,
- Breithaupt, J. L., Ketterer, M. E., Sanders, L., Marotta, H., & Silva-Filho, E.
- 932 (2014). Elevated rates of organic carbon, nitrogen, and phosphorus
- 933 accumulation in a highly impacted mangrove wetland. Geophysical Research
- 934 Letters, 41(7), 2475-2480. https://doi.org/10.1002/2014GL059789
- 935 Sanders, C.J., Smoak, J.M., Naidu, A.S., Patchineelam, S.R., 2008. Recent Sediment
- 936 Accumulation in a Mangrove Forest and Its Relevance to Local Sea-Level Rise
- 937 (Ilha Grande, Brazil). Journal of Coastal Research 24, 533–536.
- 938 https://doi.org/10.2112/07-0872.1
- 939 Santos, I. R., Maher, D. T., Larkin, R., Webb, J. R., & Sanders, C. J. (2019). Carbon
- outwelling and outgassing vs. Burial in an estuarine tidal creek surrounded by
- mangrove and saltmarsh wetlands. Limnology and Oceanography, 64(3),
- 942 996-1013. https://doi.org/10.1002/lno.11090
- 943 Sarker, S., Masud-Ul-Alam, M., Hossain, M. S., Chowdhury, S. R., & Sharifuzzaman,
- 944 S. M. (2021). A review of bioturbation and sediment organic geochemistry in

945 mangroves. Geological Journal, 56(5), 2439-2450. https://doi.org/10.1002/gj.3808 946 947 Silva-Filho, E. V., Sanders, C. J., Bernat, M., Figueiredo, A. M. G., Sella, S. M., & Wasserman, J. (2011). Origin of rare earth element anomalies in mangrove 948 949 sediments, Sepetiba Bay, SE Brazil: Used as geochemical tracers of sediment 950 sources. Environmental Earth Sciences, 64(5), 1257-1267. https://doi.org/10.1007/s12665-011-0942-y 951 952 Smith, V. H. (2003). Eutrophication of freshwater and coastal marine ecosystems a 953 global problem. Environmental Science and Pollution Research, 10(2), 126-139. https://doi.org/10.1065/espr2002.12.142 954 Sun, M.-Y. i, Aller, R. C., Lee, C., & Wakeham, S. G. (2002). Effects of oxygen and 955 956 redox oscillation on degradation of cell-associated lipids in surficial marine Cosmochimica Acta, 957 sediments. Geochimica et 66(11), 2003-2012. 958 https://doi.org/10.1016/S0016-7037(02)00830-X Sun, M.-Y. i, Lee, C., & Aller, R. C. (1993). Laboratory studies of oxic and anoxic 959 960 degradation of chlorophyll-a in Long Island Sound sediments. Geochimica et 961 Cosmochimica Acta, 57(1), 147-157. https://doi.org/10.1016/0016-7037(93)90475-C 962 Svensen, C., Viličić, D., Wassmann, P., Arashkevich, E., & Ratkova, T. (2007). 963 Plankton distribution and vertical flux of biogenic matter during high summer 964 stratification in the Krka estuary (Eastern Adriatic). Estuarine, Coastal and Shelf 965 Science, 71(3), 381-390. https://doi.org/10.1016/j.ecss.2006.07.022 966 967 Unger, D., Herbeck, L.S., Li, M., Bao, H., Wu, Y., Zhang, J., Jennerjahn, T., 2013. Sources, transformation and fate of particulate amino acids and hexosamines 968 969 under varying hydrological regimes in the tropical Wenchang/Wenjiao Rivers

and Estuary, Hainan, China. Continental Shelf Research, Land - Sea 970 971 Interactions in Tropical Ecosystems of Hainan, China 57, 44-58. https://doi.org/10.1016/j.csr.2012.02.014Volkman, J. K. (2006). Lipid Markers 972 for Marine Organic Matter. In J. K. Volkman (Éd.), Marine Organic Matter: 973 DNA 27-70). 974 Biomarkers, Isotopes and (p. Springer. https://doi.org/10.1007/698 2 002 975 Wakeham, S. G., Hedges, J. I., Lee, C., Peterson, M. L., & Hernes, P. J. (1997). 976 Compositions and transport of lipid biomarkers through the water column and 977 surficial sediments of the equatorial Pacific Ocean. Deep Sea Research Part II: 978 979 Topical Studies Oceanography, 44(9), 2131-2162. in https://doi.org/10.1016/S0967-0645(97)00035-0 980 981 Wang, F., Sanders, C.J., Santos, I.R., Tang, J., Schuerch, M., Kirwan, M.L., Kopp, R.E., Zhu, K., Li, X., Yuan, J., Liu, W., Li, Z., 2021. Global blue carbon 982 accumulation in tidal wetlands increases with climate change. National Science 983 984 Review 8, nwaa296. https://doi.org/10.1093/nsr/nwaa296 Webber, M.K., 2016. Chapter 49- Mangroves, in: First Global Integrated Marine 985 986 Assessment (First World Ocean Assessment). p. 19. Xiong, Y., Liao, B., & Wang, F. (2018). Mangrove vegetation enhances soil carbon 987 988 storage primarily through in situ inputs rather than increasing allochthonous 989 sediments. Marine Pollution Bulletin, 131, 378-385. https://doi.org/10.1016/j.marpolbul.2018.04.043 990 Xu, Y., & Jaffé, R. (2007). Lipid biomarkers in suspended particles from a subtropical 991 992 estuary: Assessment of seasonal changes in sources and transport of organic Environmental 666-678. 993 matter. Marine Research, 64(5),

https://doi.org/10.1016/j.marenvres.2007.07.004

994

Zhu, P., Wang, Y., Shi, T., Huang, G., & Gong, J. (2018). Genetic Diversity of Benthic
 Microbial Eukaryotes in Response to Spatial Heterogeneity of Sediment
 Geochemistry in a Mangrove Ecosystem. *Estuaries and Coasts*, *41*(3), 751-764.
 https://doi.org/10.1007/s12237-017-0317-z