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1 **Assessing extracted organic matter quality from river sediments by elemental and**
2 **molecular characterization: Application to the Tietê and Piracicaba Rivers (São**
3 **Paulo, Brazil)**

4

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25

27 Abstract

28 Urban river pollution causes serious problems to the environment, human health, and
29 water scarcity. Developing tools to identify and assess the health of aquatic river
30 systems is essential for monitoring the quality of rivers and implementing actions. This
31 study assesses the elemental and molecular characteristics of organic matter (OM)
32 extracted from river sediments and associates them with river quality. To assess the
33 quality of sediment cores, the most reactive and available OM from two urban rivers
34 (Tietê and Piracicaba Rivers, São Paulo, Brazil) was isolated with alkaline and water
35 solutions. It was then characterized by elemental composition, ultraviolet-visible
36 spectroscopy, and fluorescence excitation-emission matrix with parallel factor analysis.
37 The average yield of alkaline extraction was $40.71\% \pm 5.52\%$ of OM present in the bulk
38 sediments. Extracted organic matter from sediments (EOMSed) from the Tietê River
39 presented the highest average concentrations of non-purgeable organic carbon (NPOC)
40 and total organic nitrogen (TON), and the lowest average NPOC/TON molar ratios and
41 specific UV absorbance at 254 nm ($SUVA_{254}$). Considering the high degree of
42 eutrophication in the Tietê River, these results suggest a greater input of simple OM
43 with nitrogenous structures. The humic-like component in EOMSed was the most
44 abundant in both rivers. The aromaticity of EOMSed from the Piracicaba River was
45 evidenced by the greater contribution of complex structures in the form of aromatic and
46 polyaromatic moieties and higher $SUVA_{254}$. EOMSed from the Tietê River also featured
47 enhanced biological activity due to the greater contribution of microbial-derived
48 products and the presence of small molecules and nitrogenous structures. As this
49 combination of elemental and spectroscopic techniques successfully identified the

50 characteristics of extracted OM, it can be used as a tool to assess the global river
51 quality.

52 **Keywords:** River sediments, Extracted organic matter, Fluorescence, Parallel factor
53 analysis.

54

55 **1. Introduction**

56 Sediments consist of particle accumulation with different physical and chemical
57 properties that are composed of inorganic and organic material. The particles are
58 transported by water, air, erosion, and weathering processes and distributed along rivers
59 (Murdoch and MacKnight, 1991; Schorer and Eisele, 1997). The sediments are
60 biogeochemically active due to the presence of many microbes and the continuous input
61 of organic and inorganic substances (He et al., 2019; Kumwimba et al., 2017).

62 Organic matter (OM) in the sediments can originate from external sources
63 (allochthonous) or from the aquatic ecosystem itself (autochthonous) (Brailsford et al.,
64 2019; Kindler et al., 2011). Moreover, rivers are responsible for transferring carbon (C)
65 between the terrestrial biosphere and oceans, where this element is transformed and
66 stored (Cole et al., 2007). In sediments, bacteria consume or decompose organic
67 particles, thus reducing the mass of OM (Bloesch, 2009). The organic material resistant
68 to microbial action and any remaining products are deposited on the bottom of rivers,
69 along with terrestrial sediments (Burdige, 2007; Henrichs, 1992). OM is then
70 remineralized, altered, or preserved during early diagenesis, which records input history
71 (Engel and Macko, 2013).

72 The mobilization and quality of sediments are partially affected by
73 anthropogenic actions that cause extensive changes in the aquatic environment
74 (Bloesch, 2009). The excessive load of nutrients leads to the eutrophication of rivers,

75 which is a process of increasing the OM load in an aquatic ecosystem (Nixon, 1995). In
76 areas with a high population density, the main sources of nutrients are domestic sewage
77 discharge, industrial effluent, and water drained from agricultural areas (Kubo and
78 Kanda, 2020; Smith et al., 2014). Sediments with high OM content promote oxygen
79 consumption through decomposition, which can harm aquatic animals and plants
80 (Duarte, 1995).

81 Barra Bonita Reservoir in São Paulo State, Brazil, is formed by the damming of
82 the Tietê and Piracicaba Rivers, and it is the first of six reservoirs of the Middle Tietê
83 River Basin (Rodrigues et al., 2020). The Tietê and Piracicaba basins have different
84 water resource management strategies, with different types of land use and occupation
85 (Cruz et al., 2017). Both rivers receive a high degree of organic compounds, although
86 the Tietê River is more eutrophic than the Piracicaba River, because it receives a large
87 load of industrial and domestic waste (dos Santos et al., 2006; Morais et al., 2021;
88 Rodrigues et al., 2020). The Middle Tietê River had a biochemical oxygen demand
89 (BOD) of 33,636 t day⁻¹ in 2017 (CETESB, 2018). Before reaching the reservoir, the
90 Tietê River passes through the metropolitan area of São Paulo (Upper Tietê River),
91 which has a high population density and presented a BOD of 612,069 t day⁻¹. This
92 represents 57% of BOD of the Tietê River. By comparison, the Piracicaba Basin had a
93 BOD of 94,818 t day⁻¹ (CETESB, 2018). According to the State of São Paulo
94 Environmental Company (CETESB), the courses of both aquatic bodies are situated in
95 industrial areas marked by a high demographic density and intense land use (CETESB,
96 2018). However, regarding the course of the Middle Tietê River, its non-compliance
97 with water-quality standards stands at around 100% due to the untreated sewage
98 discharge in this stretch of the Tietê River (CETESB, 2018).

99 In the current scenario of scarce freshwater resources in terms of both the quality
100 and quantity available for use, it is urgent to restore water bodies. One way to do so is to
101 focus on assessing OM quality in sediments. Furthermore, finding the tools to identify
102 and assess the health of aquatic river systems is essential for the implementation of
103 actions. Molar C to nitrogen (N) ratios can be useful to identify the origin of OM
104 (Burone et al., 2003; Meyers, 1994), whereas determining the optical properties of OM
105 present in sediments is also a rapid and efficient way to assess the quality of water
106 resources and obtain information about anthropogenic activities (Du et al., 2021). OM is
107 a small fraction of the sediment compared to the inorganic fraction. The extraction is
108 carried out to isolate part of the OM and obtain information about its origin and quality.
109 For this purpose, water or basic extractants have shown their potential for determining
110 the quality and origin of OM in sediments (Brym et al., 2014; Funkey et al., 2019). The
111 neutral aqueous medium allows for the extraction of polar substances of small
112 molecular weight, which are free from the mineral fraction in the sediments. Water
113 alkaline extraction favors the extraction of more polar or reactive substances, even
114 allowing for the extraction of substances linked to minerals (Olk et al., 2019). After the
115 extraction with neutral and basic water, there remains only an insoluble organic fraction
116 that is strongly linked to minerals. This can be considered a stable or less reactive OM,
117 which will hardly influence the chemical processes in the sediment (Guigue et al., 2014;
118 Muller et al., 2014; Olk et al., 2019).

119 To assess the sediment quality, the most available and reactive OM was isolated
120 with neutral and alkaline water solutions. It was then fully characterized by elemental
121 composition, ultraviolet-visible spectroscopy (UV-Vis), and fluorescence excitation-
122 emission matrix (EEM) processed with parallel factor analysis (PARAFAC). This study
123 aimed to evaluate the elemental and molecular features of the extractable OM of

124 sediments taken from the Piracicaba and Tietê Rivers and associate this information
125 with the global river quality.

126

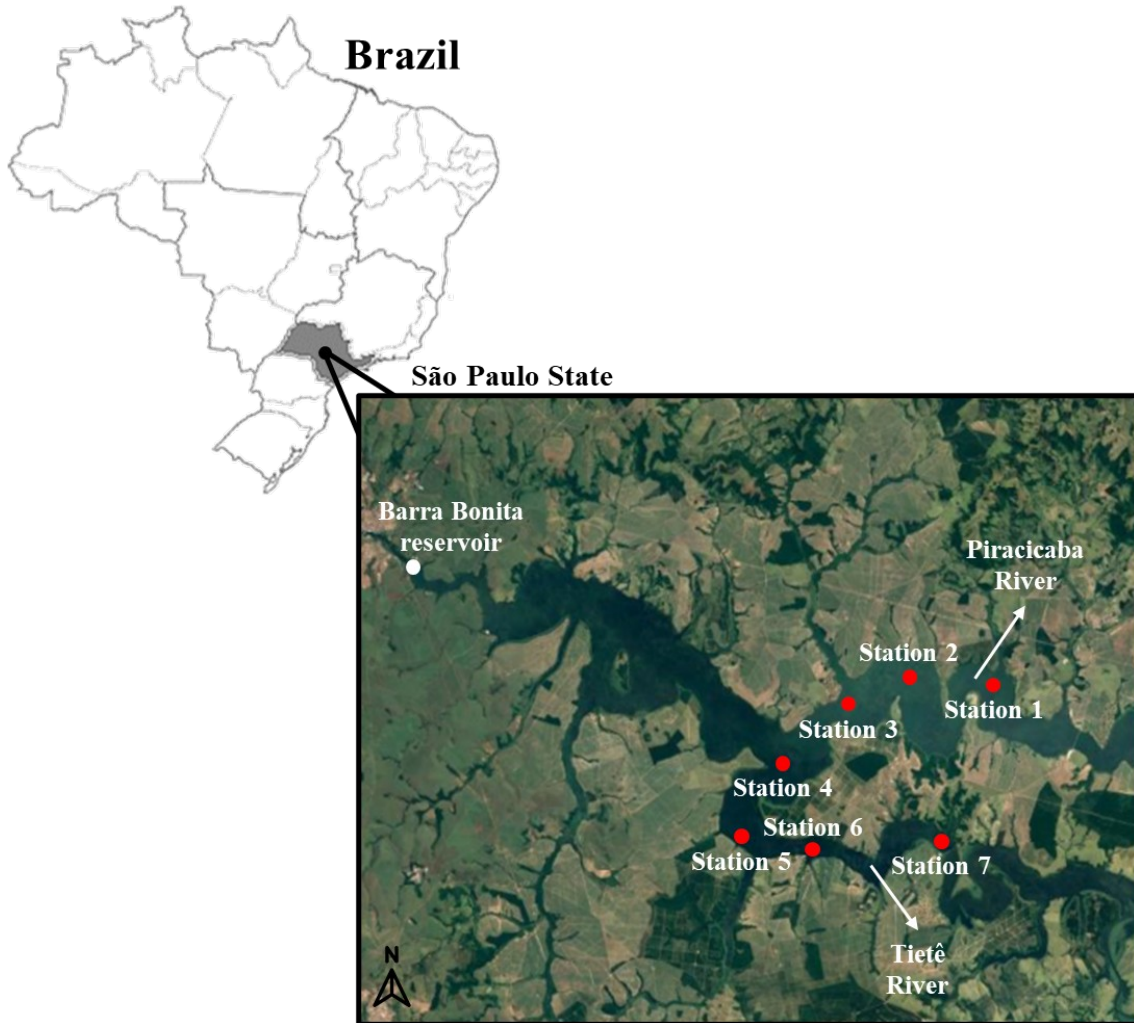
127 **2. Materials and methods**

128 *2.1. Study area description and sediment sampling*

129 The study area covers the Tietê and Piracicaba Rivers upstream from the Barra
130 Bonita Reservoir. The Barra Bonita Reservoir, located between the cities of Barra
131 Bonita and Igarapu do Tietê, was created from the flooding and damming of these rivers
132 (Bernardo et al., 2016). The Tietê and Piracicaba Rivers pass through large urban
133 centers until their confluence. Both rivers receive a large load of organic and inorganic
134 pollutants, which are delivered to the reservoir, although a greater load of pollutants is
135 dumped into the Tietê River (Smith et al., 2014). The study area was chosen due to the
136 different uses and occupations of the soil in this region, characterized by pollution
137 issues and multiple uses of water. Furthermore, this region has suffered from many
138 anthropic actions, mainly due to deforestation and flooding for the construction of six
139 successive reservoirs, with the Barra Bonita Reservoir being the first (Rodrigues et al.,
140 2020).

141 The sediment cores were collected at seven points: three on the Piracicaba River
142 (stations 1, 2, and 3), one at the confluence region (station 4), and three on the Tietê
143 River (stations 5, 6, and 7) (Figure 1) (Morais et al., 2021). The collection points were
144 georeferenced using a GPS Trimble Navigation unit as shown in the supplementary
145 material (Table S1); the sampling took place on July 25, 2017 (austral winter). The
146 sediment samples were collected using core sampling, which allowed us to maintain the
147 original deposition of sedimentary layers. The horizontal slicing was performed at the
148 same time as the sample collection, in different sizes (Table S2) under normal

149 atmosphere along the sediment cores without removing the interstitial water, thus
150 totaling 69 sample layers. The sediment samples were immediately packed into
151 polypropylene flasks and kept in a thermal box during transport to the laboratory to
152 avoid the oxidation effect.



153

154 **Figure 1:** Location of the Barra Bonita Reservoir (white dot) and sediment sample
155 collection stations (red dots).

156

157 2.2. Elemental analysis

158 The sediment samples were frozen, freeze-dried (L101, Liotop), crushed using
159 an automatic mortar grinder (RM 200, Retsch), and sieved through a 100-mesh sieve.

160 Total carbon (TC) content of the sediment samples was assessed using the dry

161 combustion method. For this purpose, 20 mg of the homogenized samples were
162 accurately weighed directly in the tin capsules. The standard used in the analysis was
163 aspartic acid, and the method was validated using the soil certified reference material
164 (ThermoFisher Soil Reference Material NC PN338 40025). All measurements were
165 performed in an elemental analyzer (Flash 2000, ThermoFisher Scientific).

166

167 *2.3. Extractable organic matter from sediment samples*

168 *2.3.1. Extraction*

169 The alkaline extraction was performed with NaOH to isolate OM in the sediment
170 samples taken from the Piracicaba and Tietê Rivers. The sediment extracts were
171 denominated EOMSed (extracted organic matter from sediments). Approximately 1.0 g
172 of each sample was placed in polypropylene flasks with 45.0 mL of 0.1 mol L⁻¹ NaOH
173 (ThermoFisher Scientific) and shaken for 24 h in an overhead shaker (Rex 20,
174 Heidolph) at 10 rpm. The samples were then centrifuged (Sigma 3-18K, Grosseron) at
175 10,000 rpm for 10 min and filtered over 0.45 µm syringe filters (Minisart NML,
176 Sartorius). Furthermore, another extraction method was conducted in the same way as
177 previously described with 45.0 mL ultrapure water (Ultrapure Water Cell, Starna Ltd) in
178 which the extracts from sediments were denominated WEOMSed (water-extracted
179 organic matter from sediments).

180

181 *2.3.2. Non-purgeable organic carbon and total organic nitrogen determination*

182 Non-purgeable organic carbon (NPOC) and total organic nitrogen (TON) from
183 EOMSed were quantified after dilution with ultrapure water to fit the standard NPOC
184 calibration curve (maximum 30 mg L⁻¹ of C). The extracts were acidified and measured
185 using an elemental analyzer (TOC-V Shimadzu). The NPOC/TON molar ratios were

186 calculated. The extraction yield was obtained by dividing the quantity of organic carbon
187 (OC) in the extracted solution in mg (NPOC multiplied by the extraction volume) by the
188 carbon content in the corresponding sediment in mg (TC multiplied by extracted mass
189 sample).

190

191 *2.3.3. UV-Vis spectroscopy*

192 Absorbance measurements were performed for all EOMsEd and WEOMsEd
193 samples using a double beam UV-Vis spectrophotometer (UV 1800, Shimadzu) with a
194 wavelength range from 200 to 700 nm in a 1 cm path length quartz cell and a scan speed
195 of 300 nm min⁻¹. A reference cell of NaOH and deionized water was used to measure
196 EOMsEd and WEOMsEd, respectively. From the absorbance measurements, it was
197 possible to define the dilution factor for fluorescence. Thus, all samples had the
198 absorbance adjusted to 0.1 at 254 nm, thus allowing their comparisons by avoiding the
199 inner filter effect for the fluorescence analysis (Kothawala et al., 2013). Specific UV
200 absorbance at 254 nm (SUVA₂₅₄) was calculated by dividing the UV absorbance
201 measured at 254 nm by the NPOC concentration (mg of C L⁻¹) and the optical path of
202 the cuvette (0.01 m) (Weishaar et al., 2003).

203

204 *2.3.4. Fluorescence spectroscopy*

205 *2.3.4.1. Sample preparation and analysis*

206 For the study of EEM, 1.0 mL of each sample diluted to absorbance at 254 nm
207 equal 0.1 (1 cm path length) was placed in quartz cells along with 1.0 mL of 0.3 mol L⁻¹
208 HEPES (Acros Organics) for pH regulation at 7 and 1.5 mL of 0.1 mol L⁻¹ NaClO₄
209 (Sigma-Aldrich) with a purity of 99.99% to fix ionic strength. The samples were
210 analyzed immediately after preparation.

211 All measured spectra were obtained with a fluorescence spectrofluorometer
212 (F4500, Hitachi). The EEM spectra were acquired with an excitation range from 200 to
213 500 nm and an emission range from 250 to 700 nm at a scan speed of 2400 nm min⁻¹.
214 The steps and slits of emission and excitation were fixed at 5 nm, and the detector
215 voltage was 700 V. Both emission and excitation detectors were corrected to prevent
216 wavelength sensitivity. The Raman spectrum of ultrapure water (Ultrapure Water Cell,
217 Starna Ltd) was measured on a daily basis with excitation at 350 nm, scan speed at
218 240 nm min⁻¹, emission from 360 to 420 nm, and excitation and emission slit fixed at
219 5 nm and 700 V to normalize the EEM intensity with the Raman scattering peak
220 (Lawaetz and Stedmon, 2009).

221

222 *2.3.4.2. Fluorescence data processing*

223 PARAFAC was conducted on the EEM dataset using PROGMEEF software
224 (<https://woms18.univ-tln.fr/progmeef/>) in Matlab language. All the EEMs were cleaned
225 from the diffusion signals using Rayleigh scattering by cutting the diffusion band in 15
226 nm and using first- and second-order Raman scattering by applying the Zeep method
227 (Mounier et al., 2011; Zepp et al., 2004). The number of evaluated components varied
228 from 2 to 5 in a spectral range from 240 to 500 nm in excitation and from 250 to 700
229 nm in emission. The number of components was defined using the core consistency
230 diagnostic (CORCONDIA). The optimal rank was the model giving the higher number
231 of components with a CORCONDIA over 60% (Mounier et al., 2011). The excitation
232 and emission of components obtained by PARAFAC were compared to the OpenFluor
233 database (Murphy et al., 2014).

234

235 *2.4. Statistical analysis*

236 Unpaired t-tests were used to determine any statistical differences between the
237 TC in bulk sediments from the Tietê and Piracicaba Rivers and NPOC, TON,
238 NPOC/TON molar ratios, and SUVA values obtained for EOM_{Sed} from the Tietê and
239 Piracicaba Rivers. The correlation coefficient between the NPOC/TON molar ratios and
240 the SUVA₂₅₄ values was calculated.

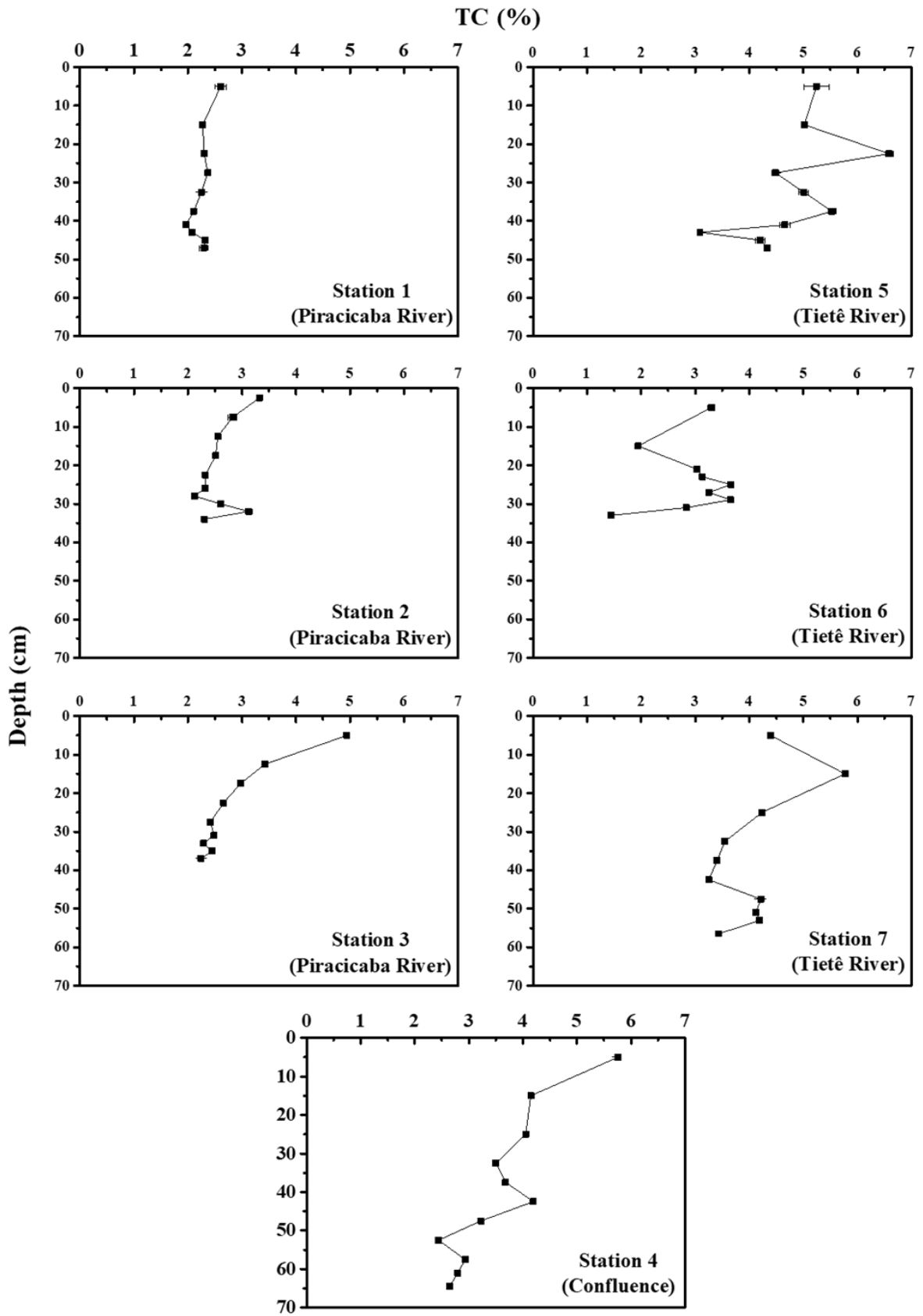
241

242 **3. Results and discussion**

243 *3.1. Total carbon characteristics in bulk sediments*

244 The distributions of TC content in the bulk sediment cores in the Piracicaba and
245 Tietê Rivers were different (Figure 2). In the collection stations of the Piracicaba River
246 (stations 1, 2, and 3), the highest TC value was found in the upper layer of the sediment
247 cores, and a decrease in TC content was observed at the lower layers of the vertical
248 distribution. In station 1, TC varied from 1.96% to 2.60% with a coefficient of variation
249 (CV) of 0.10, and the lowest value at a depth of 41 cm. In station 2, TC varied from
250 2.12% to 3.32% (CV = 0.15), and despite the decrease in TC when entering the
251 sediment, it was possible to observe an increase in TC content between the depths of 30
252 cm and 32 cm. In station 3, TC varied from 2.24% to 4.94% (CV = 0.30), although it
253 decreased exponentially from the surface to a depth of 27.5 cm, and from that depth, it
254 remained almost constant. In the confluence region, TC varied from 2.44% to 5.76%
255 (CV = 0.27), although the highest TC content is found in the surface layer, as in the
256 collection stations of the Piracicaba River. Its behavior is more similar to the collection
257 stations located on the Tietê River, which present a random TC distribution in the
258 deeper layers of the sediment cores. TC variation in the Tietê River ranged from 3.09%
259 to 6.59% (CV = 0.19), 1.44% to 3.66% (CV = 0.26), and 3.25% to 5.77% (CV = 0.19)
260 at stations 5, 6, and 7, respectively.

261 TC content is a fundamental parameter to describe the abundance of OM and
262 inorganic carbon (IC) in sediments (Veres, 2002). The random distribution of TC in the
263 Tietê River may be associated with an irregular input of OM and IC. A unpaired t-test
264 with a 95% confidence level showed that there were significant differences between the
265 average TC of the rivers. The average TC content in the Tietê River (3.96 ± 1.11) is
266 higher than in the Piracicaba River (2.57 ± 0.58). The highest TC content for the Tietê
267 River suggests that this river is more eutrophic than the Piracicaba River, since the
268 accumulation of nutrients, mainly P and N, in the aquatic bodies increases the synthesis
269 of OM (Castillo, 2020). This hypothesis is corroborated by a study that we previously
270 published on the quantification of total phosphorus (TP) in the same sediment samples
271 studied here (Morais et al., 2021). As TP is a chemical variable used to assess the
272 nutrient load and the extent of eutrophication in water bodies, the higher average TP
273 content in the Tietê River ($4316.16 \pm 1062 \text{ mg kg}^{-1} \text{ P}$) than in the Piracicaba River
274 ($1800.17 \pm 696.82 \text{ mg kg}^{-1} \text{ P}$) indicates that this river has a higher degree of
275 eutrophication (Morais et al., 2021).



276

277 **Figure 2.** Total carbon distribution inside the sediment cores at the collection stations.

278

25

26

279 3.2. Characteristics of extracted organic matter from sediments

280 Table 1 shows the average concentration of NPOC and TON, alkaline extraction
 281 yield, NPOC/TON molar ratio, and SUVA₂₅₄ of EOM_{Sed} at the different stations. These
 282 values for each sample are shown in the supplementary material (Table S3). The
 283 extraction method with alkaline solution extracted an average of 40.71% ± 5.52% of
 284 OM present in the bulk sediments. The yield of OM extraction depends on the property
 285 of the extractant and is generally low. Among the different extractants used for OM
 286 extraction, NaOH seems to be the most effective (Kurek et al., 2020; Sire et al., 2009).

287

288 **Table 1.** Average concentration of non-purgeable organic carbon (NPOC) and total
 289 organic nitrogen (TON), alkaline extraction yield, NPOC/TON molar ratio, and specific
 290 UV absorbance at 254 nm (SUVA₂₅₄) of the extracted organic matter from sediments at
 291 the collection stations.

Station	NPOC (mg C g ⁻¹)	TON (mg N g ⁻¹)	Extraction yield (%)	NPOC/TON ratio	SUVA ₂₅₄ (L mg ⁻¹ m ⁻¹)
1	9.02±0.84	1.14±0.11	40.63±5.17	6.80±0.20	6.36±0.53
2	10.65±1.71	1.25±0.24	41.03±3.58	7.37±1.00	5.99±0.69
3	12.59±1.98	1.75±0.38	45.23±6.56	6.22±0.49	6.11±1.08
4	13.54±4.82	2.40±0.76	37.17±5.61	4.78±0.30	4.54±0.73
5	19.60±5.74	3.01±0.74	40.11±5.17	5.53±0.50	3.92±0.61
6	11.90±3.54	2.00±0.52	40.50±3.96	5.05±0.37	3.70±0.51
7	16.24±2.31	2.51±0.45	41.05±6.36	5.59±0.32	4.44±0.83

292

293 A unpaired t-test at the 95% confidence level demonstrated that there were
294 significant differences in the NPOC and TON averages of EOMSed in the Tietê and
295 Piracicaba Rivers. The average concentration of NPOC and TON of EOMSed in the
296 Tietê River ($16.05 \pm 5.10 \text{ mg C g}^{-1}$ and $2.52 \pm 0.70 \text{ mg N g}^{-1}$, respectively) was higher
297 than that in the Piracicaba River ($10.69 \pm 2.11 \text{ mg C g}^{-1}$ and $1.37 \pm 0.37 \text{ mg N g}^{-1}$,
298 respectively). The highest NPOC concentrations of EOMSed in the Tietê River may be
299 due to the fact that the river passes through the metropolitan area of São Paulo, where it
300 receives a large load of domestic sewage and industrial effluents, resulting in a larger
301 biological oxygen demand than the Piracicaba River (CETESB, 2018). Furthermore,
302 taking into account the history of the Tietê River, its high degree of contamination
303 (Rocha et al., 2011, 2010) and eutrophication (Morais et al., 2021), the higher TON
304 concentration of EOMSed in the Tietê River when compared to the Piracicaba River
305 may be due to the sewage discharge containing labile and fresh OM.

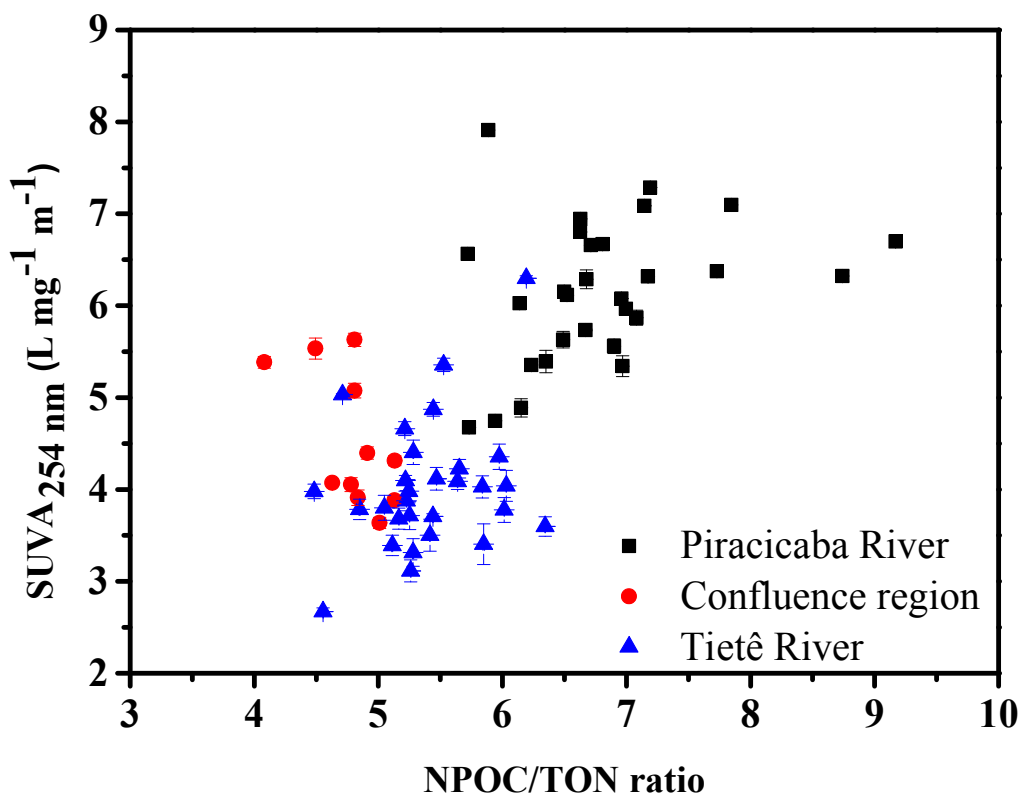
306 The average NPOC/TON molar ratios of EOMSed in the Tietê and Piracicaba
307 Rivers were statistically different (95% confidence level, unpaired t-test) and were
308 higher for the Piracicaba River (6.80 ± 0.79) compared to the Tietê River (5.39 ± 0.46).
309 Considering the historical course of the Tietê River and its high degree of
310 eutrophication (Morais et al., 2021), the lower ratios found in the river may suggest a
311 larger input of simple OM with nitrogenous structures, which may indicate effluent
312 input. In the confluence region, the NPOC/TON molar ratio of EOMSed was the lowest:
313 4.78 ± 0.30 . The lower value of the NPOC/TON molar ratio shows an increase in OM
314 deposition with nitrogenous structures, suggesting that the confluence region is
315 predominantly influenced by the Tietê River, which showed the highest nitrogen

316 concentrations (range of 2.00–3.01 mg N g⁻¹). Despite the difference in the NPOC/TON
317 molar ratios of EOM_{Sed} between the Tietê and Piracicaba Rivers, the studied EOM_{Sed}
318 showed a NPOC/TON molar ratio that varied from 4.1 to 9.2 (Figure 3). The
319 NPOC/TON molar ratios between 4 and 10 categorize the sources of C and N of algae
320 and aquatic plants (Kaushal and Binford, 1999; Meyers, 1994).

321 SUVA₂₅₄ is associated with the aromaticity of OM due to the carbon double
322 bond (C=C) of aromatic moieties or polycondensated aromatic rings that absorb light at
323 254 nm (Edzwald and Tobiasson, 2011). Therefore, high SUVA₂₅₄ values indicate an
324 OM formed by more structures that absorb light at 254 nm per unit concentration of OC
325 (Edzwald and Tobiasson, 2011). The average SUVA₂₅₄ values of EOM_{Sed} in the
326 Piracicaba and Tietê Rivers were statistically different (95% confidence level, unpaired
327 t-test) and were higher for the Piracicaba River (6.16 ± 0.78) than the Tietê River (4.02
328 ± 0.71). The confluence region showed SUVA₂₅₄ values of EOM_{Sed} closer to the Tietê
329 River (average SUVA₂₅₄ values was 4.54 ± 0.71 L mg⁻¹ m⁻¹). SUVA₂₅₄ showed
330 differences in the composition of EOM_{Sed} between the two rivers, with the higher
331 average SUVA₂₅₄ values for the Piracicaba River indicating that EOM_{Sed} has a
332 relatively high aromatic content compared to the Tietê River.

333 The NPOC/TON molar ratios of EOM_{Sed} were correlated with the SUVA₂₅₄
334 values (Figure 3). Regression analysis found a positive relationship between the
335 NPOC/TON molar ratio and SUVA₂₅₄ (r = 0.67; p < 0.001). By analogy to soil OM,
336 these results could be associated with the functional complexity of EOM_{Sed} (Dungait et
337 al., 2012; Lehmann et al., 2020). During the degradation of OM, the more polar
338 structures are more accessible to microorganisms and are thus consumed faster,
339 resulting in an accumulation of OM that is thermodynamically unfavorable to
340 microorganisms (hydrophobic and aromatic moieties). The relatively lower presence of

341 N suggests that these structures have already been totally or partly assimilated, resulting
 342 in the selective preservation and accumulation of more chemically stable structures,
 343 which led to greater aromaticity in the Piracicaba River. Conversely, the lower $SUVA_{254}$
 344 and NPOC/TON molar ratio in the Tietê River suggest the addition of fresh OM. This
 345 evidence is supported by the high BOD value of the Tietê River.



346
 347 **Figure 3.** Relationship between specific UV absorbance at 254 nm ($SUVA_{254}$) and non-
 348 purgeable organic carbon (NPOC) and total organic nitrogen (TON) molar ratios of
 349 extracted organic matter from sediments.

350

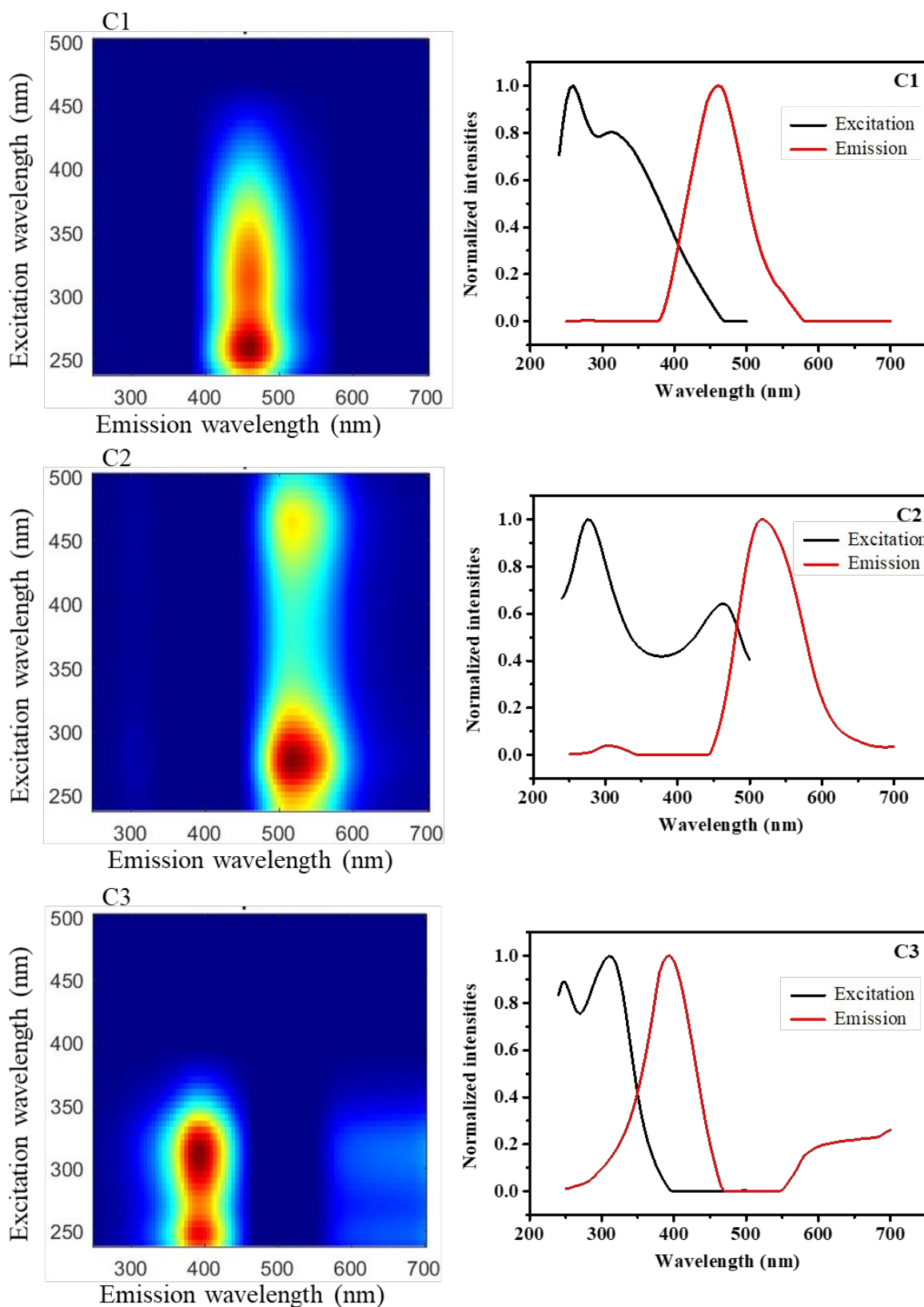
351 *3.3. Fluorescence excitation-emission matrix spectra of organic matter extracted from*
 352 *sediments with alkaline and neutral water solutions*

353 The PARAFAC model adjusted for EEM (N= 138) from EOMSed and
 354 WEOMSed diluted to the same optical density resulted in three fluorescent components
 355 (Figure 4) with a CORCONDIA of 89.98%. The spectral characteristics of the three

356 components were compared to the OpenFluor database (Murphy et al., 2014), and
357 similarity was measured with the PARAFAC models from different aquatic
358 environments using the EEM similarity score of 0.95. Components 1, 2, and 3
359 respectively corresponded to PARAFAC models 35, 5, and 25 from the OpenFluor
360 database.

361 Component 1 (C1) had two excitation maxima: one in 260 nm stimulated by UV
362 excitation (peak A), and the other in 310 nm stimulated by visible excitation, with an
363 emission maximum in the visible range at 465 nm for both excitation peaks (Coble,
364 1996). Component 2 (C2) was comprised of two excitation maxima at 285 nm and 465
365 nm, and an emission maximum at 520 nm (Osburn et al., 2011; Walker et al., 2013).
366 The fluorescence emission is useful to access the structural arrangement of OM due to
367 the fluorophore emission in short (blue-shift) or long wavelength (red-shift). C1 and C2
368 had similar characteristics to soil fulvic and humic acids, respectively. C1 resembles
369 fulvic acids due to the shorter wavelength emission, and the blue-shifted component is
370 attributed to the lower molecular weight and a structural arrangement comprised of
371 more alkyl moieties (Borisover et al., 2009; Kowalczyk et al., 2009; Osburn et al., 2016,
372 2011; Shutova et al., 2014; Yamashita et al., 2010b, 2010a). C2 resembles humic acids
373 from the soil due to the red-shifted component, which is attributed to a more complex
374 structural arrangement mainly composed of aromatic moieties (Soares da Silva et al.,
375 2020). Furthermore, the shift in the wavelength concerns the aggregation of humic
376 structures in solution; a red-shifted humic structure can show a molecular arrangement
377 with higher molecular aggregation, while a shorter wavelength suggests smaller
378 molecules (Bento et al., 2020; Boguta and Sokołowska, 2020, 2016). Component 3 (C3)
379 demonstrated two excitation maxima at 250 nm and 315 nm, and an emission maximum
380 at 395 nm. C3 resembled microbial humic-like compounds from aquatic environments

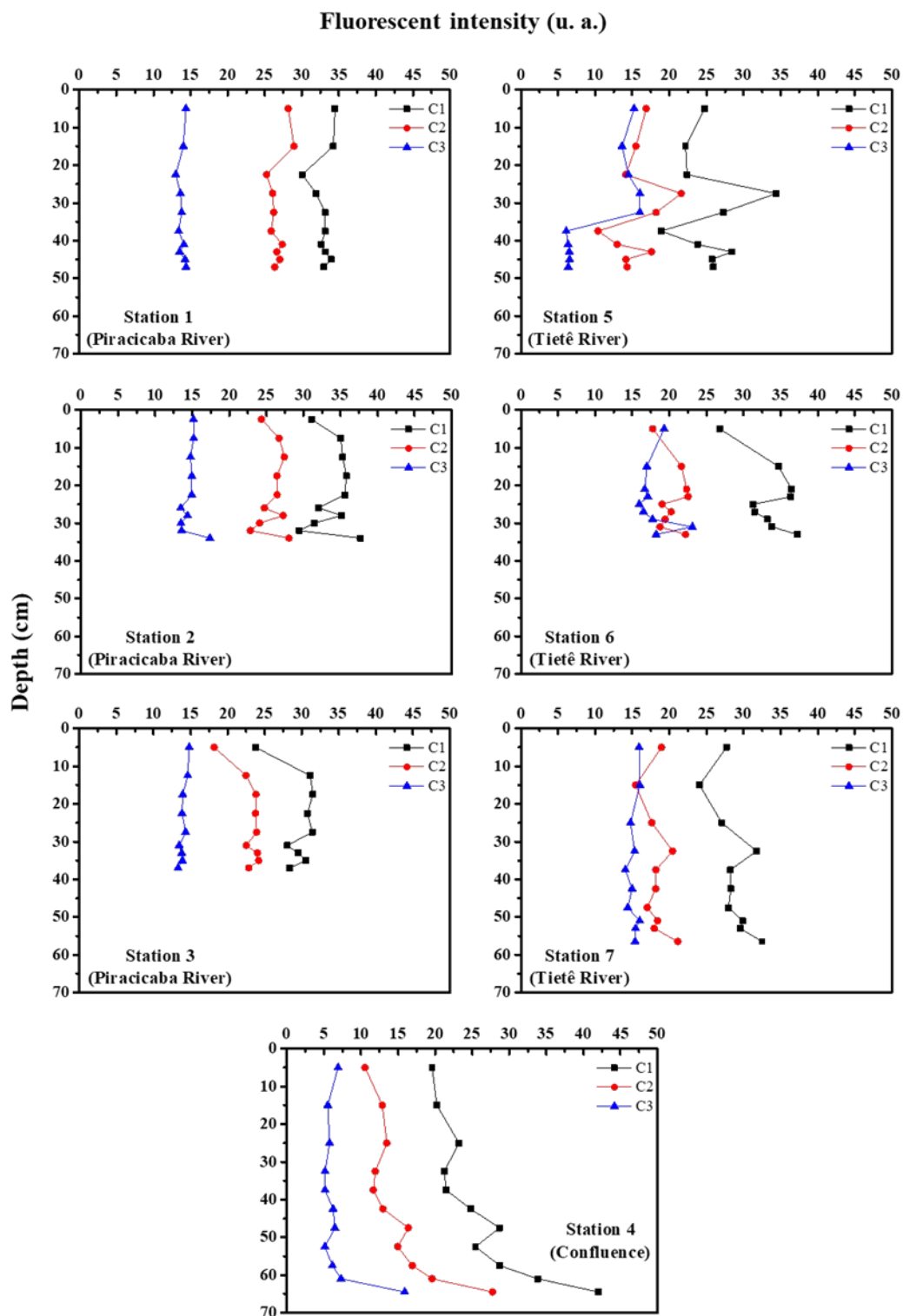
381 (Coble, 1996; Osburn et al., 2011). This component is probably a product of microbial
382 activity and thus of autochthonous origin (Yamashita et al., 2008).



383

384 **Figure 4.** Excitation-emission matrix contour plots of the three parallel factor analysis
385 components (left) and their excitation and emission spectra (right).

386 The PARAFAC model was made for a dataset with all samples, thus allowing us
387 to compare the component contributions. Figures 5 and 6 show the fluorescent
388 contributions of each component identified by PARAFAC for EOMSed and
389 WEOMSed, respectively, along with the sediment cores in the different stations,
390 corrected for the analytical dilution factor. For EOMSed (Figure 5), the average
391 fluorescent contribution of C1 was higher in decreasing order for the Piracicaba River >
392 Tietê River > confluence region. This shows that small molecules make a greater
393 contribution to the EOMSed arrangement of the Piracicaba River. The average
394 fluorescent contribution of C2 had the same decreasing order as that of C1 (Piracicaba
395 River > Tietê River > confluence region), showing that complex structures in the form
396 of aromatic and polyaromatic moieties make a greater contribution to the EOMSed
397 arrangement of the Piracicaba River. The average fluorescent contribution of C3 was
398 higher in decreasing order for the Tietê River > Piracicaba River > confluence region,
399 showing that microbial-derived products make a greater contribution to the EOMSed
400 arrangement of the Tietê River. Thus, EOMSed from the Piracicaba River contains
401 more aromatics, while EOMSed from the Tietê River contains more microbial-derived
402 products. These results are in agreement with the $SUVA_{254}$ values and NPOC/TON
403 molar ratios, which showed less aromatic EOMSed with more nitrogenous structures for
404 the Tietê River compared to the Piracicaba River. The low NPOC/TON molar ratio may
405 be the main reason for the higher microbial activity and the consequent presence of
406 microbial derivatives (C3).

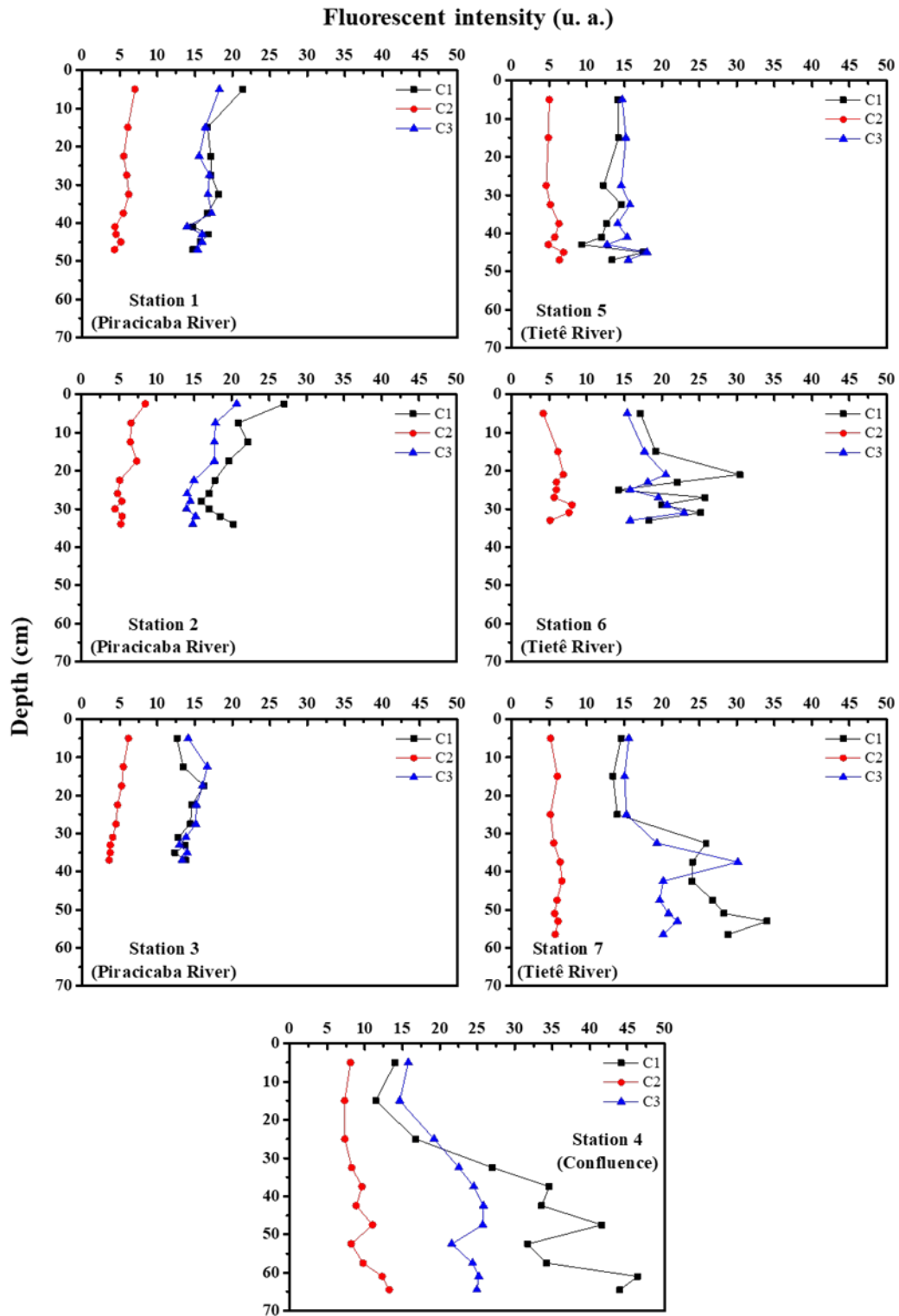


407

408 **Figure 5.** Fluorescent intensity of components (C1, C2, and C3) taken from the
 409 extracted organic matter from sediments along with the sediment core identified by
 410 parallel factor analysis.

411 In WEOMsEd (Figure 6), the average fluorescent contributions of C1, C2, and
412 C3 were higher in decreasing order for the confluence region > Tietê River > Piracicaba
413 River. The extraction of microbial-derived products (C3) was greater for WEOMsEd
414 than for EOMsEd, and the C3 values were higher at the stations of the Tietê River than
415 the Piracicaba River, indicating its greater microbial activity. The low abundance of C2
416 can be ascribed to the component structure, because humic-like substances with high
417 aromaticity are more soluble in alkaline solution than in water, which may result in the
418 higher relative content of C2 in alkaline solution; furthermore, the higher C2
419 concentration in alkaline extracts obfuscates the C3 concentration. The alkaline medium
420 favored the greater extraction of C1 and C2 (humic-like compounds) due to the
421 hydrolysis caused in the functional groups of humic molecules bonded to the surface of
422 the mineral from sediment (Kleber and Lehmann, 2019; Olk et al., 2019).

423 The optical properties of EOMsEd proved to be more efficient for assessing the
424 quality and composition of sediments than those of WEOMsEd due to the better
425 discrimination between the fluorescence components in the alkaline extracts. Although
426 water extraction has been used to assess OM sources and link contamination in polluted
427 urban rivers (Chen et al., 2019; Zhang et al., 2020), in our study, alkaline extracts were
428 better at describing the properties of OM.



429

430 **Figure 6.** Fluorescent intensity of components (C1, C2, and C3) taken from water-
 431 extracted organic matter from sediments along with sediment core identified by parallel
 432 factor analysis.

45

46

23

433 *3.4. Features of extractable organic matter from sediments from the Piracicaba and*
434 *Tietê Rivers*

435 The neutral water solution enabled the better extraction of small molecules
436 (blue-shifted), which are free from the mineral fraction in the sediments. While the
437 alkaline solution favors the extraction of more complex substances (red-shifted). The
438 results obtained with EEM-PARAFAC together with $SUVA_{254}$ values and NPOC/TON
439 molar ratio allowed for the total assessment of EOMSed quality.

440 The differences between the EOMSed compositions in sediments were
441 highlighted by the $SUVA_{254}$ values, NPOC/TON molar ratios, and EEM-PARAFAC.
442 Although the most abundant component in EOMSed from the two rivers is humic-like
443 with the lowest molecular weight (C1), the aromaticity of EOMSed from the Piracicaba
444 River was evidenced by the greater contribution of C2 and $SUVA_{254}$ values. Conversely,
445 EOMSed from the Tietê River had greater microbial activity due to the greater
446 contribution of C3, the presence of small molecules (lower C2 contribution), and the
447 presence of nitrogenous structures. Based on the analyses performed, it was not possible
448 to further identify the compositional alteration of EOMSed and WEOMSed, which may
449 be related to their similar deposition.

450 The origin of EOMSed is inferred from the results obtained here. The
451 NPOC/TON molar ratios calculated for EOMSed from the Piracicaba River indicate
452 that EOMSed can form in the aquatic body (autochthonous). The contributions of two
453 humic-like components in alkaline extracts indicate that EOMSed may also originate
454 from soil OM (allochthon). According to the NPOC/TON molar ratios calculated for
455 EOMSed from the Tietê River as well as the greater microbial activity in this aquatic
456 ecosystem, it can be inferred that the origin of EOMSed is predominantly

457 allochthonous, mainly due to the discharge of domestic sewage, which is indicated by
458 the higher content of TC present in the Tietê River sediments.

459

460 **4. Conclusion**

461 EOMSeD from the Piracicaba and Tietê Rivers was mainly characterized by an
462 arrangement of low molecular weight compounds. However, EOMSeD from the
463 Piracicaba River presented more aromatic moieties and fewer nitrogenous structures
464 compared to the Tietê River. The presence of nitrogenous structures and fluorophores
465 related to microbial activity can be an indicator of OM quality, which could be used as a
466 global indicator of the river state. Thus, the combination of elemental and spectroscopic
467 techniques allows for the successful deciphering of extracted OM characteristics. This
468 approach can therefore be used as a tool to assess the quality of aquatic bodies.

469

470 **Declaration of competing interest**

471 The authors declare that they have no known competing financial interests or
472 personal relationships that could have appeared to influence the work reported in this
473 paper.

474

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481

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