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

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Abstract

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

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

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

1. Introduction

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

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

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

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

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

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

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

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

2. Materials and methods

2.1. Study area description and sediment sampling

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

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

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

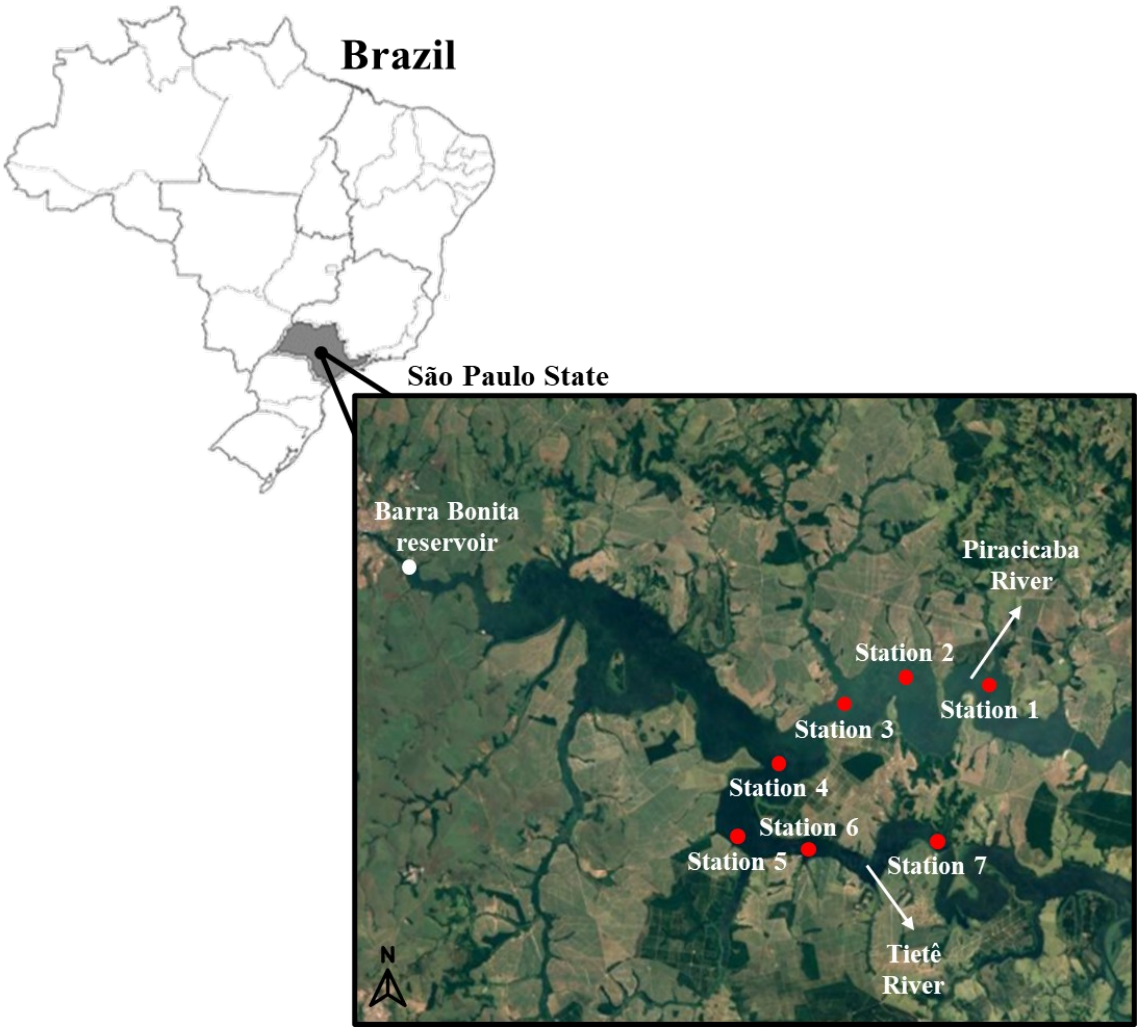

Figure 1: Location of the Barra Bonita Reservoir (white dot) and sediment sample collection stations (red dots).

2.2. Elemental analysis

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

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

2.3.3. UV-Vis spectroscopy

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

2.3.4. Fluorescence spectroscopy

2.3.4.1. Sample preparation and analysis

For the study of EEM, 1.0 mL of each sample diluted to absorbance at 254 nm equal 0.1 (1 cm path length) was placed in quartz cells along with 1.0 mL of 0.3 mol L^{-1} HEPES (Acros Organics) for pH regulation at 7 and 1.5 mL of 0.1 mol L^{-1} $NaClO_4$ (Sigma-Aldrich) with a purity of 99.99% to fix ionic strength. The samples were analyzed immediately after preparation.

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

2.3.4.2. Fluorescence data processing

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

2.4. Statistical analysis

Unpaired t-tests were used to determine any statistical differences between the TC in bulk sediments from the Tietê and Piracicaba Rivers and NPOC, TON, NPOC/TON molar ratios, and SUVA values obtained for EOMSed from the Tietê and Piracicaba Rivers. The correlation coefficient between the NPOC/TON molar ratios and the $SUVA_{254}$ values was calculated.

3. Results and discussion

3.1. Total carbon characteristics in bulk sediments

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

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

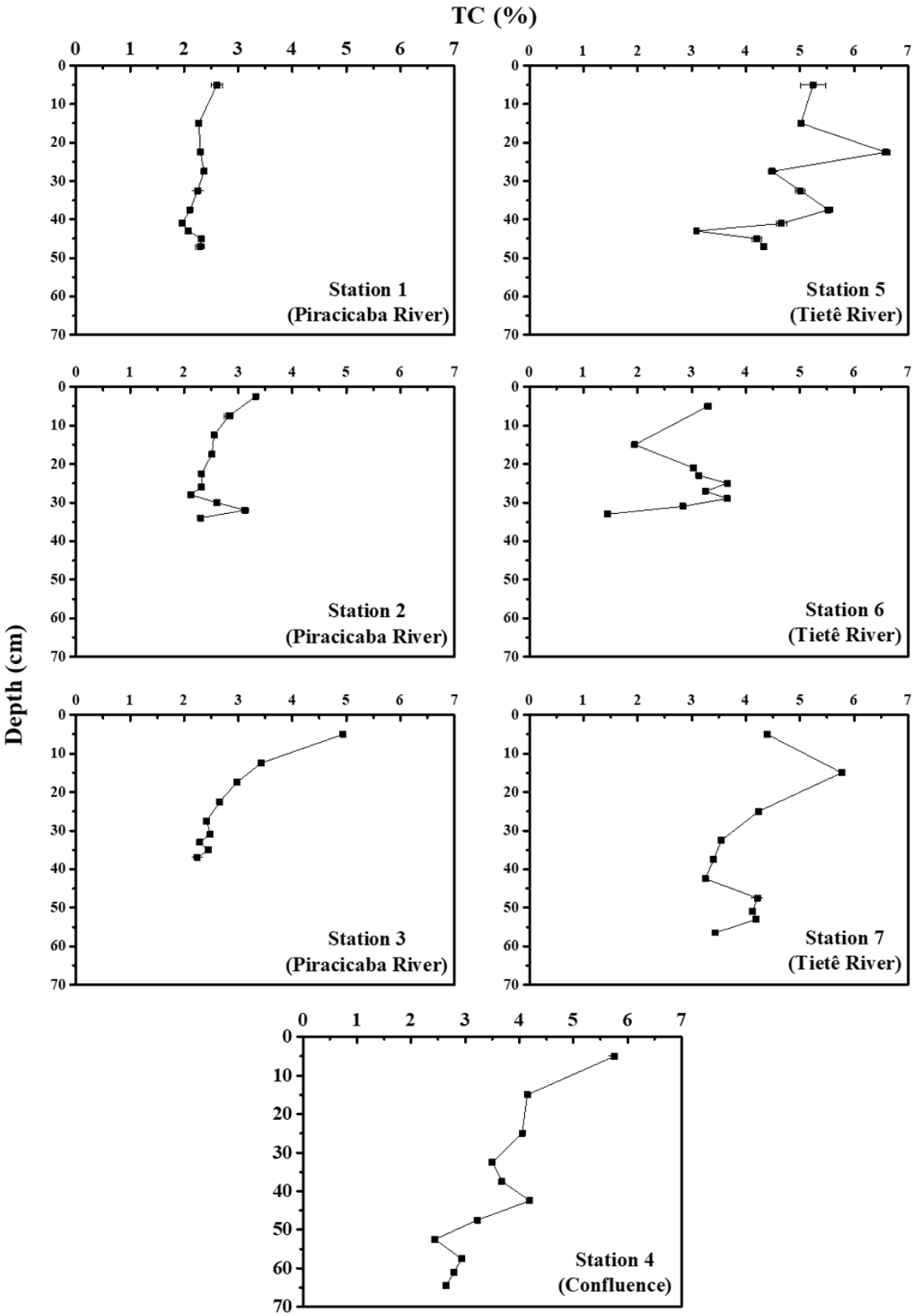

Figure 2. Total carbon distribution inside the sediment cores at the collection stations.

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 $SUVA_{254}$ of EOMSed 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 ($SUVA_{254}$) 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

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

The average NPOC/TON molar ratios of EOMSed in the Tietê and Piracicaba Rivers were statistically different (95% confidence level, unpaired t-test) and were higher for the Piracicaba River (6.80 ± 0.79) compared to the Tietê River (5.39 ± 0.46). Considering the historical course of the Tietê River and its high degree of eutrophication (Morais et al., 2021), the lower ratios found in the river may suggest a larger input of simple OM with nitrogenous structures, which may indicate effluent input. In the confluence region, the NPOC/TON molar ratio of EOMSed was the lowest: 4.78 ± 0.30. The lower value of the NPOC/TON molar ratio shows an increase in OM deposition with nitrogenous structures, suggesting that the confluence region is 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 EOMSed between the Tietê and Piracicaba Rivers, the studied EOMSed
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 $SUVA_{254}$ 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 Tobiason, 2011). Therefore, high $SUVA_{254}$ values indicate an
324 OM formed by more structures that absorb light at 254 nm per unit concentration of OC
325 (Edzwald and Tobiason, 2011). The average $SUVA_{254}$ values of EOMSed 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 $SUVA_{254}$ values of EOMSed closer to the Tietê
329 River (average $SUVA_{254}$ values was 4.54 ± 0.71 L mg^{-1} m^{-1}). $SUVA_{254}$ showed
330 differences in the composition of EOMSed between the two rivers, with the higher
331 average $SUVA_{254}$ values for the Piracicaba River indicating that EOMSed has a
332 relatively high aromatic content compared to the Tietê River.

333 The NPOC/TON molar ratios of EOMSed were correlated with the $SUVA_{254}$
334 values (Figure 3). Regression analysis found a positive relationship between the
335 NPOC/TON molar ratio and $SUVA_{254}$ ($r = 0.67$; $p < 0.001$). By analogy to soil OM,
336 these results could be associated with the functional complexity of EOMSed (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

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

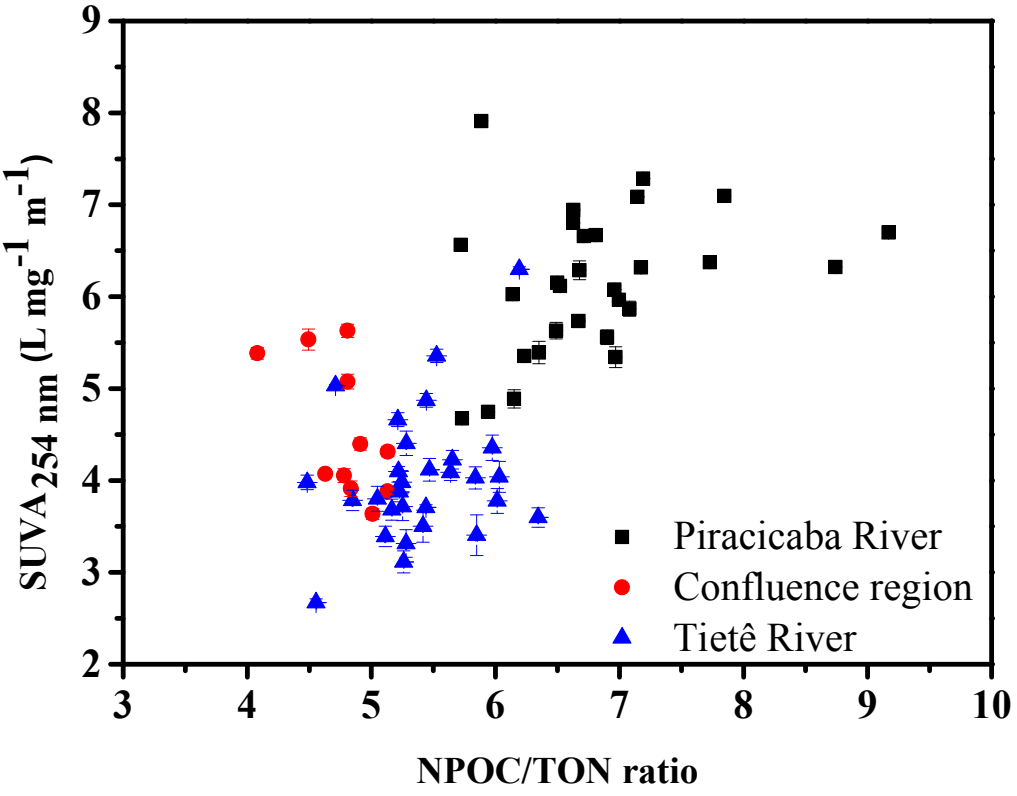

Figure 3. Relationship between specific UV absorbance at 254 nm ($SUVA_{254}$) and non-purgeable organic carbon (NPOC) and total organic nitrogen (TON) molar ratios of extracted organic matter from sediments.

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

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

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

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

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

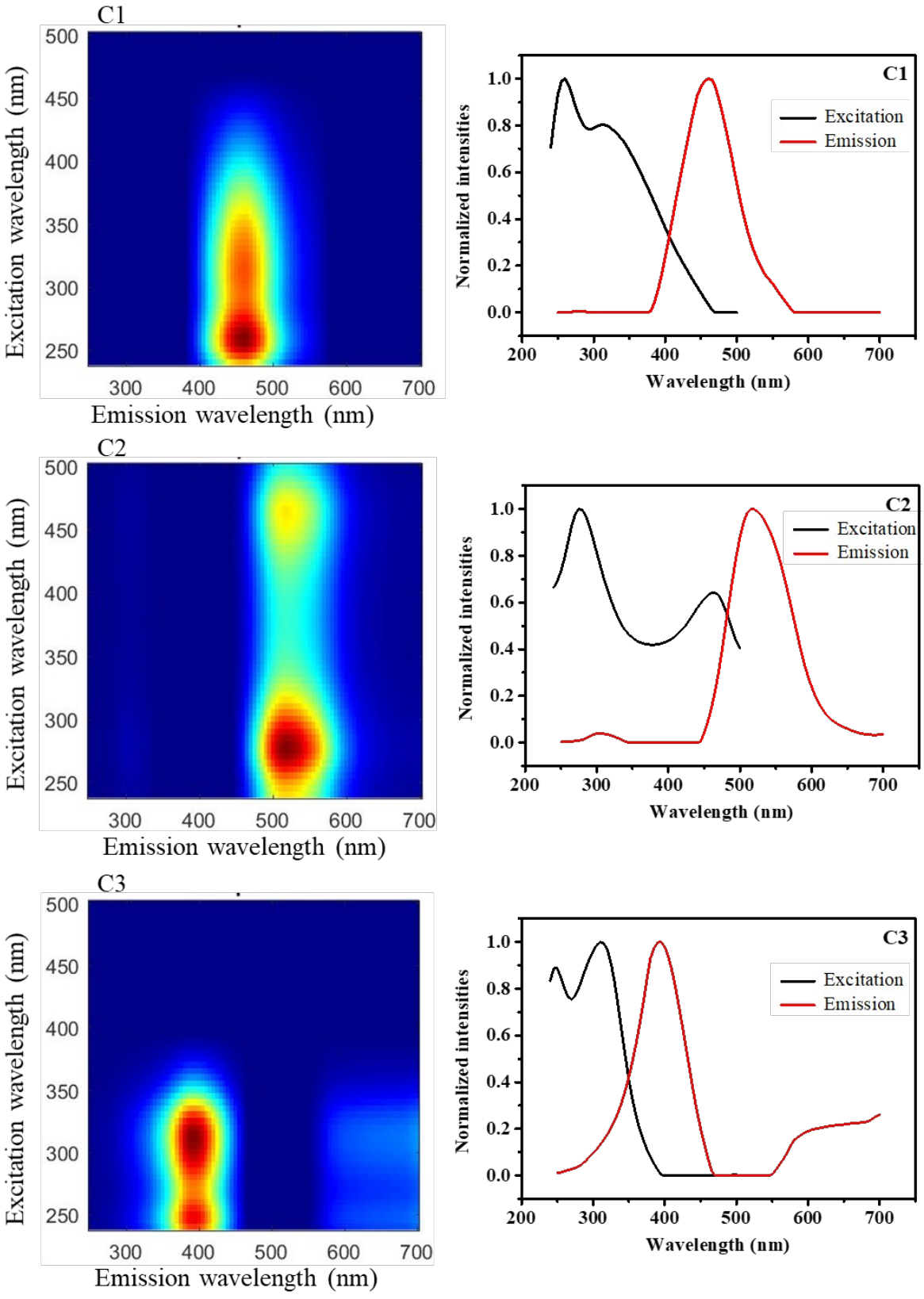

Figure 4. Excitation-emission matrix contour plots of the three parallel factor analysis components (left) and their excitation and emission spectra (right).

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

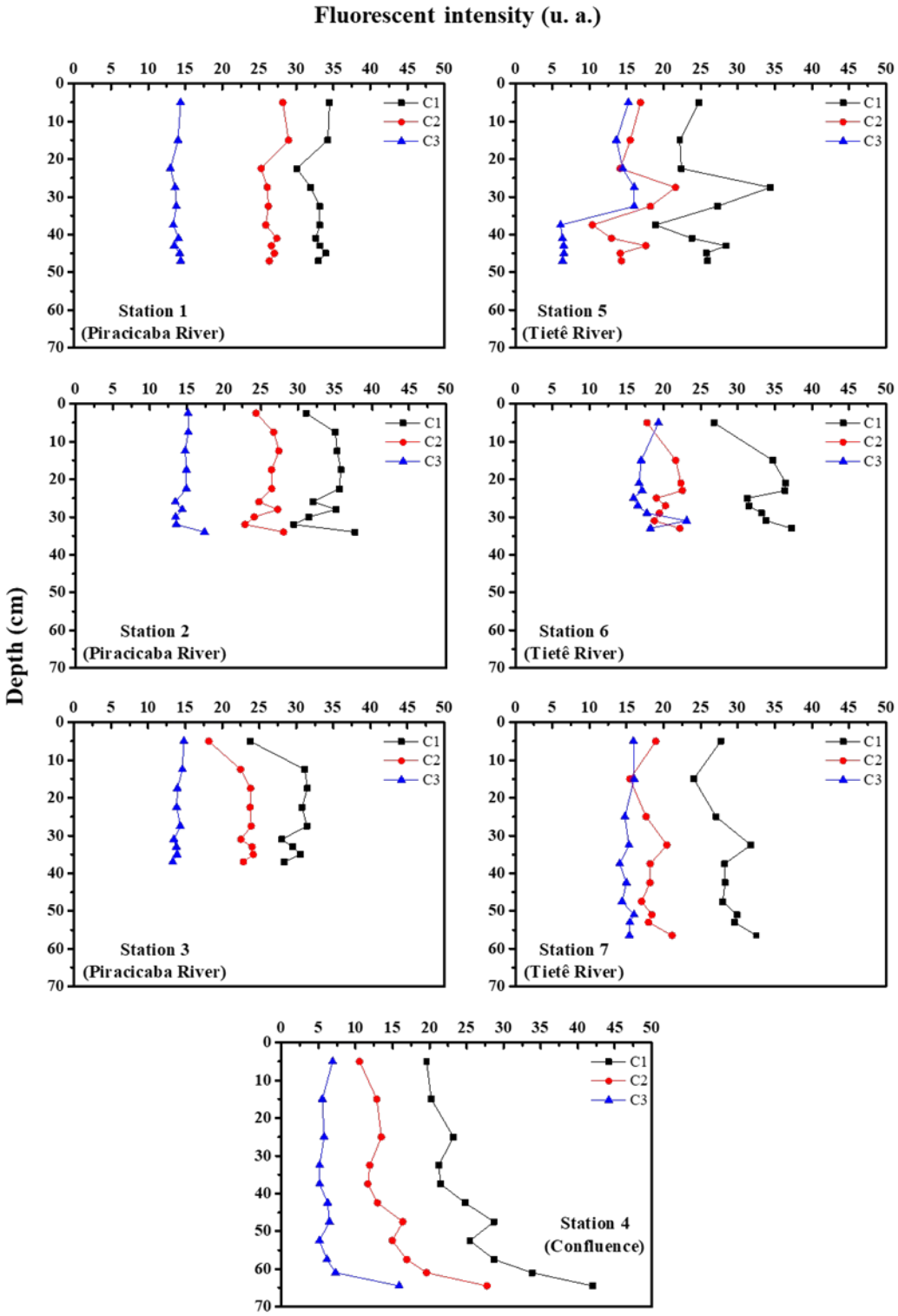

Figure 5. Fluorescent intensity of components (C1, C2, and C3) taken from the extracted organic matter from sediments along with the sediment core identified by parallel factor analysis.

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.

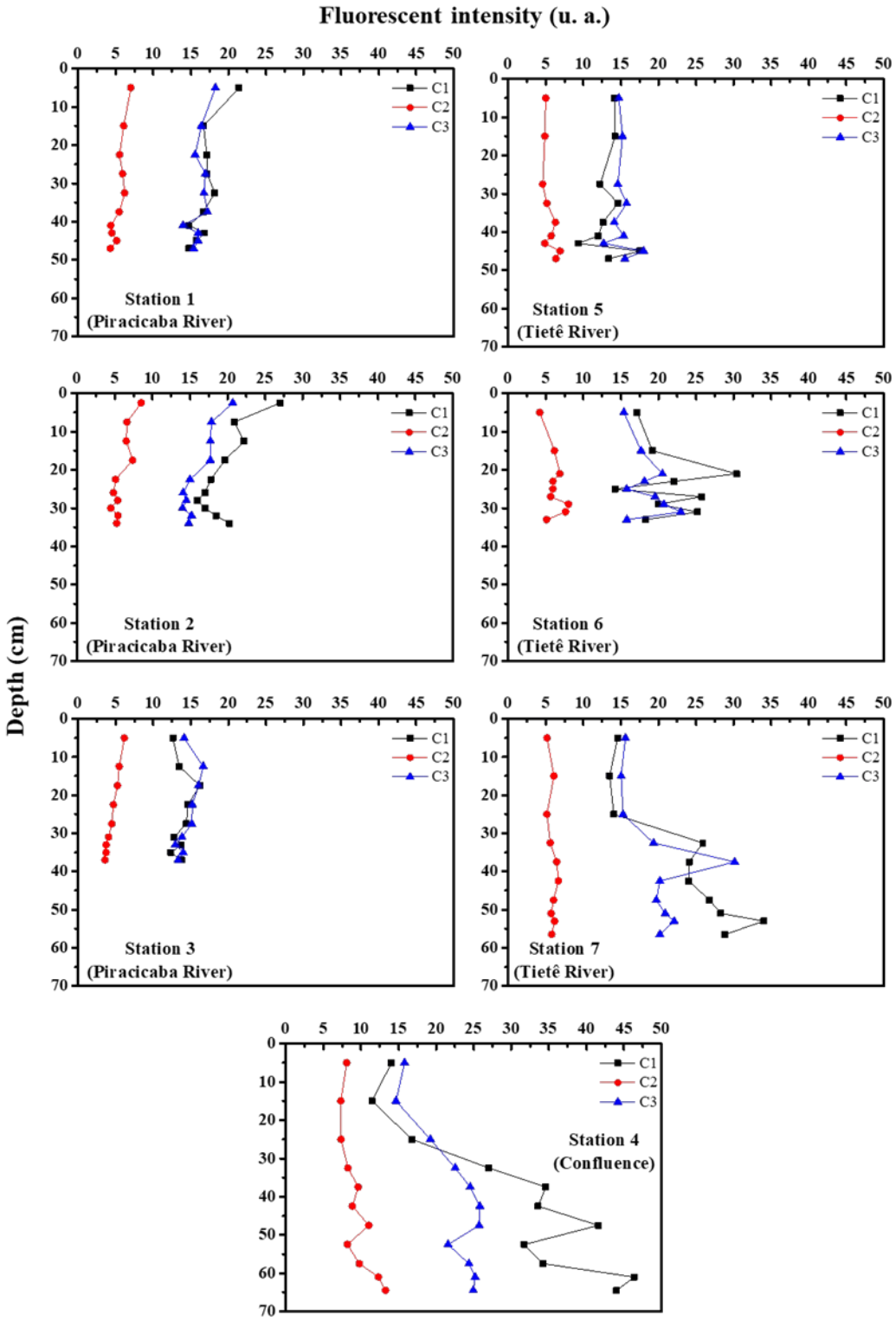

Figure 6. Fluorescent intensity of components (C1, C2, and C3) taken from water-extracted organic matter from sediments along with sediment core identified by parallel factor analysis.

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

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

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

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

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

4. Conclusion

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

Declaration of competing interest

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

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