# Organic water features of three adjacent Eastern Mediterranean urbanized watersheds

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## Abstract

Landscape urbanization broadly affects watersheds ecosystems, but until now the influence of nonpoint source urban inputs on dissolved organic matter (DOM) amount, composition and source is poorly understood. To understand how DOM composition varied with urbanization, fluorescence excitation emission matrices (EEMs) was collected from two types of waters: urban and non-urban waters from upstream to downstream sites along three adjacent watersheds that pour into the Mediterranean Sea. Two humic-like DOM fluorescent components (C1 and C4), two protein-like components (C5 and C7) and two microbial components (C2 and C3) were identified by parallel factor analysis (PARAFAC). The results indicated that urbanization had an important influence on DOM concentration and composition, with urban waters having a high degree of DOM variation due to different land use surrounding each body of water. Urban waters presented higher DOM fluorescence index (FI), a greater proportion of protein-like manifested by BIX values, and less proportion of humic-like (demonstrated by HIX values) than non-urban waters which were dominated by allochthonous inputs. In addition, the EEM was compared in dry and wet season where higher DOM amount and FI appeared in summer due to autochthonous production coming from algae growth compared to allochthonous input from rainfall dominated in wet season.

## Article Highlights

- Ibrahim, Kaleb and Beirut watersheds are located in a semiarid region at the East of the Mediterranean Sea
- Ibrahim, Kaleb and Beirut watersheds are impacted by urban effluents and agricultural soil leachates
- DOC in the downstream sites reflects the strong impact of urban discharges into the receiving waters where the dilution is affected during the dry period
- Fluorescence EEM results confirm that humic character of DOM is mainly linked to terrestrial runoff, while DOM low aromaticity and non-humic character is correlated to urban discharges
- Higher DOM fluorescence index FI, a greater proportion of protein-like manifested by BIX values, and less proportion of humic-like measured by HIX values are shown for urban DOM
- Allochthonous inputs distinguished by high HIX humidification index is shown for natural DOM
- Seasonal variation is highlighted for DOM characteristics by comparison of wet and dry seasons results

## Introduction

Rivers have a major role in carbon cycles by transporting carbon from land to the seas representing a reactive flux and dissolved organic matter DOM is an inevitable carbon flux source. DOM is highly reactive in ecosystem processes such as bacterial respiration, photochemical oxidation and primary production (McDowell 2023). DOM are very dynamic, and they change by nature from upstream to downstream and even after entering the marine. So, DOM nature differs between freshwater and urban water.

DOM concentration, composition and chemistry are highly variable depending on the source of organic matter if terrestrial (allochthonous) or from aquatic biota (autochthonous) or from human activities (anthropogenic). The allochthonous is the major source of DOC input in streams and rivers that comes from plants or soil. The DOM from soil is decomposed for a longer time. Algae is the major source of autochthonous organic matter and major input in lakes. Note that DOM in freshwater is from autochthonous source (rich in N) and its humic acid fraction is smaller compared to DOM from plant and soil origin (Thurman 2012).

DOM is a heterogeneous mixture of aromatic and aliphatic organic compounds containing oxygen, nitrogen and sulfur functional groups (Chen et al. 2003). The hydrophobic DOM dominated in natural water is from plant origin and has a large amount of aromatic carbon, high phenolic content, and low N – content while the hydrophilic DOM dominated in urbanized water comes mainly from bacteria and algae and has low phenolic content, low aromatic C, large N and a carboxylic content (Croué et al. 2003).

Many studies have been done concerning DOM characterization in fresh and urban water showing the great ability in binding to organic pollutants thus affecting their accumulation and toxicity (Romero González-Quijano et al. 2022; Zhang et al. 2022; Lyu et al. 2021). Freshwater is rich in humic acid which constitutes a major part of hydrophobic fraction of DOM. Unlike waste water in urbanized areas which has a large amount of hydrophilic fraction and a greater potential to form metal complexes by binding to organic micro pollutants that affect their bioavailability and toxicity (De Paiva Magalhães et al. 2015). It also depends on pH, temperature and climate change, ionic strength, major cation composition of water, surface chemistry of sediment sorbents that act as solubility controls on the presence of photolytic and microbiological degradation processes (Croué et al. 2003).

Various fluorescence spectroscopy techniques have been used to characterize sources of marine, fresh, and urban DOM samples. To gain information on DOM origin, dynamics and degree of transformation, excitation emission matrix (EEM) fluorescence spectroscopy combined with parallel factor analysis (PARAFAC) is used to characterise DOM in the three studied watersheds. Fluorescence indices were used to track changes of the origin and transformation degree of DOM by distinguish: 1) the humidification level using HIX humidification index, 2) the biological activity by BIX biological index and 3) microbially derived DOC sources from terrestrially derived sources by FI fluorescence index (Zsolnay 2003). Therefore, EEM fluorescence spectroscopy technique was used in this study to differentiate natural organic matter from urban DOM coming from urban discharges.

This work will focus on the impact of urbanization on the characterization of dissolved organic matter in three Eastern Mediterranean watersheds taking into consideration spatial and seasonal variability of DOM. The functional analysis of DOM using fluorescence EEMs will be used to characterize DOM to delineate EEMs into many regions. It also highlights the contrast of the spectral analyses of organic matter from water origin affected by wastewater and from those unaffected by urban discharges. The analysis will be done from upstream to downstream along three adjacent rivers: Ibrahim, Kaleb and Beirut in sampling campaigns done in dry and wet season.

# 1. Materials and methods

## 1.1 Study Area

Along with Lebanon's small surface (10,452 km²) and large coastline (210 km), our study area is related to three coastal river watersheds that flow from Mount Lebanon into the Mediterranean Sea: Ibrahim River, Kaleb River, and Beirut River presented in Fig. 1. The three studied rivers follow a defined hydrologic regime which is controlled by their geomorphology where the three of them are coastal rivers that flow in one regional direction eastward towards the Mediterranean.

- Ibrahim River is known for its highest water flow among all Lebanese rivers (Darwish et al. 2015). It has been studied several times before (Hanna et al. 2018). The studies showed that human activities have a great impact on water resources in this area quantitatively and qualitatively.
- Kaleb River is characterized by its urban and agricultural activities along its sides, touristic sites and the animal farms and quarries. The nature of activities at this Basin and the elements released in water and in soil vary from upstream to downstream.
- Finally, Beirut River is characterized by an average flow in wet season and a flow almost null in the dry season. It crosses the capital beirut so it has the highest population (Shaban 2020), industrial, agricultural (Frem 2009) and touristic activities along its side which reveals very high amounts of discharges.

A total of 23 samples were collected at different sampling points in these three rivers in such a way that they represent the river's source, outlet, and in-between locations based on the river's accessibility. The sampling sites were chosen to represent the highly populated urban area at the downstream, while the upstream sampling site is mostly representative for forest and agricultural zones. As shown in (Fig. 1a), four sites were considered along Ibrahim River where IS1 and IS2 represent two karstic sources Afqa (1400m) and Roueiss (1600m) respectively (impacted by farm and agriculture waste). The third site IS3 was taken at Jannah Dam (800m) (hugely impacted by vegetation) and the fourth site IS4 at the outlet of the river (slightly impacted by industrial waste and urbanization). As for Kaleb River (Fig. 1b), also four sampling points were taken. The first sampling point was taken at the source in Sannine called Nabaa Joz Al-Namel (KS1) which is 1600 m above sea level (geoview.info 2022) where the water is potable. The second site (KS2) is at Abou Mizane (1200m above sea level). This site dries out in the dry season, and it is populated (impacted by vegetation waste and tourism). Moreover, the third site (KS3) is located near Jeita Grotto (380m above sea level) which is a popular touristic destination throughout the year and hugely affected by urban activities. And the last site (KS4) is in Zikrit area just before the river empties into Mediterranean Sea (higher pollution than Ibrahim). Finally, three sites were collected along Beirut River (Fig. 1c). The site at the source BS1 was located at Nabaa Fawar mountain (1623 m above sea level) (possibly contaminated by infiltration water from irrigation due to compost usage). The second site BS2 was at Kanater Zbeidy (150m above sea level) (highly contaminated due to industrial waste and wastewater). Last, the third site was located at the port of Beirut at sea level BS3. A special case was observed at BS3 where a second river consisting of wastewater from the sewer network is joining the main river creating an additional flow (all types of contamination). The calculation of the flow at this site was done as by (Maatouk, 2014). Two sampling campaigns were conducted during 2 seasons: the wet season in May 2020 and the dry season in October 2021.

## 1.2 Physico-chemical properties

The parameters measured for each water sample are the following: temperature (T˚), pH, electrical conductivity (EC), total suspended solids (TSS) and DOC. Temperature, pH and EC measurements were made on site with a TRACER pocket tester. To reduce the sources of error, we have ensured that the field equipment, pH case (Tracer LaMotte, USA), and electrical conductivity (Tracer LaMotte, USA) are used in accordance with the instructions and in accordance with the "quality" procedures recommended by the suppliers. Total suspended solid (TSS) was determined according to the corresponding standard methods (APHA/AWWA/WEF, 2005). DOC dissolved organic carbon content was determined using the O.I. analytical carbon analyzer by a Shimadzu V-CPH analyzer (quantification limit = 0.5 $mgC.L^{-1}$).

## 1.3 Fluorescence Spectral and Parallel Factor Analysis

All fluorescence spectra were recorded on a Fluorolog fluorescence spectrophotometer equipped with both excitation and emission monochromators (FL3–22 SPEX-Jobin-Yvon instruments). A 450-W Xenon arc lamp was used as the excitation source. A series of emission spectra were collected over a range of excitation wavelengths to provide a complete representation of the fluorescence of a sample in the form of an excitation emission matrix (EEM), in which fluorescence intensity was presented as a function of excitation wavelength on one axis and emission wavelength on the other. The samples are placed in 1cm optical path quartz cell and thermostated at 20°C. The glassware used must be clean, this cleaning is carried out by baths of detergent, RBS 50, at a concentration of 2–3%. Cleanliness is then tested by fluorescence before using the glassware. 3D fluorescence spectra are generated upon 75 minutes by the successive registration of 17 emission spectra (260-700nm) at wavelengths of excitation between 250 and 410nm. A wavelength step size of 10 nm was used for the collection of EEM spectra.

After obtaining the spectrum, it is necessary to correct it by eliminating the scattering bands resulting from the Rayleigh, Raman and Tyndall effects. The EEM spectra of the sample are obtained by subtraction of the spectrum of a blank of ultrapure water (Millipore, Milli-Q) and instrumentally corrected. Samples with absorbance higher than 0.1 at 254 nm were diluted to avoid any inner filter effect. The intensities of fluorescence are given in Raman unit.

EEM spectroscopy allows observing fluorescence regions characteristic of the main classes of compounds constituting the dissolved organic matter DOM. EEM were decomposed into 2 to 6 underlying components using PARAFAC models conducted with MATLAB software with DOM fluor toolbox. The spectra obtained were divided into six regions. The regions are characterized as following and represented in the Figure below (Fig. 2). C1 represent the marine humic-like, terrestrial, microbial and highly processed material ($\lambda ex$ / $\lambda em$) = (≤ 230 (340)/425) (Hu et al. 2017). C2 represent microbial reduced Quinone ($\lambda ex$ / $\lambda em$) = (245 (305)/325) and C3 reflects the microbial processed substances ($\lambda ex$ / $\lambda em$) = (260 (320)/ 350–450) (Yang et al. 2015). Moreover, C4 represent the uvc-uva humic like substances (λex / λem) = (230, 290/450–500). Finally, C5 reflects the Tyrosine material (λex / λem) = (270/300–320) whereas C7 the Tryptophan (λex / λem) = (250–270/370–400) (Peng et al. 2020). And finally, peaks at shorter excitation wavelengths (< 250nm) and longer emission (> 350nm) are related to fulvic acid materials (region three) (Chen et al. 2003). The regions' intensities and percentages were determined for all samples of the three studied rivers.

Humic compounds represent the final stage of degradation of DOM that has undergone many transformation and this has caused the introduction of humification index (HIX) which allows DOM maturation (Zsolnay 2003) .

Humification index HIX is the ratio of the areas between H and L domains of the emission spectrum at a specific excitation wavelength 254nm. The H domain is between 435 nm and 480 nm and the L domain is between 300-345nm. This ratio reflects the increase in CH ratio that occur during humification showing the relative stability of organic compounds with respect to microbial activity. According to (Ayah et al. 2015), HIX was affected by the season where in winter it was higher due to the availability of more humified organic matter from the leaching of soils mainly from terrigenous source. The low value of HIX in summer is due to poor organic matter maturation thus reflecting the autochthonous and recent sources. The high values of HIX are between 10–16. The low values are less than 4. The intermediate values reflect mixture of both components. Also Fluorescence index (FI) was indicated, which indicates if precursor material for DOM is of a more microbial (FI ~ 1.8) in nature or more terrestrially derived (FI ~ 1.2) (Cory and McKnight 2005). FI is the ratio of emission intensity at 470 nm to that at 520 nm under the excitation wavelength of 370 nm (Jaffé et al. 2008). Biological index BIX was calculated as the ratio of fluorescence intensity of emission at 380 nm to that at 430 nm (f (380)/ f (430)) under the excitation wavelength of 310 nm, which corresponded to 0.6–0.7 for DOM of low biological components and > 1 for DOM of biological or aquatic bacterial origin (Huguet et al. 2010).

## 2. Results and Discussion

# 2.1 Hydrochemistry of watersheds

The temperature of the different sites along the three river watersheds was measured during dry and wet season as shown in Table 1. The temperature at the outlet of each river was higher compared to the source and the middle of each stream. In addition, the highest temperatures were found along Beirut River during both dry and wet season ranging from 15.8 to 25.1 ºC and from 18.8 and 25 ºC respectively. Many activities cause the change of water temperature including the discharge of warmer cooling water, the removal of riparian planting that shades and maintains temperatures and the reduction of water levels due to abstraction or diversion of water used for irrigation (Pletterbauer et al. 2018).

Regarding the conductivity values (Table 1), the values during the dry season were more pronounced than that of the wet season, due to the dilution of the ions by the increased water flow during the wet season. Also, it was noticed that the values at the sources of the three rivers are in the same range whereas they tend to increase downstream to be the highest at the outlets. For example, EC value BS3 in the dry season at the outlet is around 502 μS/cm, fourteen times higher than the value at the source of the river (BS1) 37.8 μS/cm and five times higher than that in the wet season (BS3:100 μS/cm). This significant increase is due to the urban discharges by the sewer network, which is than mixed with river water before being discharged into the Mediterranean Sea and to the marine intrusion at the outlet of the river. This is aligned with (El-Nakib et al. 2018) where the variation between the seasons was important and higher in the dry season since the flow in this season is lower and highly affected by the anthropogenic discharges where the river becomes a lentic system at the sea level. As for Ibrahim River the EC at the sources is lower than that taken down streams and the value of EC is higher in the dry season which is aligned with (Hanna et al. 2018). As for Kaleb River, it is also influenced by the soil nature and leaching as well as by the anthropogenic inputs. For this reason, the EC is highest at its outlet at sea level where the retention time tend to increase.

As for the pH values, they were also measured in both seasons (Table 1). It was noticed that all three rivers were mildly alkaline especially in the wet season. The highest pH was recorded at Ibrahim River outlet (9.08) in the dry season and at Kanater Zbeidy (BS2) in the wet season (9.25). The basic pH at Ibrahim river outlet is aligned with those previously reported for Ibrahim river watershed by (Daou et al. 2013), (Hanna et al. 2018) and (Houri and El Jeblawi 2007). This basic pH is due to karstic nature of the basins and the marble factory on the outlet. Moreover, the high pH at Kanater Zbeidy river site (BS2) is detected since this site is a collector of wastewater coming from all surrounding adjacent areas such as Burj Hammoud, Sin El Fil and Ashrafieh, highly populated zones in Beirut capital. Moreover, the pH value at Jeita site (KS3) is aligned with (Daou et al. 2013) where pH in this site is highly affected by the nature of the soil and the various reactions that take place in the water (physico-chemical and biological reactions). The pH here in Jeita touristic site is also affected by wastes from anthropogenic origin and mineral substances from endogenous origin.

Table 1
Global parameters of Ibrahim, Kaleb and Beirut River in dry and wet season

| Sampling sites | | Temperature(˚C) | | Conductivity (µS/cm) | | pH | | TSS (mg/L) | | DOC (mgC/L) | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | | *dry* | *Wet* | *Dry* | *wet* | *dry* | *wet* | *dry* | *wet* | *dry* | *wet* |
| **Ibrahim River** | *NI S1* | 8.9 | 8.5 | 28 | 18.5 | 7.3 | 8.8 | 0.2 | 0.1 | 0.98 | 7.39 |
| | *NI S2* | 9.1 | 8.5 | 32 | 17.5 | 7.1 | 8.5 | 0.2 | 2.6 | 1.10 | 1.39 |
| | *NI S3* | 15 | 12.1 | 43 | 23 | 8.9 | 8.9 | 0.4 | 0.2 | 1.18 | 0.61 |
| | *NI S4* | 16.6 | 14.8 | 42 | 30 | 9.1 | 9.0 | 0.2 | 3.6 | 1.37 | 20.79 |
| **Kaleb River** | *NK S1* | 7 | 6.4 | 14 | 13.5 | 8.6 | 8.5 | 0.2 | 0.1 | 1.27 | 9.33 |
| | *NK S2* | dry | 9.8 | Dry | 20.1 | Dry | 9.0 | dry | 3 | | 1.43 |
| | *NK S3* | 16 | 14.2 | 44 | 24 | 8.7 | 8.6 | 2.8 | 10.8 | 1.01 | 2.59 |
| | *NK S4* | 22.2 | 15.7 | 87 | 38.7 | 7.7 | 8.9 | 23.4 | 6 | 4.15 | 21.03 |
| **Beirut River** | *NB S1* | 15.8 | 11 | 32 | 16.4 | 7.9 | 8.5 | 0.2 | 1.2 | 0.93 | 0.91 |
| | *NB S2* | 22.6 | 23.8 | 130 | 64.5 | 8.5 | 9.2 | 62 | 5.6 | 8.91 | 8.90 |
| | *NB S3* | 25.1 | 25 | 504 | 100 | 8 | 7.8 | 639 | 690 | 39.89 | 19.2 |

TSS concentration is more relevant during wet season compared to the dry (Table 1). In addition, this concentration is higher at the three river outlets than their sources. The low TSS concentration could be assigned to the dilution effect of a larger body of water or the site location within a forested area. This is the case of the sites at the sources of Ibrahim, Kaleb and Beirut Rivers. The decrease of TSS concentration along the down streams of Ibrahim and Kaleb Rivers could be explained by the possible change in the river gradient near the downstream where it is less steep than the upper streams and where the current doesn't move as swiftly as above. Another reason could be the fact that the river becomes wider at the down streams thus the sediments will tend to settle down compared to upstream. Contrarily, the highest TSS concentration was found at the Beirut River outlet (BS3), during both wet and dry season (690 and 639 mg/L respectively) and this due to the mixture of the sewer wastewater and the river water, hence increasing the quantity of organic and inorganic matter (urban development and heavy agricultural use). For such sites with TSS concentration above 50 mg/L, the urban land use was dominant versus sites with less than 50 mg/L with agricultural land use is dominant (Hart 2006).

DOC concentration was also measured for all the sites along the three watersheds in both dry and wet seasons. For Ibrahim and Kaleb Rivers, DOC concentrations are related to the river flow, where it's shown that they are higher in wet season than in dry season. Organic materials present at this period may come either from autochthonous origin (in-stream production) or from allochthonous origin. The latter could be provided from a natural source as soil runoff (surface and sub-surface soil erosion), litter erosion, etc., or from anthropogenic source as urban discharges which are dominant in downstream. In fact, the high values of DOC in wet season at upstream of Kaleb and Ibrahim rivers, IS1 and KS1, could be explained by the dominance of organic matter that may be leached already during the first runoff of the wet weather season. Unlike, Beirut River didn't show this difference between dry and wet seasons for the upstream sites. That's because it's all the year impacted by urban releases. Regarding the spatial variation, it can be observed that DOC concentrations at downstream sites for all rivers (IS4, KS4 and BS3) are systematically higher than that observed for the upstream sites. Downstream sites of all these watersheds are strongly impacted by urbanization. Indeed, massive urban discharges of domestic and industrial activities, rich in organic materials, are rejected directly without any treatment into receiving waters at downstream of these small Mediterranean karstifed watersheds (Merhabi et al 2019), explaining the high DOC concentrations measured at downstream, and especially at the outlet of Beirut River. In this latter, the urban pressure is more pronounced in dry season where is no effect of dilution; DOC measures 39,9 mgC/L. These results are consistent with other studies done on the downstream of coastal Mediterranean karst watersheds highly affected by urban pressure (Carrasco et al. 2008; Mustapha et al. 2014; Tzortziou et al. 2015).

## 2.2 Variation in Fluorescence Indices of DOM

All surface waters were analyzed using fluorescence spectroscopy EEM as previously described. Spatial and temporal variations of DOM quality were highlighted according to hydrological conditions. In general, higher intensities of fluorescent materials were found for waters collected in dry season in comparison to those sampled in the wet season due to the dilution effect in wet season. The HIX and BIX indices were calculated to provide information on DOM origin and transformation. In both seasons, there is a pronounced biological activity that produces biological material from humification processes that results in humic compounds. In the table below (Table 2), we notice that the HIX values (humification level) differ in both seasons along Ibrahim River and remains almost the same along Kaleb and Beirut rivers. This is related to the dominant forest zone in the Ibrahim River watershed highlighting the excessive input of humic organic matter showed by the higher values of HIX in wet season.

The humification index (HIX) in the three rivers was less than 4 in the dry season, supporting the strong autochthonous component character and the weak humus property of DOM. It is obvious that in dry season, the HIX values are lower compared to the wet season. The high values of HIX in winter are strongly associated to the predominance of humic organic matter resulting from the leaching of soils where there is a terrigenous allochthonous humic character unlike the dry periods where it shows a greater presence of autochthonous component of DOM. From the dry season to the wet season, the autochthonous component character of DOM in the rivers displayed an attenuating tendency, and the external source contributions were strengthened. DOM mainly come from internal sources during the dry season, while it covers both origins from in-situ biological production and external input during the wet season.

The biological index (BIX) ranged from 0.8 to 1.0 at the three river sources and middle sites, revealing the strong autochthonous component characteristics of the rivers (He et al. 2022). As for the spatial variation of BIX, it decreases at upstream of the three rivers and it increases in the middle sites and downstream in both periods wet and dry. That’s reflect high phytoplankton activity and strong organic origin at downstream.

Table 2
HIX and BIX values for all sites of Ibrahim, Kaleb and Beirut Rivers in dry and wet seasons

| **Sampling sites** | | **HIX dry** | **BIX dry** | **HIX wet** | **BIX wet** |
|---|---|---|---|---|---|
| **Ibrahim** | *IS1* | 0.93 | 0.93 | 2.2 | 0.22 |
| | *IS2* | 0.88 | 0.71 | 2.1 | 1.86 |
| | *IS3* | 2.31 | 0.98 | 2.78 | 1.73 |
| | *IS4* | 2.5 | 1.3 | 3 | 0.67 |
| **Kaleb** | *KS1* | 0.42 | 0.85 | 0.62 | 0.38 |
| | *KS2* | n.d. | n.d. | 1.54 | 0.65 |
| | *KS3* | 1.12 | 1.2 | 1.35 | 1.9 |
| | *KS4* | 1.96 | 1.12 | 2.35 | 1.18 |
| **Beirut** | *BS1* | 1.98 | 0.93 | 2.14 | 0.59 |
| | *BS2* | 1.29 | 1.04 | 1.42 | 1.41 |
| | *BS3* | 0.99 | 1.40 | 1.18 | 1.31 |

The fluorescence index (FI) ranged from 1.6 to 1.8 in the rivers (Fig. 3), indicating that DOM along three rivers is a combination of internal release and external inputs (autochthonous and allochthonous) (He et al. 2022). In general, the FI value was slightly higher in the dry season than in the wet season, implying that DOM is primarily obtained from internal inputs during the dry season. The terrigenous humic-like substances abundance is linked to river inflow during rainfall events, in this instance the external sources play a larger role. According to (Lin et al. 2022), FI values above 2.1 represent wastewater and this is hugely manifested at downstream sites of Beirut River. It should be mentioned that the time of sampling at the different sites is different and not punctual so there is a probable variation in the impact of pollution sources. For most of the sampling sites, the high FI values, the low HIX values (< 4) and the high

BIX values (> 0.9) noticed explain that DOM has been coming from urban origin and/or freshly produced from biological activity.

## 2.3 Fluorescence spectroscopy EEM - PARAFAC components

A six-component model was determined by PARAFAC analysis. The EEM spectra contour plots of the six components are given in Fig. 4 in dry and wet seasons respectively. The six components determined showed similarities, with peaks identified in previous studies and related in the literature which shows that fluorescence band intensities of wastewater effluents are very high and considered as a reference point in the determination of anthropogenic DOM and as a differentiation between urban discharges and natural water (Goldman et al. 2012). Components C2 and C3 were related to biological activity, while components C1 and C4 to humic material and C5 and C7 to protein material. In other words, C1 and C4 will reflect the humic character whereas the remaining will reflect the non-humic material.

There is a clear seasonal effect on DOM quality showed by the variation of fluorescence intensities (Fig. 4). First, the fluorescence intensities are weaker in the wet season due to dilution effect. Also, it was noticed that the upstream fluorescence intensities are lower than that at downstream affected by urbanization. This is also explained by a lower presence of humic substances due to predominance of non-humic compounds at downstream. This is due strongly to the fact that the downstream sites are affected by urban DOM from wastewater discharges. The difference in the fluorescence intensity illustrates the variation in the urban/natural DOM impact on each site. Indeed, with the most intensive human activity (agricultural and industrial discharges) being located at the outlet's rivers, fluorescence components C5 and C7 could be derived from any combination of terrestrial, anthropogenic, and microbial sources. It was also observed that both Ibrahim and Kaleb River share a similar natural watershed due to the behavioral resemblance whereas Beirut River is considered as a highly urbanized watershed. This is clearly shown in the intensities' values of the six fluorescence components (Fig. 5). Concerning the spatial variation, we find for the three rivers, that C1 and C4 fluorescent components' values almost increase from source to outlet (upstream to downstream) in both dry and wet season with more pronounced values in the dry season. This means that the humic character increase from source to outlet due to the large agricultural land and increased vegetation cover in these watersheds. The high values of C1 and C4 at the source could be explained by compost usage and fertilizers that are loaded in humic DOM. Moreover, if we compare C2 and C3 intensities, the values increase from source to outlet along Kaleb and Beirut Rivers and there is an absence of C2 component at sites of Ibrahim River (IS3 and IS4) in the dry season and almost negligible values of component C2 and C3 along all site except BS3 along Beirut River in the wet season. This could be explained by dilution impact that is revealed at Beirut and Kaleb River unlike Ibrahim River where the values are almost similar in both seasons. The C2 and C3 components reflect the presence of microbial substances that are biologically active where component C2 is mainly linked to anthropogenic sources such as urban runoff and sewage. Also, microbial activity and degradation of phytoplankton in natural aquatic systems contribute to C2. Whereas C3 is related to autochthonous labile DOM produced by biological processes. So this pattern is attributed to both extensive grassland and forest cover which affects the bare soil surfaces and the distance from anthropogenic pollution which together highly affects the importance of biological processes (Niu et al. 2022). Finally, components C5 and C7, reflecting the proteinic DOM materials, increase from source to outlet along the three rivers and mainly along Beirut River with more pronounced values in the dry season (Fig. 5). So based on the analysis, obviously, Beirut River is highly polluted followed by Kaleb River then by Ibrahim River.

The relative distribution of the six PARAFAC components in each site was calculated in accordance with the literature (Fig. 6). The average proportional distribution of components C1 (C1%), C2 (C2%), C3 (C3%), C4 (C4%), C5 (%C5) and C7 (C7%) in each site was calculated to clearly compare between upstream and downstream of Ibrahim, Kaleb and Beirut Rivers.

We can easily relate components C1 and C4 to humic character and C2, C3, C5 and C7 to non-humic character. Moreover, a pronounced resemblance in the behavior of components percentages is shown along Ibrahim and Kaleb rivers in both seasons. The humic character increases from source to outlet. The origin of this humified material might be biological, microbial, terrestrial, or even from meat processing industry. The terrestrial origin is more likely to be manifested during the wet season (Peer 2022). As for Beirut river, the humic character decreases from source to outlet and this is predicted since the industrial input and the anthropogenic impact increases from source to outlet along Beirut River that passes in the capital city of Lebanon. As for the non-humic character, the components C5 and C7 exists at the outlets of Ibrahim and Kaleb due to industrial and urbanization impact but it is more pronounced at Beirut Outlet in both seasons. The protein-like components of DOM (tryptophan and tyrosine, C5 and C7) are often associated with sewage input and biological activity. The discharge of urban industrial wastewater and domestic sewage also promoted the increase of the proportion of tyrosine-like and tryptophan-like components. The proportion of DOM protein-like components in the middle reaches of the Beirut and Kaleb river Basin is relatively high in summer, which may be due to the strong urbanization degree in the middle reaches and large domestic sewage discharge (Xiaxia et al. 2022). Also, according to (Peer 2022), components C5 and C7 are related to the influence of discharges from several industries and that the fluctuation is more related to the production cycle than to seasonal conditions. In addition, C5 component at Kaleb river outlet (KS3) is relatively high since at this point, there is a by-pass for the river into a water treatment plant where the waste is rejected directly at this site into the river stream. Also, it was mentioned that the protein like compounds predominate in the dry season, and this is obviously manifested in our study. Furthermore, according to (Carstea et al. 2020), Tryptophan (C7) indicates possible microbial contamination in the water sample and has been associated with an autochthonous source. This component is highly present at Beirutoutlet.

# 3. Conclusion

Based on EEM fluorescence with PARAFAC analysis, two types of DOM were identified in the three adjacent rivers according to fluorescence components classification: humic-like components C1 and C4 and protein-like components C2, C3, C5 and C7. The fluorescence intensity of DOM in water gradually increased along the flow direction, and the lower reaches were significantly higher than the upper and middle reaches. The areas with a high urbanization impact in the middle reaches have higher protein-like components and are highly affected by human activity. Urbanization played an important role in driving the DOM variability. As a result, Beirut and Kaleb River showed a similar behavior unlike that of Ibrahim watershed. The urbanization affected DOM quantity and quality by content of DOM and the fluorescent ratios (HIX, BIX and FI) in one hand and DOM nature and origin in other hand. This caused a decrease in the amounts of natural humic-like DOM and an enrichment in the amounts of anthropogenic and protein-like DOM. In addition, urban water DOM had a high degree of spatial and temporal variation due to different surrounding land use types on each water body and seasons. DOM concentration and fluorescence intensity were rich in the dry season compared to that in the wet season. These ratios revealed that the humic DOM are attributable to both terrestrial and autochthonous inputs, with the latter being dominant. Also, the ratios showed that high temperature in dry season made the endogenous input more obvious. These changes were remarkably observed at Beirut River which reflected the highest pollution followed by Kaleb then by Ibrahim rivers. These conclusions give us a better understanding of urbanized aquatic systems, emphasizing of protection and management of water resources in urban development. The prevention and management of urban water pollution, strictly implement the national laws and regulations on water pollution prevention and control, make rational use of new water pollution prevention and control technologies, and reduce the urban discharges should be strengthened.

# Declarations

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### Data availability

All data generated or analyzed during this study are included in this published article.

### Conflict of Interest

The authors declare that they have no conflict of interest.

# References

1. Ayah, Ayah, M. Grybos, M Bawa, H. Bril, and G. Djaney. 2015. “Characterization of Dissolved Organic Matter in the Waters of Lomé Lagoon System (Togo).” *American Journal of Environmental Protection* 3 (4): 145–50. https://doi.org/10.12691/env-3-4-5.

2. Carstea, Elfrida M., Cristina L. Popa, Andy Baker, and John Bridgeman. 2020. “In Situ Fluorescence Measurements of Dissolved Organic Matter: A Review.” *Science of The Total Environment* 699 (January): 134361. https://doi.org/10.1016/j.scitotenv.2019.134361.
3. Chen, Wen, Paul Westerhoff, Jerry A. Leenheer, and Karl Booksh. 2003. “Fluorescence Excitation−Emission Matrix Regional Integration to Quantify Spectra for Dissolved Organic Matter.” *Environmental Science & Technology* 37 (24): 5701–10. https://doi.org/10.1021/es034354c.
4. Cory, Rose M., and Diane M. McKnight. 2005. “Fluorescence Spectroscopy Reveals Ubiquitous Presence of Oxidized and Reduced Quinones in Dissolved Organic Matter.” *Environmental Science & Technology* 39 (21): 8142–49. https://doi.org/10.1021/es0506962.
5. Croué, J.-P., M. F. Benedetti, D. Violleau, and J. A. Leenheer. 2003. “Characterization and Copper Binding of Humic and Nonhumic Organic Matter Isolated from the South Platte River: Evidence for the Presence of Nitrogenous Binding Site.” *Environmental Science & Technology* 37 (2): 328–36. https://doi.org/10.1021/es020676p.
6. Daou, Claude, Marise Salloum, Abdul Halim Mouneimne, and Bernard Legube. 2013. “Multidimensionnal Analysis Of Two Lebanese Surface Water Quality: Ibrahim And El- Kalb Rivers,” 12.
7. Darwish, Talal, Amin Shaban, Ivan Portoghese, Michele Vurro, Roula Khadra, Sagedah Saqallah, Laurent Drapeau, Simon Gascoin, and Nabil Amacha. 2015. “Inducing Water Productivity from Snow Cover for Sustainable Water Management in Ibrahim River Basin, Lebanon,” January.
8. De Paiva Magalhães, D., M. Da Costa Marques, D.F. Baptista, and D. Buss. 2015. “Metal Bioavailability and Toxicity in Freshwaters.” *Environmental Chemistry Letters* 13 (1): 69–87. https://doi.org/10.1007/s10311-015-0491-9.
9. El-Nakib, Sania, Ibrahim Alameddine, Majdi Abou Najm, and May Massoud. 2018. “Quantifying the spatio-temporal variability of water quality in an urbanized perennial Mediterranean river: the case of the Beirut River.” In , 187–97. A Coruña, Spain. https://doi.org/10.2495/WP180191.
10. Frem, S. 2009. “Nahr Beirut : Projections on an infrastructural landscape.”
11. info. 2022. “Nabaa Jaouz En Niml Spring(s), Mont-Liban, Lebanon.” 2022. https://lb.geoview.info/nabaa_jaouz_en_niml,273380.
12. Goldman, Jami H., Stewart A. Rounds, and Joseph A. Needoba. 2012. “Applications of Fluorescence Spectroscopy for Predicting Percent Wastewater in an Urban Stream.” *Environmental Science & Technology* 46 (8): 4374–81. https://doi.org/10.1021/es2041114.
13. Hanna, N., B. Lartiges, V. Kazpard, E. Maatouk, N. Amacha, S. Sassine, and A. El Samrani. 2018. “Hydrogeochemical Processes in a Small Eastern Mediterranean Karst Watershed (Nahr Ibrahim, Lebanon).” *Aquatic Geochemistry* 24 (5–6): 325–44. https://doi.org/10.1007/s10498-018-9346-x.
14. Hart, Heather Melanie. 2006. “Effect of Land Use on Total Suspended Solids and Turbidity in the Little River Watershed, Blount County, Tennessee,” 144.
15. He, J., X. Wu, G. Zhi, Y. Yang, L. Wu, Y. Zhang, B. Zheng, et al. 2022. “Fluorescence Characteristics of DOM and Its Influence on Water Quality of Rivers and Lakes in the Dianchi Lake Basin.” *Ecological*

*Indicators* 142 (September): 109088. https://doi.org/10.1016/j.ecolind.2022.109088.

16. Houri, Ahmad, and Saadieh W. El Jeblawi. 2007. “Water Quality Assessment of Lebanese Coastal Rivers during Dry Season and Pollution Load into the Mediterranean Sea.” *Journal of Water and Health* 5 (4): 615–23. https://doi.org/10.2166/wh.2007.047.
17. Hu, Bin, Peifang Wang, Chao Wang, Jin Qian, Jun Hou, Xiaoai Cui, and Nannan Zhang. 2017. “The Effect of Anthropogenic Impoundment on Dissolved Organic Matter Characteristics and Copper Binding Affinity: Insights from Fluorescence Spectroscopy.” *Chemosphere* 188 (December): 424–33. https://doi.org/10.1016/j.chemosphere.2017.09.023.
18. Huguet, A., L. Vacher, S. Saubusse, H. Etcheber, G. Abril, S. Relexans, F. Ibalot, and E. Parlanti. 2010. “New Insights into the Size Distribution of Fluorescent Dissolved Organic Matter in Estuarine Waters.” *Organic Geochemistry* 41 (6): 595–610. https://doi.org/10.1016/j.orggeochem.2010.02.006.
19. Jaffé, R., D. McKnight, N. Maie, R. Cory, W. H. McDowell, and J. L. Campbell. 2008. “Spatial and Temporal Variations in DOM Composition in Ecosystems: The Importance of Long-Term Monitoring of Optical Properties.” *Journal of Geophysical Research: Biogeosciences* 113 (G4). https://doi.org/10.1029/2008JG000683.
20. Lin, Yuye, En Hu, Changshun Sun, Ming Li, Li Gao, and Linhua Fan. 2022. “Using Fluorescence Index (Fi) of Dissolved Organic Matter (Dom) to Identify Non-Point Source Pollution: Effects of Land Use and Correction by Nitrogen and Oxygen Stable Isotopes.” *SSRN Electronic Journal*, January. https://doi.org/10.2139/ssrn.4226844.
21. Lyu, Lili, Ge Liu, Yingxin Shang, Zhidan Wen, Junbin Hou, and Kaishan Song. 2021. “Characterization of Dissolved Organic Matter (DOM) in an Urbanized Watershed Using Spectroscopic Analysis.” *Chemosphere* 277 (August): 130210. https://doi.org/10.1016/j.chemosphere.2021.130210.
22. McDowell, William H. 2023. “DOM in the Long Arc of Environmental Science: Looking Back and Thinking Ahead.” *Biogeochemistry* 164 (1): 15–27. https://doi.org/10.1007/s10533-022-00924-w.
23. Merhabi F, Amine H, Halwani J (2019) Evaluation de la qualité des eaux de surface de la rivière Kadicha. J Sci Libanais 20(1):10–34
24. Niu, Xiaoying, Wei pu, Pingqing Fu, Yang Chen, Yuxuan Xing, Dongyou Wu, Ziqi Chen, et al. 2022. “Fluorescence Characteristics, Absorption Properties, and Radiative Effects of Water-Soluble Organic Carbon in Seasonal Snow across Northeastern China,” June. https://doi.org/10.5194/acp-2022-336.
25. Peer, S. 2022. “Enhanced Statistical Evaluation of Fluorescence Properties to Identify Dissolved Organic Matter Dynamics during River High-Flow Events - ScienceDirect.” https://www.sciencedirect.com/science/article/pii/S0048969722051154.
26. Peng, Na, Kaifeng Wang, Ningyu Tu, Yang Liu, and Zhuanling Li. 2020. “Fluorescence Regional Integration Combined with Parallel Factor Analysis to Quantify Fluorescencent Spectra for Dissolved Organic Matter Released from Manure Biochars.” *RSC Advances* 10 (52): 31502–10. https://doi.org/10.1039/D0RA02706E.
27. Pletterbauer, Florian, Andreas Melcher, and Wolfram Graf. 2018. “Climate Change Impacts in Riverine Ecosystems.” In *Riverine Ecosystem Management: Science for Governing Towards a Sustainable*

*Future*, edited by Stefan Schmutz and Jan Sendzimir, 203–23. Aquatic Ecology Series. Cham: Springer International Publishing. https://doi.org/10.1007/978-3-319-73250-3_11.

28. Romero González-Quijano, Clara, Sonia Herrero Ortega, Peter Casper, Mark Gessner, and Gabriel Singer. 2022. "Dissolved Organic Matter Signatures in Urban Surface Waters: Spatio-Temporal Patterns and Drivers." Preprint. Biogeochemistry: Limnology. https://doi.org/10.5194/bg-2021-340.
29. Shaban, A. 2020. *Water Resources of Lebanon*. Vol. 7. World Water Resources. Cham: Springer International Publishing. http://link.springer.com/10.1007/978-3-030-48717-1.
30. Thurman, E. M. 2012. *Organic Geochemistry of Natural Waters*. Springer Science & Business Media.
31. Tronczynski, J. 1992. "Interactions between Dissolved Organic Matter and Organic Contaminants."
32. Xiaxia, L., Y. Keting, and C. Beibei. 2022. "Spatiotemporal Variation of Riverine Dissolved Organic Matter Degradation Based on EEMs-PARAFAC: A Case Study of Shili River in Jiujiang, Jiangxi Province, China, as a Typical Demonstration City of the Yangtze River Protection Strategy." https://www.mdpi.com/2073-4441/15/1/33.
33. Yang, Liyang, Jin Hur, and Wane Zhuang. 2015. "Occurrence and Behaviors of Fluorescence EEM-PARAFAC Components in Drinking Water and Wastewater Treatment Systems and Their Applications: A Review." *Environmental Science and Pollution Research* 22 (9): 6500–6510. https://doi.org/10.1007/s11356-015-4214-3.
34. Zhang, Liuqing, Y. Jun Xu, and Siyue Li. 2022. "Riverine Dissolved Organic Matter (DOM) as Affected by Urbanization Gradient." *Environmental Research* 212 (September): 113457. https://doi.org/10.1016/j.envres.2022.113457.
35. Zsolnay, Ádám. 2003. "Dissolved Organic Matter: Artefacts, Definitions, and Functions." *Geoderma* 113 (3–4): 187–209. https://doi.org/10.1016/S0016-7061(02)00361-0.

# Figures

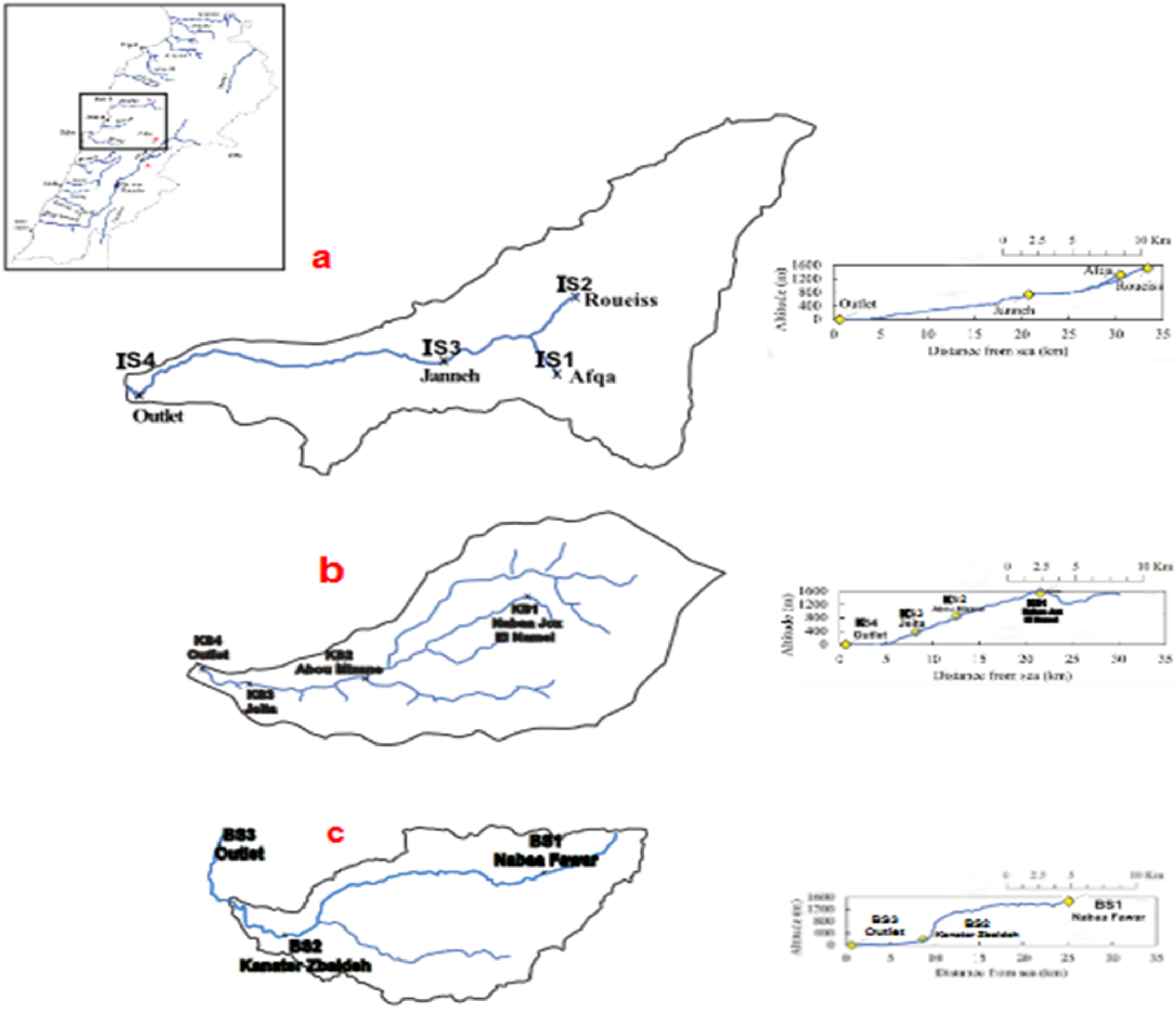



Figure 1

(a) Ibrahim River Watershed (b) Kaleb River Watershed (c) Beirut River Watershed

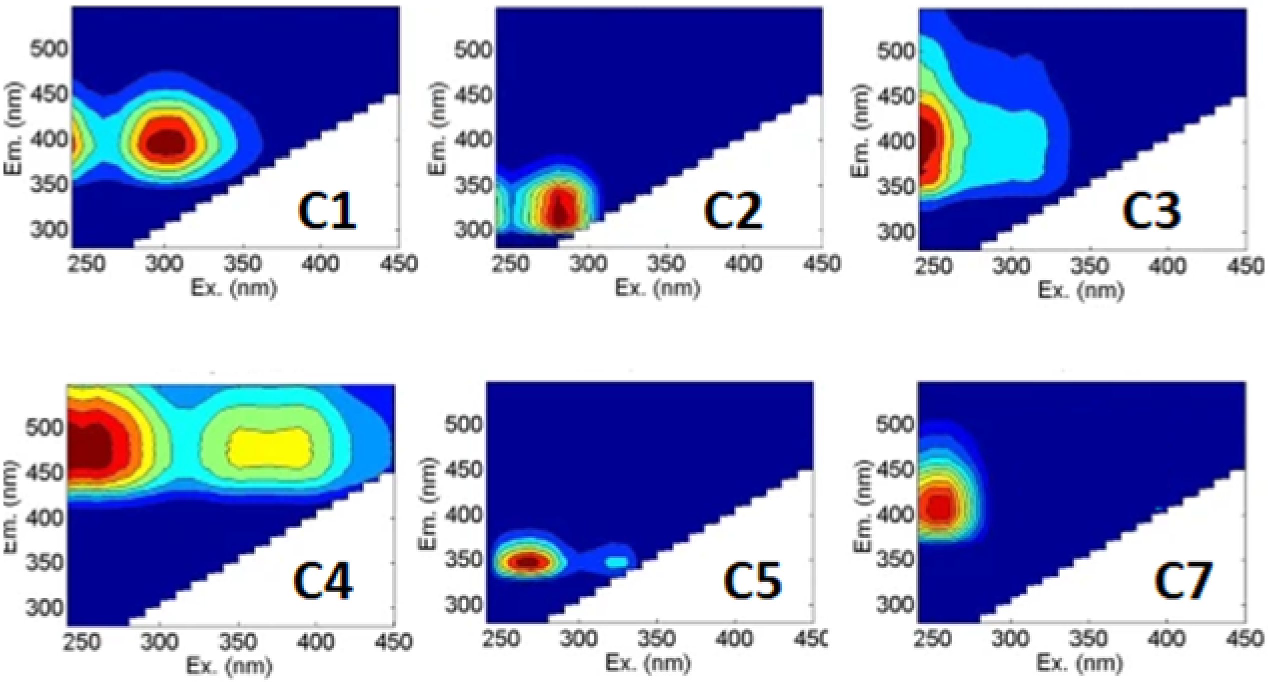



Figure 2

Distribution of PARAFAC components

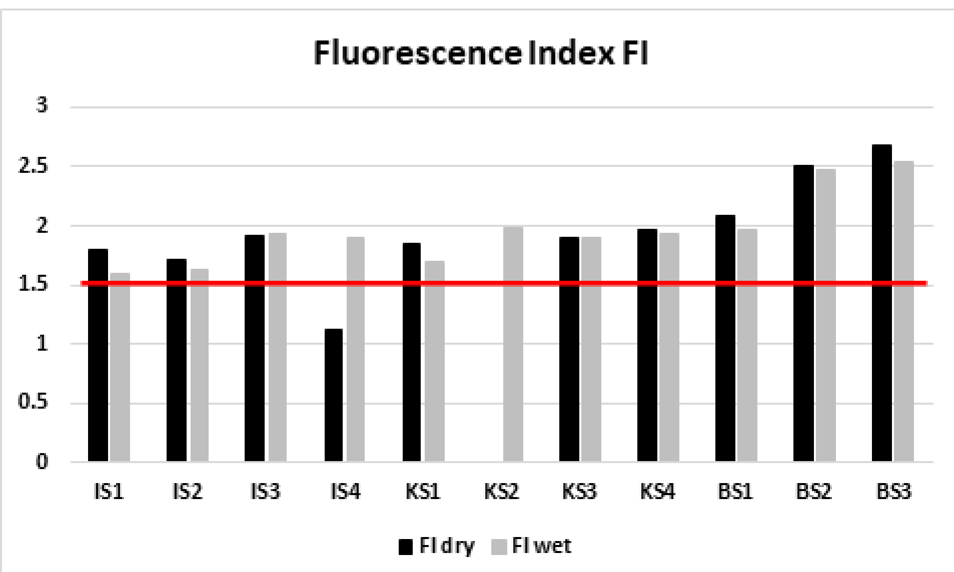
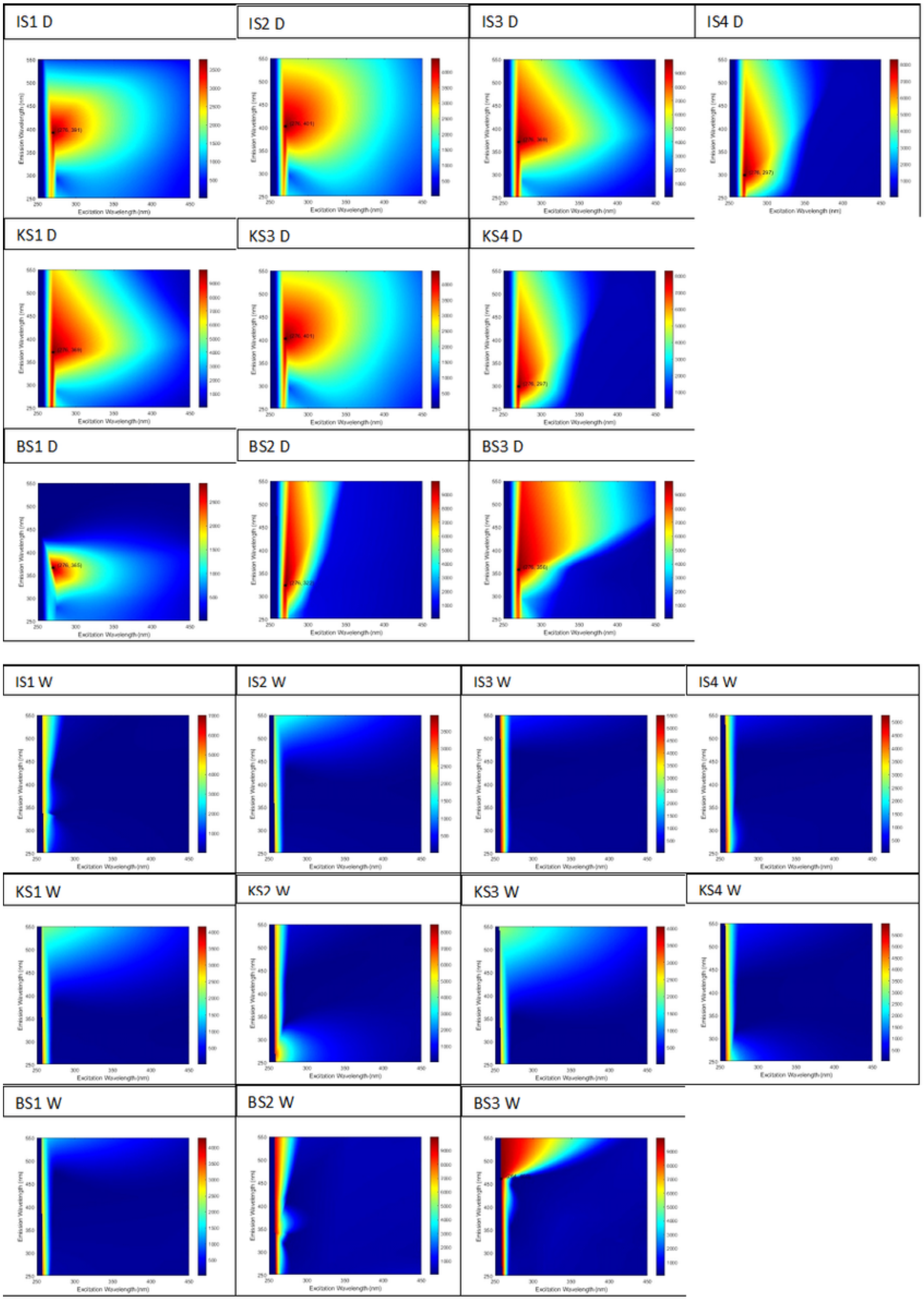


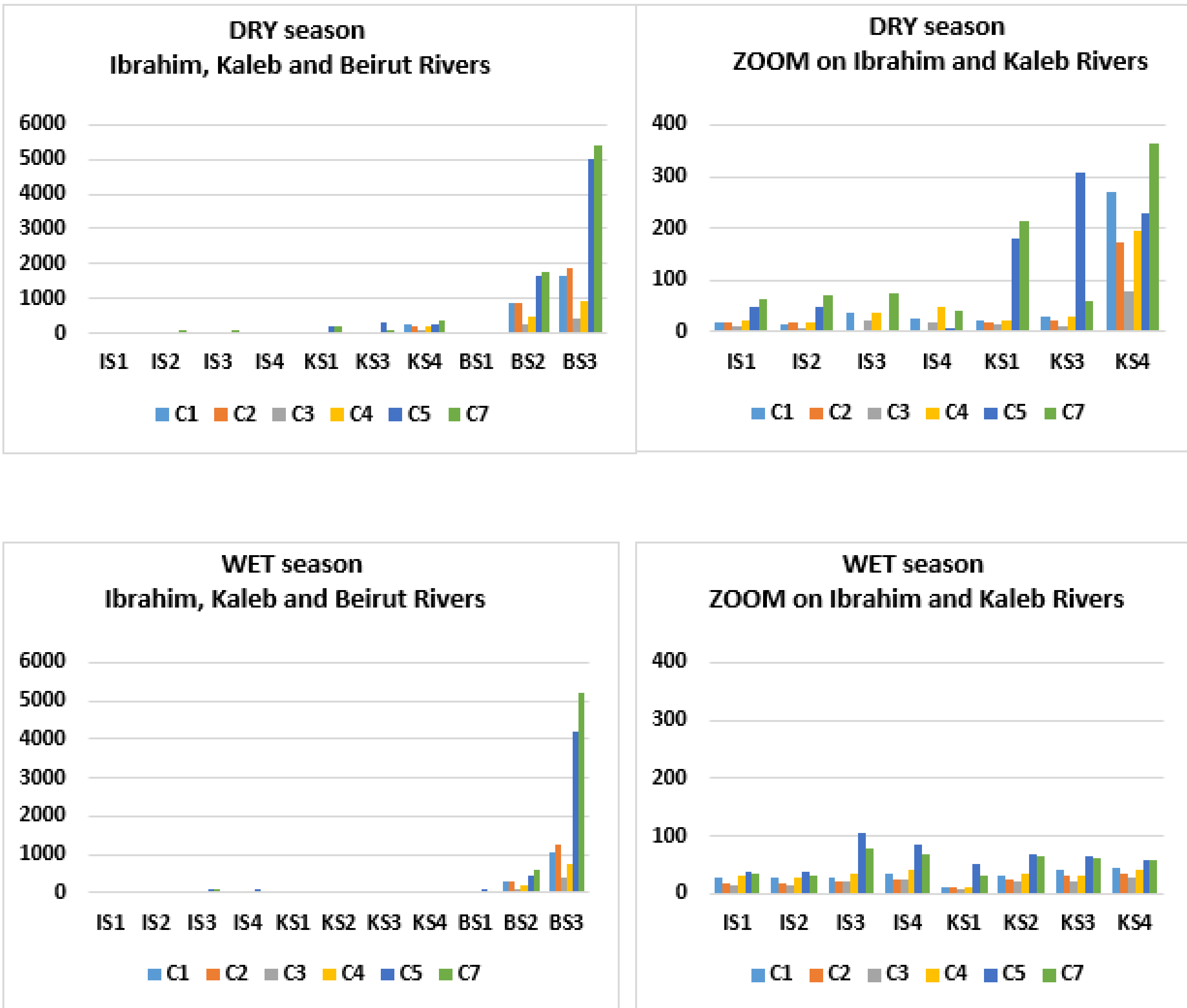

Figure 3

Fluorescence index for Ibrahim, Kaleb and Beirut Rivers in dry and wet seasons




## Figure 4

**EEM fluorescence intensities of DOM for all rivers sites along Ibrahim (IS1, IS2, IS3 and IS4), Kaleb (KS1, KS2, KS3 and KS4) and Beirut (BS1, BS2 and BS3) in dry (D) and wet (W) seasons**




## Figure 5

Fluorescence intensities of PARAFAC components C1, 2, 3, 4, 5 and 7 for all rivers sites along Ibrahim, Kaleb and Beirut in dry and wet seasons

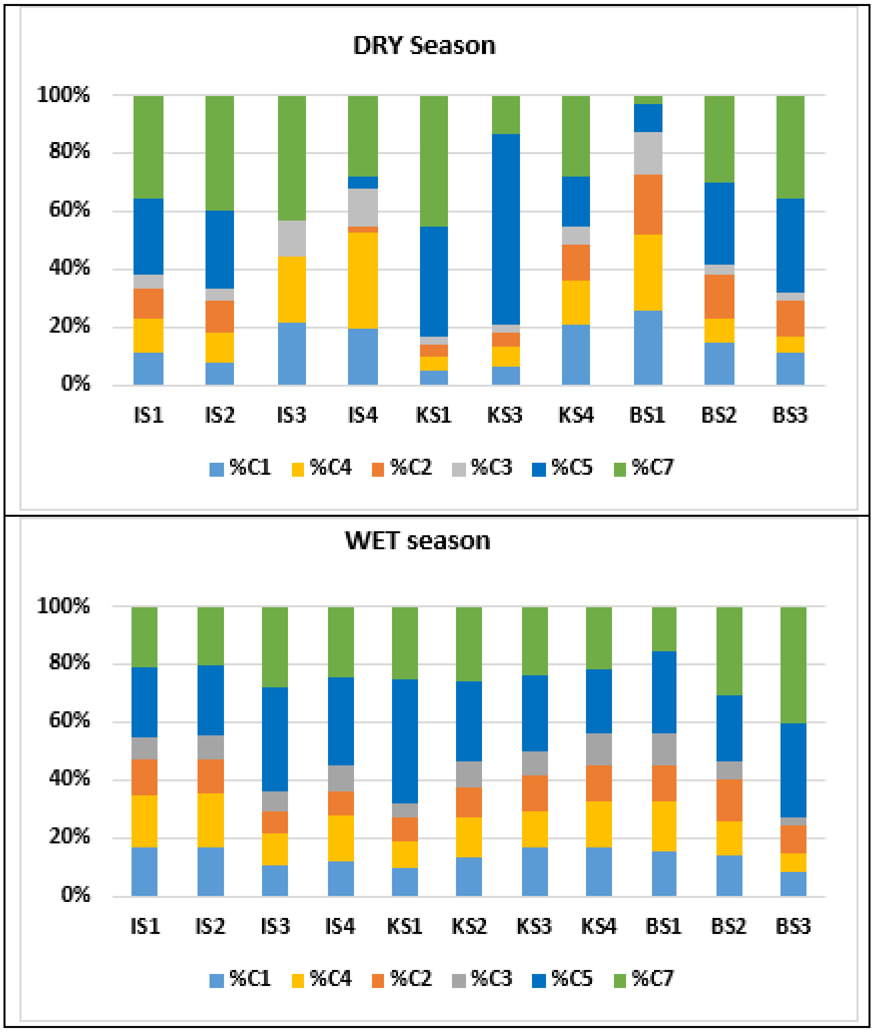



Figure 6

Percentage of PARAFAC components C1, C2, C3, C4, C5 and C7 in dry and wet seasons at Ibrahim, Kaleb and Beirut Rivers