Open Journal of Modern Hydrology, 2024, 14, 153-173
https://www.scirp.org/journal/ojmh
ISSN Online: 2163-0496
ISSN Print: 2163-0461

Dissolved Organic Matter Features of Three Adjacent Eastern Mediterranean Urbanized Watersheds

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How to cite this paper: Abboud, N., Maatouk, E.M., Matar, Z. and Kazpard, V. (2024) Dissolved Organic Matter Features of Three Adjacent Eastern Mediterranean Urbanized Watersheds. *Open Journal of Modern Hydrology*, **14**, 153-173.
https://doi.org/10.4236/ojmh.2024.143009

Received: February 28, 2023
Accepted: May 13, 2024
Published: May 16, 2024

Abstract

Landscape urbanization broadly affects ecosystems in coastal watersheds, 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) were determined for urban and non-urban waters from upstream to downstream sites along three adjacent coastal watersheds that flow into the Mediterranean Sea. Two humic DOM fluorescent components (humic-like and fulvic-like peaks) and two proteinic components (tyrosine-like and tryptophane-like peaks) were identified by EEM fluorescence. 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 uses surrounding each body of water. Urban waters show a higher DOM fluorescence index (FI), the highest fluorescence intensity of protein-like manifested also by BIX values, and a lower value of the humification index (HIX) than non-urban waters which were dominated by allochthonous inputs. In addition, the EEM was compared in dry and wet season where higher DOM amounts and FI appeared in summer due to autochthonous production coming from algae growth compared to allochthonous input from rainfall dominated in wet season. The concentration of DOC increased from upstream to downstream for the three rivers, especially Beirut River. The increase in DOC values was observed in both dry and wet seasons by 39 and 19 times respectively compared to upstream (0.93 - 0.91 mgC/L).

Keywords

Dissolved Organic Matter DOM, EEM Fluorescence Spectroscopy, Autochthonous/Allochthonous DOM, Urbanization, Upstream/Downstream, Wet/Dry Season

1. Introduction

Rivers have a major role in carbon cycles by transporting carbon from land to the seas. The flux of dissolved organic matter (DOM) is a major carbon flux source. DOM is highly reactive in ecosystem processes such as bacterial respiration, photochemical oxidation and primary production [1]. DOM is very dynamic, and they change by nature from upstream to downstream and even after entering the marine environment. So, DOM nature differs between freshwater and urban water.

DOM concentration, composition, and chemistry are highly variable depending on the source of organic matter. DOM may be terrestrial (allochthonous), 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 [2]. Algae is the major source of autochthonous organic matter. Note that if DOM in freshwater is from autochthonous sources, it is often rich in nitrogen (N) and its humic acid fraction is smaller compared to DOM from plant and soil origins [3] [4].

DOM is a heterogeneous mixture of aromatic and aliphatic organic compounds containing oxygen, nitrogen, and sulfur functional groups [5]. 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 [6].

DOM composition was strongly dependent on the land use structure and varied seasonally but the seasonal variation pattern could be altered by human activities in the massively urbanized catchments [7].

Numerous studies have investigated the characterization of DOM in both fresh and urban water, revealing its significant capacity to bind with organic pollutants, thereby influencing their accumulation and toxicity [8] [9] [10]. Many studies have been done concerning DOM characterization in fresh and urban water showing the great ability to bind to organic pollutants thus affecting their accumulation and toxicity [8] [9] [10]. Freshwater is rich in humic acid which constitutes a major part of the hydrophobic fraction of DOM, unlike wastewater in urbanized areas which has a large amount of hydrophilic fraction and a greater potential to form metal complexes by binding to organic micropollutants that affect their bioavailability and toxicity [11]. DOM-metal interaction also depends on pH, temperature and climate change, ionic strength, major cation composition of water, and the surface chemistry of sediment sorbents that act as solubility controls on the presence of photolytic and microbiological degradation processes [6].

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 is used to characterise DOM in the three studied watersheds. Fluorescence indices were used to track changes in the origin and transformation degree of DOM by distinguishing: 1) the humification level using HIX Humification Index, 2) the biological activity by BIX Biological Index, and 3) microbially derived DOC sources from terrestrially derived sources by FI Fluorescence Index [12]. Therefore, EEM fluorescence spectroscopy technique was used in this study to differentiate natural organic matter from urban DOM coming from urban discharges.

The focus of this work is 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. Urbanization is an extensive form of land-cover and land-use alteration that is rapidly growing and correlating very closely with increases in non-point sources of polluted runoffs which degrade the quality of aquatic resources [7]. The functional analysis of DOM using fluorescence EEMs will be used to characterize DOM and highlight 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 conducted from upstream to downstream along three adjacent coastal rivers—Ibrahim, Kaleb, and Beirut—during both dry and wet seasons in the sampling campaigns. The aim of this work is to understand the impact of pollution from these three coastal rivers on the Mediterranean Sea, to have a database about DOM behavior in these watersheds and to stress on the importance of introducing water treatment plants at the mouth of these three rivers.

2. Materials and Methods

2.1. Study Area

Along with Lebanon's small surface (10,452 km^2) 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 (**Figure 1**). The three studied rivers follow a defined hydrologic regime which is controlled by their geomorphology where each coastal river flows easterly towards the Mediterranean. **Table 1** summarizes the nature of activities at the three watersheds and the elements emitted to water and soil based on literature for a) Ibrahim River, b) Kaleb River, and c) Beirut River.

Ibrahim River is known for its highest water flow among all Lebanese rivers [13]. It has been studied several times before [14]. The studies showed that human activities have a great impact on water resources in this area quantitatively and qualitatively (Table 1). The second river will be Kaleb River, which is characterized by urban and agricultural activities along its watershed, including tourism, animal agriculture, and limestone quarries (Table 1). 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 [15], industrial, agricultural [16], and touristic activities along its side which reveals very high amounts of discharges (Table 1).

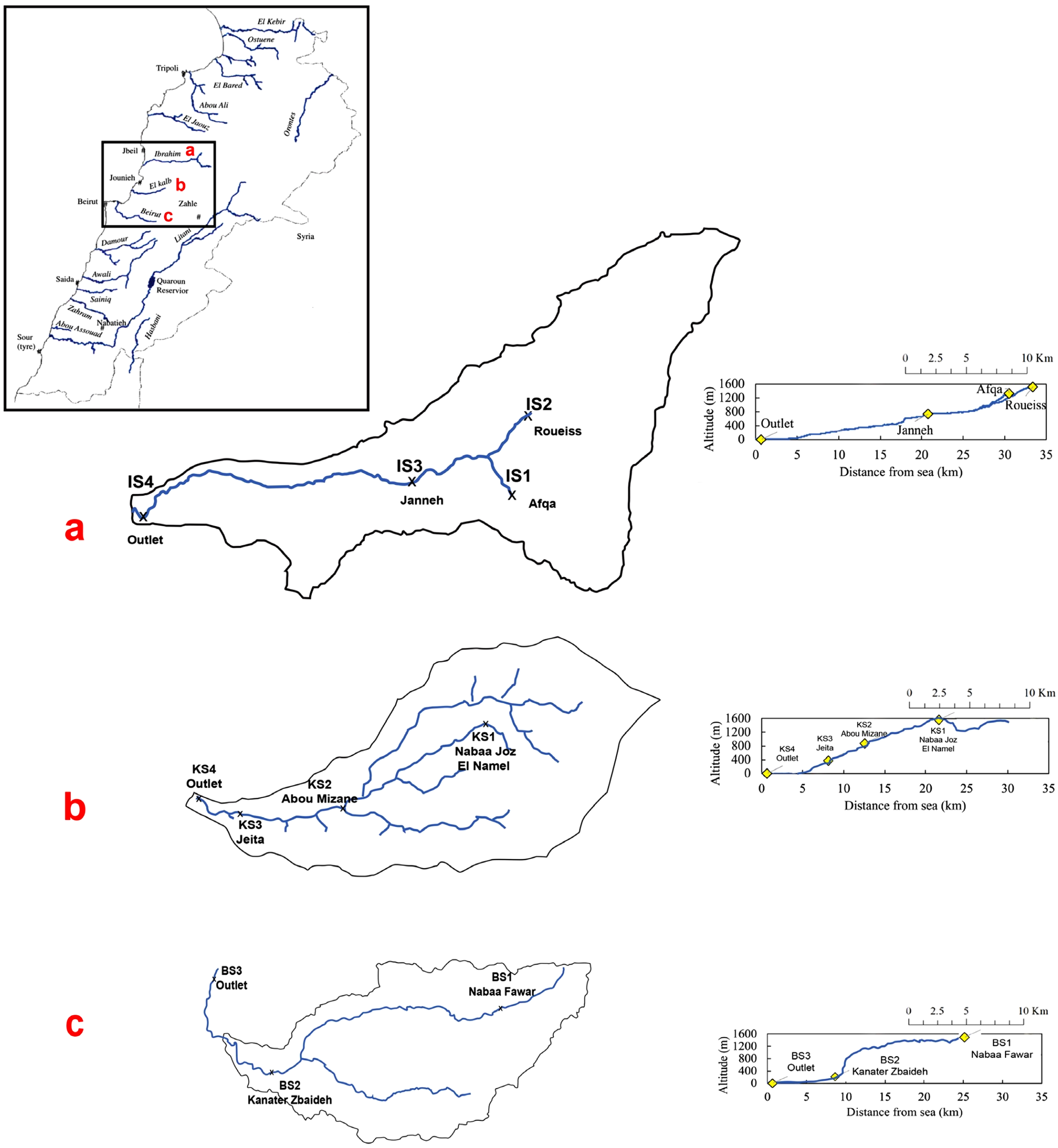

Figure 1. (a) Ibrahim River Watershed (b) Kaleb River Watershed (c) Beirut River Watershed [19].

Table 1. Nature of activities at the three watersheds and the elements emitted to water and soil based on literature for a) Ibrahim River, b) Kaleb River, and c) Beirut River [19].

Rivers	Surface (Km^2)	Length (Km)	Nature of Activity in the Basin	Elements released in water based on bibliography	Elements released in sediments based on bibliography
a-Ibrahim	330	30	*Agricultural Land*	*nitrogenous fertilizers and chlorinated pesticides* [20], *Downstream contamination with nitrates* [21]	*Fe, Mn, Zn and Pb* [21]
			Industrial facilities [22]	*Caries high concentration of Cd and Hg to the sea* [23].	
			Heritage Sites [25]		*Cd, Cr, Cu, Ni, Pb and Zn* [24]
			Residential Areas	*solid effluents* [25], *domestic wastewater* [20]	*Fe* [26]
			Vehicle Exhaust Fume	*High Pb deposition due to leaded petrol usage* [26]	
b-Kaleb	257	31	*Urban Activities*	*Domestic and wastewater discharge*	
			Touristic sites	*Solid wastes*	
			Agricultural activities	*nitrogenous fertilizers and chlorinated pesticides* [20] *Downstream contamination with nitrates* [21]	*. nitrates* [20]
			Animal farms and quarries	*organic wastewater discharge* [27]	
c-Beirut	217	25	*Urbanization and high population* [28]	*domestic and wastewater discharges*	
			Industrial activities	*chemical effluent, solid waste from construction material and fabrication* [29]	
			Agricultural activities [16]	*Nitrates and phosphates*	*Rich in Cd, Pb and Hg* [30]
			Slaughterhouse wastes	*organic waste*	
			wastewater from sewer network [18]	*Sewage*	
			Hospital debris	*organic wastes*	

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 downstream, while the upstream sampling site is mostly representative of forest and agricultural zones. As shown in (**Figure 1(a)**), four sites were considered along Ibrahim River where IS1 and IS2 represent two karstic sources Afqa (1400 m) and Roueiss (1600 m) respectively (impacted by farm and agriculture waste). The third site, IS3, was taken at Jannah Dam (800 m) (hugely impacted by vegetation) and the fourth site, IS4, at the outlet of the river (slightly impacted by industrial waste and urbanization).

For Kaleb River (**Figure 1(b)**), four sampling points were also 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 [17] where the water is potable. The second site (KS2) is at Abou Mizane (1200 m above sea level). This site dries out in the dry season and is populated (impacted by vegetation waste and tourism). Moreover, the third site (KS3) is located near Jeita Grotto (380 m above sea level) which is a popular tourist destination throughout the year and hugely affected by urban activities. Lastly, site (KS4) is in Zikrit area just before the river empties into the Mediterranean Sea (higher pollution than Ibrahim). Finally, three sites were collected along Beirut River (**Figure 1(c)**). 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 (150 m 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 by Maatouk (2014) [18]. Two sampling campaigns were conducted during 2 seasons: the wet season in May 2020 and the dry season in October 2021.

2.2. 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 calibrated according to the manufacturer's instructions. The accuracy of measurements was ±0.01 for pH, ±0.1˚C for temperature, and ±2% for electrical conductivity. 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 $mgC \cdot L^{-1}$).

2.3. EEM Fluorescence Spectral

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 was 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 a 1 cm optical path quartz cell and thermostated at 20˚C. The glassware used must be clean; cleaning is performed using detergent baths, specifically RBS 50, at a concentration of 2% - 3%. Cleanliness is assessed through fluorescence testing before using the glassware. 3D fluorescence spectra are generated over 75 minutes by successively recording 17 emission spectra (260 - 700 nm) with excitation wavelengths ranging from 250 to 410 nm. 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). 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 [31].

EEM spectroscopy allows observation of fluorescence regions characteristic of the main classes of compounds constituting the dissolved organic matter DOM. EEM spectra showed four peaks indicating humic acid-like, fulvic acid-like, and protein-like fluorophores, tyrosine and tryptophane. The humic acid-like peak is centered at 230 - 245 nm EX/ 400 - 460 nm EM. The fulvic acid-like peak is centered on 305 - 325 nm EX/ 410 - 430 nm EM. These two peaks compare well with earlier studies of natural waters as outlined in work by [12]-[32]. They are also similar to humic acid-like and fulvic acid-like peaks from river water collected for this study. The tyrosine-like peak is centered at 275 nm EX/305 nm EM [33]. This is nearly identical to the fluorescent center of the dissolved free amino acid tyrosine [31]. The tryptophan-like peak has been well documented from several urban water sources such as WWTP influent [34], WWTP effluent [35] and river water impacted from WWTP discharge [36]. Each study reports this fluorescent peak at 275 - 280 nm EX/ 340 - 350 nm EM [37]. This tryptophan fluorophore has also been attributed to surface marine estuary environments that support high biological activity [38].

Information on the origin and the transformation degree of DOM can be obtained through the calculation of the Humification Index (HIX) [39], Fluorescence Index (FI), and the Biological Index (BIX) [40]. Humification Index (HIX) is the ratio of the areas between H and L domains of the emission spectrum at a specific excitation wavelength at 254 nm. The H domain is between 435 nm and 480 nm and the L domain is between 300 - 345 nm. This ratio reflects the increase in CH ratio that occurs during humification showing the relative stability of organic compounds with respect to microbial activity. According to [41], HIX was influenced by the season; it was higher in winter due to the increased availability of humified organic matter resulting from soil leaching, primarily from terrigenous sources. 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, the Fluorescence Index (FI) was indicated, which indicates if the precursor material for DOM is of a more microbial (FI ~1.8) nature or more terrestrially derived (FI ~1.2) [42]. FI is the ratio of emission intensity at 470 nm to that at 520 nm under the excitation wavelength of 370 nm [43]. 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 [40].

3. Results and Discussion

3.1. Hydrochemistry of Watersheds

The temperature of the different sites along the three river watersheds was measured during dry and wet seasons as shown in **Table 2**. 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 seasons ranging from 15.8˚C to 25.1˚C and from 18.8˚C and 25˚C 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 [44].

Regarding the conductivity values (**Table 2**), the values during the dry season were more pronounced than those 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, in the dry season, the electrical conductivity (EC) value at the outlet (BS3) is approximately 502 μS/cm, which is fourteen times higher than the value at the source of the river (BS1) at 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 then mixed with river water before being discharged into the Mediterranean Sea and to the marine intrusion at the outlet of the river. This aligns with [45], where the variation between seasons was significant, particularly in the dry season. The lower flow during this season is highly influenced by anthropogenic discharges, transforming the river into a lentic system at 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 [14]. As for Kaleb River, it is also influenced by the soil nature and leaching as well as by anthropogenic inputs. For this reason, the EC is highest at its outlet at sea level where the retention time tends to increase.

As for the pH values, they were also measured in both seasons (**Table 2**). It was noticed that all three rivers were mildly alkaline, especially in the wet season.

Table 2. 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

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 [14] [20] [46]. This basic pH is due to the 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 the capital Beirut. Moreover, the pH value at Jeita site (KS3) is aligned with [20] where pH in this site is highly affected by the nature of the soil and the various reactions that take place in the water (physicochemical and biological reactions). The pH in Jeita touristic site is also affected by wastes of anthropogenic origin and mineral substances from endogenous origin.

TSS concentration is more relevant during wet season compared to the dry (**Table 2**). In addition, this concentration is higher at the three river outlets than at 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 in Total Suspended Solids (TSS) concentration along the downstream sections of the Ibrahim and Kaleb Rivers can be attributed to several factors. One possible explanation is the change in river gradient near the downstream areas, where the terrain is less steep than in the upper streams, resulting in slower water flow. Additionally, the widening of the river downstream may contribute to sediment settling compared to the upstream regions. Contrarily, the highest TSS concentration was found at the Beirut River outlet (BS3), during both wet and dry seasons (690 and 639 mg/L respectively) and this was 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 where agricultural land use is dominant [47].

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, such as urban discharges, which are dominant downstream. In fact, the high values of DOC in wet season 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. On the contrary, Beirut River didn't show this difference between dry and wet seasons for the upstream sites. This is due to continuous urban releases throughout the year. A changing pattern of DOM in surface water was observed throughout the year [48]. In terms of spatial variation, it is evident that DOC concentrations at downstream sites for all rivers (IS4, KS4, and BS3) are consistently higher than those observed at upstream sites. Downstream sites of all these watersheds are strongly impacted by urbanization and anthropogenic input. Indeed, massive urban discharges of domestic and industrial activities, rich in organic materials, are rejected directly without any treatment into receiving waters downstream of these small Mediterranean karstified watersheds [49], explaining the high DOC concentrations measured downstream, and especially at the outlet of Beirut River. In the latter, the urban pressure is more pronounced in dry seasons where no effect of dilution was observed; 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 [50]. DOC is capable of participating in pollutant migration and transformation [51].

3.2. EEM Fluorescence Spectroscopy

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. EEM fluorescence intensities of DOM for all river sites along Ibrahim, Kaleb, and Beirut in dry season are given in **Figure 2**.

In general, higher intensities of fluorescent materials were found for waters collected in dry season in comparison to those sampled in the wet season. In addition, the four determined peaks exhibit similarities with those identified in previous studies and documented in the literature. This similarity highlights that fluorescence peak intensities of wastewater effluents are notably high, serving as a reference point for the determination of anthropogenic dissolved organic matter (DOM) and as a means to differentiate between urban discharges and natural water [52]. Tyrosine and Tryptophane-like peaks were related to biological activity, while humic and fulvic-like peaks to humic material. The composition and sources of riverine DOM are affected by the different types of land use. More protein like DOM was found in sections of urban rivers.

There is a clear seasonal effect on DOM quality shown by the variation of fluorescence intensities (**Figure 3**). First, the fluorescence intensities of fulvic-like and protein-like (tyrosine and tryptophane) peaks are weaker in the wet season due to the dilution effect. In addition, the higher fluorescence intensities observed in dry season could also be explained by an important contribution in the summer of recent organic material coming from the increase of autochthonous biological activity (**Figure 3**). In contrast, the pattern is different for the humic-like peak between the dry and wet seasons for most samples of Ibrahim and Kaleb Rivers and for the upstream site of Beirut River (**Figure 3**). Its highest intensity at the wet season could be due to the greater presence of humic substances in the high-flow period coming from soil leaching. That means that DOM in the wet season was sourced from plant degradation from forest land or from urban green belts. The seasonality altered the DOM composition, with protein-like components emerging only in stream waters during the dry season, while microbial humic-like components exclusively occurred during the wet season [53].

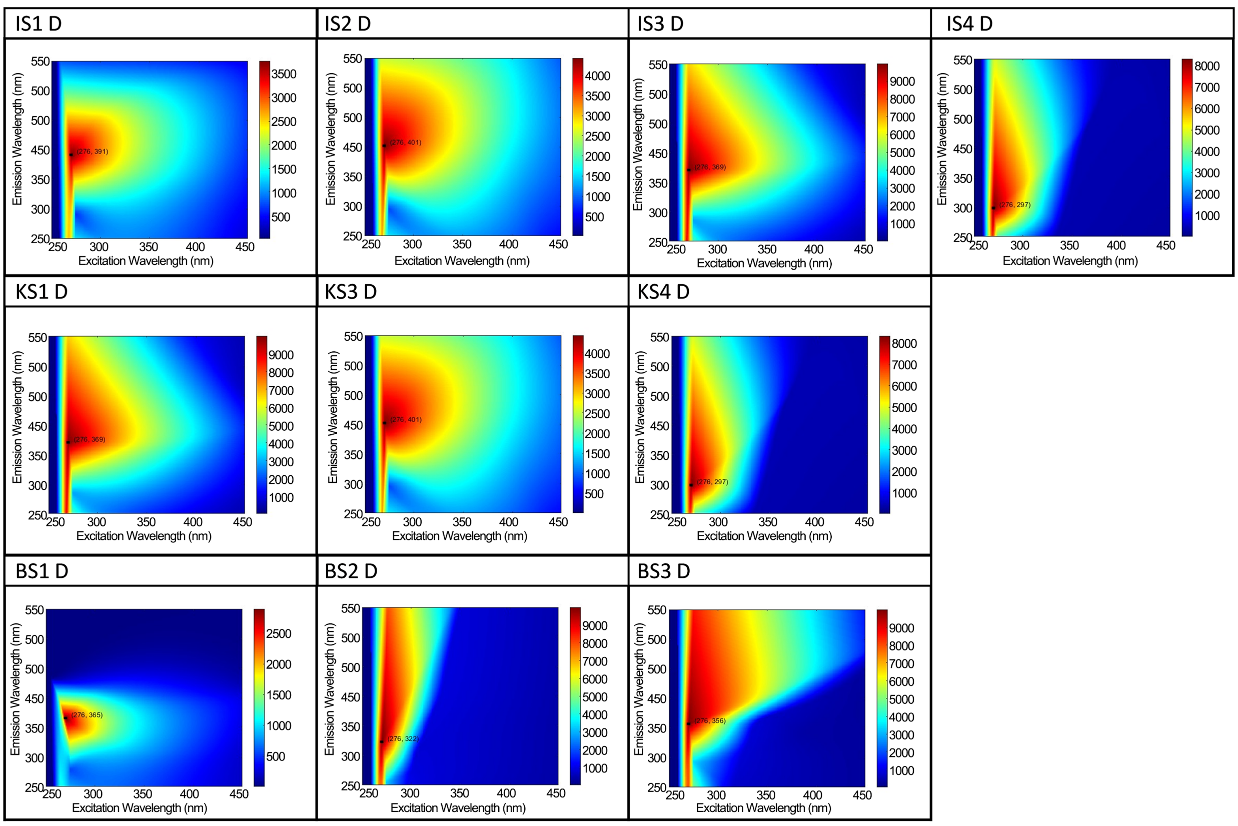

Figure 2. EEM fluorescence intensities of DOM for all rivers sites along Ibrahim (IS1, IS2, IS3 and IS4), Kaleb (KS1, KS2, KS3 and KS4) and Beirut (BS1, BS2 and BS3) in dry (D) season.

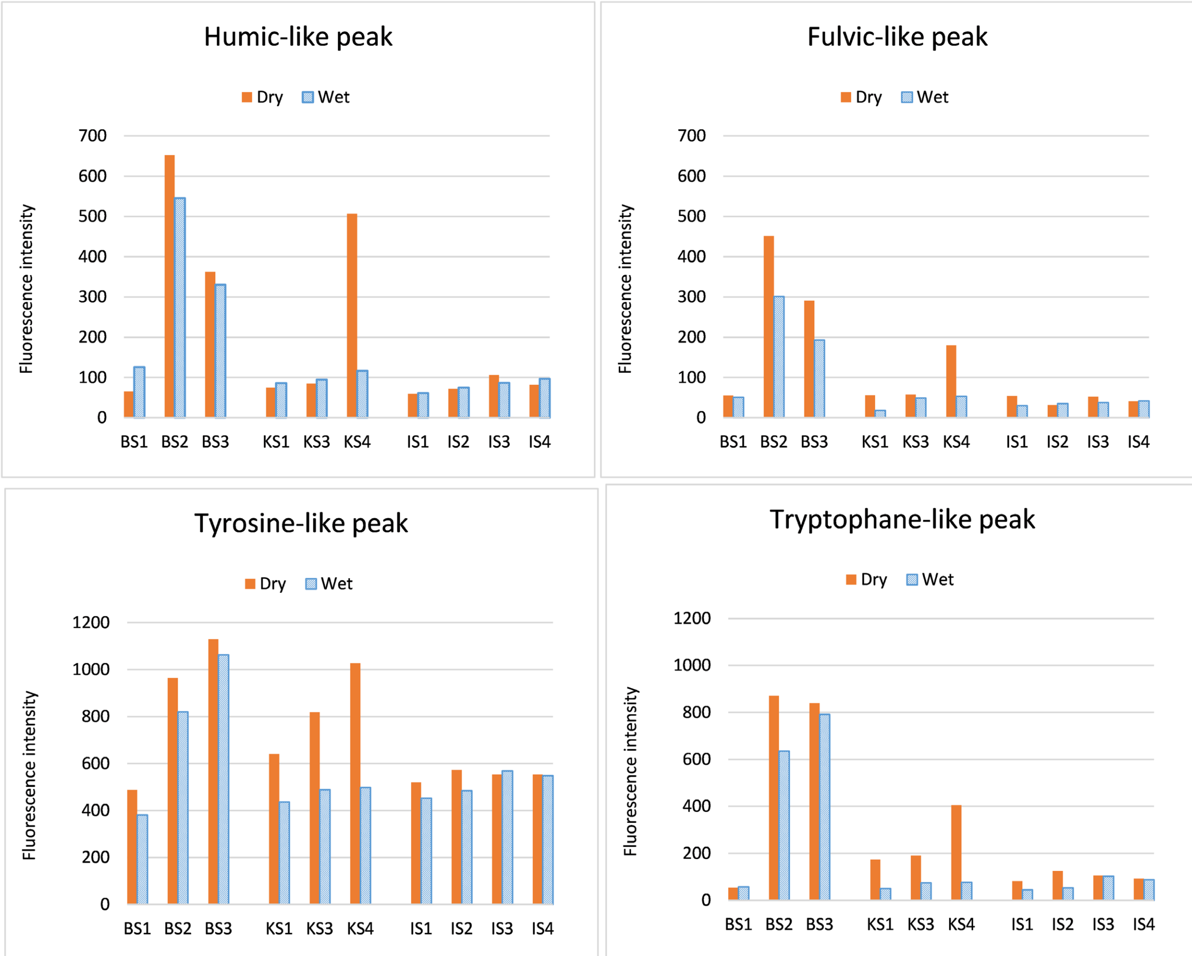

Figure 3. Fluorescence peaks intensities for all rivers sites along Ibrahim, Kaleb and Beirut Rivers in dry and wet seasons.

Regarding the spatial variation, it was noticed that fluorescence intensities for most of the upstream sites are lower than that at downstream (Figure 3). The difference in the fluorescence intensity between upstream and downstream sites illustrates the variation of DOM quality from natural to urban origin respectively. The downstream sites are affected by urban DOM coming from wastewater discharges enriched by non-humic compounds. Indeed, with the most intensive human activity (agricultural and industrial discharges) being located at the outlet's rivers, fluorescence DOM could be derived from a combination of terrestrial, anthropogenic, and microbial sources. Furthermore, it was observed that both Ibrahim and Kaleb River share approximately similar natural watersheds due to their behavioral resemblance whereas Beirut River is considered a highly urbanized watershed (Figure 2). This is clearly shown in the intensities' values of all four peaks which were higher for Beirut River in comparison to Kaleb and Ibrahim Rivers (Figure 3). The results showed that forested catchments had higher humic-like and lower protein-like than urbanized and mixed forest-agriculture catchments whereas the urbanized catchments showed an inverse trend.

The intensities of humic-like peaks increase from upstream to downstream for the three rivers in both seasons. This suggests an enhancement of the humic character from the source to the outlet, attributed to extensive agricultural land, increased vegetation covering these watersheds, and the use of compost and fertilizers containing humic dissolved organic matter (DOM). Regarding the tyrosine-like and tryptophane-like peaks, reflecting the proteinic DOM materials, they increase from source to outlet along the three rivers and mainly along Beirut River with more pronounced values in the dry season (**Figure 3**). These protein-like components of DOM predominant in Beirut River, reflect the presence of microbial substances biologically active, and are associated to anthropogenic sources such as urban runoff and sewage input [54]. In fact, the discharge of urban industrial wastewater and domestic sewage promoted the increase of fluorescence intensities of tyrosine-like and tryptophane-like components [55] [56]. According to [57], tryptophane-like peak indicates microbial contamination in the water sample and has been associated with an autochthonous source, which is highly present at the Beirut outlet. Protein-like substances originate from sewage discharge and microbial substances and are an important indicator of human activity [58].

By comparing the rivers, the fluorescence intensities of fulvic-like and tyrosine-like peaks for Ibrahim River don't present nor a significant spatial variation between upstream and downstream, nor a significant temporal variation for the two seasons, as shown by Kaleb and Beirut rivers. This pattern for Ibrahim River is attributed to both extensive grassland and forest cover which affects the bare soil surfaces and the far distance from anthropogenic pollution which together highly affect the importance of biological processes [59]. For Beirut River, the increasing nature of non-humic character from source to outlet is predicted due to the huge industrial input and anthropogenic impact along this watershed that passes in the capital city of Lebanon. Concerning Kaleb River, the high values of fluorescence intensities measured at KS4 are attributed to the fact that at KS3, there is a by-pass point for the river into a water treatment plant where the waste is rejected directly at this site into the river stream. Based on the analysis, obviously, Beirut River is highly polluted, followed by Kaleb River, then, by Ibrahim River. The high level of pollution was due to domestic effluents and sewer discharge particularly from the informal settlements that lack proper mechanisms of sewer disposal. Moreover, the open dumpsites along the river sites and the industrial discharge were major contamination sources and affected the water quality.

3.3. DOM Fluorescence Indices

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 3**), 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 shown by the higher values of HIX in the 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 the 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 an 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 comes from internal sources during the dry season, while it covers both origins from in-situ biological production and external input during the wet season.

Table 3. 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	*IS*1	0.93	0.93	2.2	0.22
	*IS*2	0.88	0.71	2.1	1.86
	*IS*3	2.31	0.98	2.78	1.73
	*IS*4	2.5	1.3	3	0.67
Kaleb	*KS*1	0.42	0.85	0.62	0.38
	*KS*2	n.d.	n.d.	1.54	0.65
	*KS*3	1.12	1.2	1.35	1.9
	*KS*4	1.96	1.12	2.35	1.18
Beirut	*BS*1	1.98	0.93	2.14	0.59
	*BS*2	1.29	1.04	1.42	1.41
	*BS*3	0.99	1.40	1.18	1.31

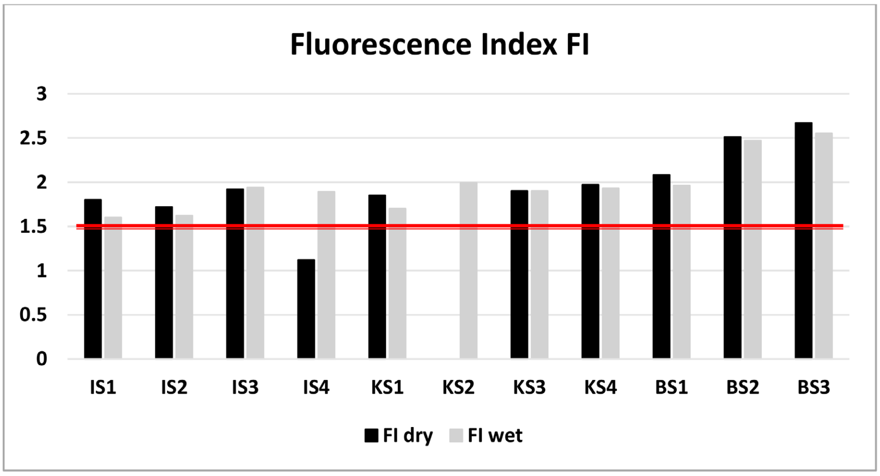

Figure 4. Fluorescence index for Ibrahim, Kaleb and Beirut Rivers in dry and wet seasons.

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 [60]. As for the spatial variation of BIX, it decreases upstream of the three rivers and it increases in the middle sites and downstream in both periods wet and dry. That reflects high phytoplankton activity and strong organic origin downstream.

The Fluorescence Index (FI) ranged from 1.6 to 1.8 in the rivers (**Figure 4**), indicating that DOM along three rivers is a combination of internal release and external inputs (autochthonous and allochthonous) [60]. 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 [61], 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.

4. Conclusion

Based on EEM fluorescence spectra, two types of DOM were identified in the three adjacent rivers according to fluorescence components classification: humic components (humic-like and fulvic-like) and proteinic components (tyrosine-like and tryptophane-like). 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) on one hand, and DOM nature and origin on the other hand. This caused 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 attributed to the diverse land use types surrounding each water body and seasonal changes. 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 attributed to both terrestrial and autochthonous inputs, with the latter being dominant. Also, the ratios showed that high temperatures in dry season made the endogenous input more obvious. Significant changes were notably observed in Beirut River, reflecting the highest pollution, followed by

Kaleb and then Ibrahim Rivers. These findings contribute to a better understanding of urbanized aquatic systems, underscoring the importance of protecting and managing water resources in urban development. To address urban water pollution, it is crucial to rigorously enforce national laws and regulations on water pollution prevention and control, adopt rational approaches to new technologies for pollution prevention and control, and actively work towards reducing urban discharges. It is necessary that urban and regional planners prioritize the preservation of natural ecosystems in their practices and take the ecological repercussions of their decisions into account. Sustainable land use practices can help lessen the detrimental effects of industrialization and urbanization on the availability and quality of water. Much research was done and confirmed that the degree of environmental conservation and water resources management techniques, like ecosystem-based approaches and integrated water resources management (IWRM), are significantly correlated.

Acknowledgement

This work was financed by the research grant programs of the Lebanese University (le projet est soutenu par le programme de subvention de la recherche scientifique à l'Université Libanaise). The funding source was not involved in the study design, writing of the report, and decision to submit the article for publication. We thank the research assistants of the Research and Analysis Platform for Environmental Sciences (PRASE).

Data Availability

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

Conflicts of Interest

The authors declare that they have no conflict of interest.

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