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Surface Water Processes in Coping with Anthropogenic Impact in a Coastal Eastern Mediterranean Region

Nour Abboud[1,2], Zeinab Matar[1,2,3], Elias Maatouk[1,2,3*], Véronique Kazpard[1,2,3]

[1]Research and Analysis Platform for Environmental Sciences (PRASE), Doctoral School of Sciences and Technology (EDST), Lebanese University, Hadat, Lebanon
[2]Laboratory of Georessources, Geosciences and Environment (L2GE), Faculty of Sciences, Lebanese University, Fanar, Lebanon
[3]Department of Earth and Life Sciences, Faculty of Sciences, Lebanese University, Hadat, Lebanon
Email: *Elias.maatouk.1@ul.edu.lb

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Abstract

Rivers are progressively being exposed to increased anthropogenic pollution stresses that are undermining their designated uses and affecting sensitive coastal areas. In this study, three adjacent eastern Mediterranean coastal rivers, Ibrahim, Kaleb and Beirut, were evaluated. Water quality samples were collected in dry and wet seasons from different sampling sites along the river from the source to the outlet which represent a gradient of increased urbanization. The spatiotemporal variability of the physio-chemical properties, heavy metals (Zn, Pb, Cu, Cr, and Cd) and organic matter (DOC) were statistically analyzed to better understand the contribution of point and nonpoint pollution sources. The three rivers (Beirut, Kaleb and Ibrahim) show a similar behavior in calcium and carbonate alkalinity due to the carbonate mineral weathering effect, so they are of calcium bicarbonate type due to their calcareous geological nature. The speciation of anions was affected by temporal variation. Moreover, it is obvious that the Beirut River has a different behavioral characteristic where the water is a sulfate type water with a preferable metal-OM complexation mainly with lead, zinc and copper, whereas Kaleb and Ibrahim are considered to be of a nitrate phosphate type with a preferable metal inorganic complexation, especially copper, that has a consistent behavior in both types of waters. This difference is attributed to the urbanization effect highly impacting the Beirut River.

Keywords

Anions/Cations, Metals, DOC, Complexation, Coastal Rivers, Spatiotemporal Variability

1. Introduction

Anthropogenic activities are increasingly modifying nutrient cycles in freshwater bodies. Lebanon generated a volume that varied between 275 and 328 Mm^3 of wastewater, of which 80% was domestic and 20% industrial [1]. Only 8% of the total generated wastewater was treated, although 60% of the population was connected to a sewage collection network. In the absence of operational wastewater treatment plants, coastal agglomerations are discharged into the sea, and effluents from inland communities are disposed of in rivers, streams and cesspits [2]. Additionally, the overexploitation of water resources due to excessive drilling and pumping is mainly concentrated in coastal areas, and saltwater intrusion affects a large stretch of aquifers along the Lebanese coastline [3]. Aside from the major pollution sources, what makes Lebanon's water quality deterioration problem more drastic is the prevalence of fissured limestone formations, which facilitate the seepage of liquid wastes into groundwater where they reappear in surface water and potable drinking water, resulting in a widening of the contaminated section [4].

On the other hand, rivers become enriched in metal after leaching from agricultural land, which is affected by the use of fertilizers and the discharge of industrial wastewater. The behavior of these metals is highly affected by pH and organic content, where their adsorption and bioavailability differ [5]. Additionally, alkalinity may have an effect on the behavior of metals, where major cations such as calcium might compete with metals [6]. Additionally, pH can affect the bioavailability of metals in freshwater. Therefore, as the pH decreases, the free metal ion concentration might increase, which leads to metal desorption from colloidal and particulate matter and to the dissociation of some inorganic and organic metal complexes [7]. Furthermore, organic matter (OM) is well known for its ability to interact with metallic micropollutants, affecting their transport and fate in the aquatic environment [8] [9] as well as their bioavailability, biodegradation, and toxicity towards organisms [10] [11] [12] [13]. The metal affinities to anthropogenic OM are larger than those to natural OM, which is relevant for environmental conditions. Organic matter quality and quantity have almost the same impact on trace metal mobilization [14]. Based on Chang 2005, when comparing the Zn complexation properties of natural OM from different surface waters, they found that at the same pH and ionic strength, natural OM from different surface water sources is similar in complexation to Zn with the same mechanisms of metal binding independent of NOM origin. Zinc binds to OM in natural water, so a very small quantity of zinc remains free, bioavailable or toxic

[15]. According to [16], there was a positive correlation between dissolved zinc and dissolved organic carbon (DOC) concentration, which indicates the capacity of some metals to remain in their dissolved form. Copper has a high affinity for binding to OM [10] [17]. When studying the Parisian aquatic system [18], they emphasized that DOM from urban water has proteinaceous structures that are highly reactive to copper and lead and organic pollutants. The windermere humic aqueous model (WHAM IV) gives a better prediction of complexation at low copper concentrations for samples of natural water.

In addition to copper and zinc, lead-NOM complexes account for most of the dissolved lead in freshwater, and it is strongly adsorbed to humic acids in sediments. In urban water, lead has a great capacity to bind to hydrophilic fractions of DOM, so all fractions must be considered when studying surface water. In addition, in surface water and ground water, lead carbonate complexes will dominate the lead hydroxy species formed in the absence of DOM. Lead bioavailability is highly dependent on the hydrophilic fraction of DOM, which plays a main role in transport and interaction with particles and in metal uptake by aquatic organisms as a result of both the decrease in free lead concentration and the ability of lead to form complexes [18]. For chromium, its adsorption and complex formation are highly dependent on the presence of natural organic ligands such as fulvic acids and on pH, which affects the oxidation state of chromium [19].

This work will focus on the hydrogeochemical composition of coastal rivers in the Eastern Mediterranean region to show the demographic impact. The spatial variability of organic and metallic micropollutants will be highlighted from upstream (source) to downstream (Mediterranean Sea) of three adjacent rivers: the Ibrahim River, Kaleb River (both located north of the capital city) and Beirut River. These rivers are located in three cities in the coastal part of Mount Lebanon [20]. Many sites along each river have been analyzed to be able to compare and understand the difference in pollution impact, nature and effect of urban discharges on water quality a) upstream and downstream of each river b) between three rivers and c) with respect to temporal variability where two campaigns took place in the period extended from 2020 to 2022. 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 heavy metals 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 a large coastline (210 km), our study area is related to three coastal river watersheds that flow from Mount Lebanon into the Mediterranean Sea: The Ibrahim River, Kaleb River, and Beirut River, as presented in **Figure 1**. The three studied rivers follow a defined hydrologic regime that is controlled by their geomorphology, where the three of them are coastal rivers that flow in one regional direction eastward towards the Mediterranean (Table 1).

- The Ibrahim River is known for its highest water flow among all Lebanese rivers [34]. It has been studied several times before [35] (Table 1). The studies showed that human activities have a great quantitative and qualitative impact on water resources in this area. A summary of water chemistry along the Ibrahim River is shown in Table 1.
- The Kaleb River is characterized by its urban and agricultural activities along its sides, touristic sites and animal farms and quarries. The nature of activities in this basin and the elements released in water and soil are described in Table 1.
- Finally, the Beirut River is characterized by an average flow in the wet season and a flow almost null in the dry season. It crosses the capital Beirut, so it has the highest population [36], industrial, agricultural [31] and touristic activities along its side, which reveals very high amounts of discharges, as shown in Table 1.

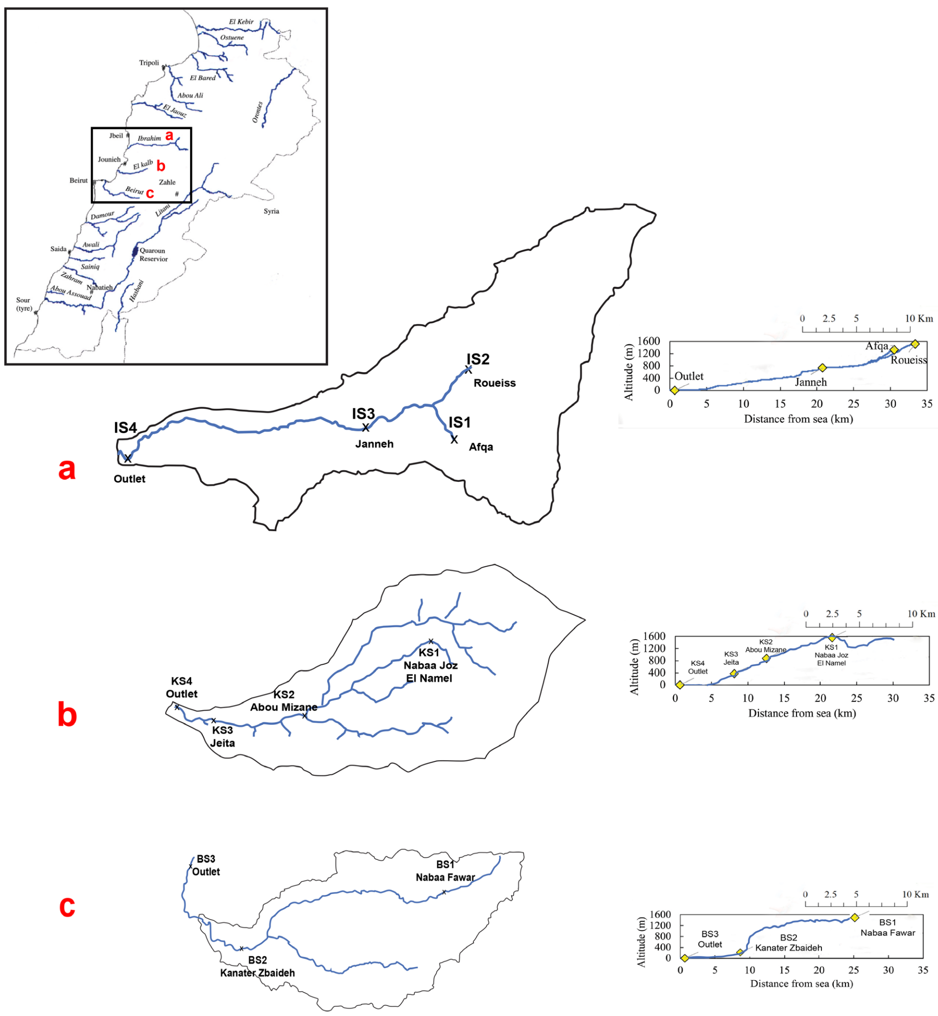

Figure 1. Ibrahim River, Kaleb River, and Beirut River Watersheds.

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 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 was mostly representative of forest and agricultural zones. As shown in **Figure 1(a)**, four sites were considered along the Ibrahim River, where IS1 and IS2 represent two karstic sources, Afqa (1400 m) and Roueiss (1600 m), respectively. The third site IS3 was taken at Jannah Dam (800 m), and the fourth site IS4 was taken at the outlet of the river. For the 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 [37] 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 it is populated. 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 is greatly affected by urban activities. The last site (KS4) is in the Zikrit area just before the river empties into the Mediterranean Sea. Finally, three sites were collected along the Beirut River (**Figure 1(c)**). The site at source BS1 was located at Nabaa Fawar Mountain (1623 m above sea level). The second site BS2 was at Kanater Zbeidy (150 m above sea level). 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 joins the main river, creating an additional flow. The calculation of the flow at this site was performed by [33]. Two sampling campaigns were conducted during two seasons: the wet season in May 2020 and the dry season in October 2021.

2.2. Physicochemical Properties

The parameters measured for each water sample are the following: major cations (K^+, Ca^{2+}, Na^+), major anions ($H_2PO_4^-$, F^-, Cl^-, NO_2^-, Br^-, NO_3^-, SO_4^{2-}), dissolved organic carbon (DOC), total heavy metals (T) (Cr, Pb, Zn, Cu, Cd), and their distribution between dissolved (D) and particulate (P) phases.

Calcium, magnesium, chloride, sulfate, nitrate, and phosphate were analyzed as stated by the standard guidelines of water sampling and physicochemical parameter evaluation (Reasoner 2004). Mg^{2+} and Ca^{2+} were analyzed by atomic absorption spectroscopy (AAS-Rayleigh WFX-210; Shimadzu, China), while flame photometry (Sherwood Flame Photometer Model 420) with a precision of ±1% and a repeatability of 0.3% was used to measure K^+ and Na^+. All on board, it is necessary to undergo acidification of these samples at pH. using 1% HNO_3 (grade). Cl^-, NO_3^-, SO_4^{2-}, and HPO_4^{2-} were measured in non-acidified water samples by using ion chromatography (Shimadzu LC-20AD-Shim-pack IC-A3 (S)) with a typical accuracy of ±0.5%. Repeated measurements of the blanks show that, in general, the accuracy is ±3% for cations and ±4% for anions.

DOC dissolved organic carbon content was determined using the O.I. analytical carbon analyzer by a Shimadzu V-CPH analyzer (quantification limit = 0.5 $mgC \cdot L^{-1}$).

Table 1. Nature of activities at the three watersheds and the elements emitted to water and soil based on literature: Ibrahim River, Kaleb River, and Beirut River.

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
			Agricultural Land	*nitrogenous fertilizers and chlorinated pesticides* [21], *Downstream contamination with nitrates [22]*	*Fe, Mn, Zn and Pb* [22]
			Industrial facilities [23]	*Caries high concentrations of Cd and Hg to the sea* [24]	*Cd, Cr, Cu, Ni, Pb and Zn* [25]
Ibrahim	330	30	*Heritage Sites* [26]		
			Residential Areas	*solid effluents* [26], *domestic wastewater* [21]	*Fe [27]*
			Vehicle Exhaust Fume	*High Pb deposition due to leaded petrol usage* [27]	
			Urban Activities	*Domestic and waste water discharge*	
			Touristic sites	*Solid wastes*	
Kaleb	257	31	*Agricultural activities*	*nitrogenous fertilizers and chlorinated pesticides* [21] *Downstream contamination with nitrates* [22]	*nitrates* [21]
			Animal farms and quarries	*organic waste water discharge* [28]	
			Urbanization and high population [29]	*domestic and wastewater discharges*	
			Industrial activities	*chemical effluent, solid waste from construction material and fabrication* [30]	
Beirut	217	25	*Agricultural activities [31]*	*Nitrates and phosphates*	*Rich in Cd, Pb and Hg* [32]
			Slaughterhouse wastes	*organic waste*	
			wastewater from sewer network [33]	*Sewage*	
			Hospital debris	*organic wastes*	

2.3. Metal Analysis

To prepare the various standard solutions necessary for the quantification of heavy metals, we used high-purity solvents: HNO_3 suprapur 65% (Fisher Scientific) and HCl 30% (Merck). Many steps were followed to determine the concentration of heavy metals in the different phases or fractions: total, dissolved, and particulate using AAS (Maatouk, 2014). To determine the total metal concentration (T), we mineralized the raw (unfiltered) sample with a Digiprep system. The procedure entails heating for two and a half hours at 95˚C 50 mL of sample, to which 1.15 mL of HNO_3 (65%) and 0.62 mL of HCl (30%) are added. The sample is placed in a high-purity polypropylene mineralization tube (resistant to high temperatures). The tubes are then placed in the digestion block, and the heating program is started. Using a probe positioned in a control tube, it is possible to monitor the temperature. Once mineralization was complete, the sample was filtered using a Teflon filter (PTFE) of 0.45 µm. To determine the concentration of the dissolved fraction [D], a similar protocol was applied by filtration on a 0.45 µm cellulose acetate membrane to remove the total suspended solids. The analysis of heavy metals was performed on the filtrate by AAS. Finally, the particulate fraction of heavy metals [P] was determined by the difference between total and dissolved metals noted as [T] and [D], respectively. The heavy metal content was also determined for each fraction in mg/kg, according to the formula below. For the particulate fraction [P*], *i.e.*

[P*] (mg/kg) = $\{10^3 \times [P]$ (µg/l)}/[TSS] (mg/L) (Maatouk, 2014). The flux of heavy metals into the Mediterranean Sea was calculated for the sampling points located at the river outlet into the Mediterranean according to the formula: Flux (kg/year) = Q (m^3/year)*[P] (kg/m^3), where Q is the flow at the studied site and P is the particulate concentration fraction of each heavy metal.

3. Results

3.1. Calcium Flux

The assessment of naturally weathered limestone outcrops in the study area and the resultant input into the Mediterranean Sea is referred to as calcium flux channeled by surface water of the coastal rivers from the source to the outlet. Two-thirds of riverine calcium is derived from the weathering of carbonate rocks [38] [39] [40]. Lebanon's watersheds are made up of exposed carbonate rocks where limestone, dolomitic limestone and dolomite are distributed on field surfaces. More than 85% of these rocks are karstified, and the dissolution of carbonates is very noticeable [36]. Calcium and carbonate alkalinity show a similar behavior along the three rivers, which indicates that they are controlled by almost identical factors as carbonate mineral weathering, which gives $CaCO_3$ precipitation as a sink.

Among the cations studied, it was clearly observed that the highest cation concentration was calcium among the three rivers, and it generally increased from the source to the outlet (**Figure 2**), except for the Ibrahim River, where the calcium concentration did not vary much throughout its pathway. It is known that the Ibrahim River has Ca^{2+} in both Afqa and Roueiss sources, and the seasonal comparison shows that the samples taken in the dry season are Ca^{2+}-depleted [35]. This aligns with the results of our study, where the concentration of calcium was lower at these sites in the dry season. In the other two rivers, Beirut and Kaleb, the calcium concentration at the outlet was almost three times and two times that at the source of the Beirut River and Kaleb River, respectively. Additionally, there was an important difference between the outlet site and the site just before it, specifically for the Beirut River (**Figure 2**), where the calcium concentrations were 50.7 mg/L and 185 mg/L at BS2 and BS3, respectively.

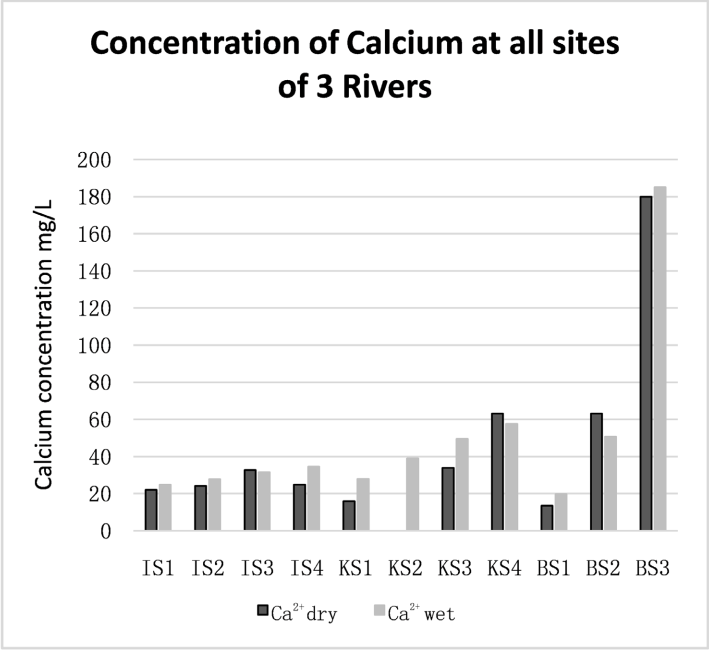

Figure 2. Calcium concentration in mg/L at all sites of the Ibrahim, Kaleb and Beirut Rivers in the dry and wet seasons.

These values show the intervention of anthropogenic effects at these sites and the impact of human activities in the lower part of the river. Moreover, in the Beirut River, the high concentration of calcium at the outlet was accompanied by a very high concentration of sulfate (215 mg/L). According to [41], sulfate can lead to fast calcium leaching from soils into the water. This also explains the obvious perturbation at the outlets and specifically Beirut outlet BS3.

3.2. River Water Chemical Facies

The three rivers are studied for their cationic and anionic chemical facies (**Figure 3**). Concerning the cationic typology, and for the two sampling periods (dry and wet), water samples are of calcium type. For the anionic composition, all the samples, except (BS3 in dry) and (BS2 in wet), are of a bicarbonate nature. The three rivers are calcium bi/carbonate type. This hydrochemical composition reflects the calcareous geological nature of the sampling areas [42] [43]. Moreover, the mean pH values in both seasons are approximately 8, indicating that the surface water of the study area of Ibrahim, Kaleb and Beirut is mainly alkaline in nature (pH at outlets is 9.05+/−0.035, 7.7+/−0.84 and 8.3+/−0.14, respectively).

To better understand the anthropogenic impact on the surface water of the three studied areas and to overcome the screening effect of the bi/carbonate facies, the hydrochemistry is studied by introducing nitrate and phosphate components into the anionic composition of the water (**Figure 4**). When the cationic parameters are unchanged, the cationic facies in **Figure 4** remain the same as the previous facies. However, the anionic facies show a separation of the typology according to the sampling periods (dry and wet). The waters in the northern

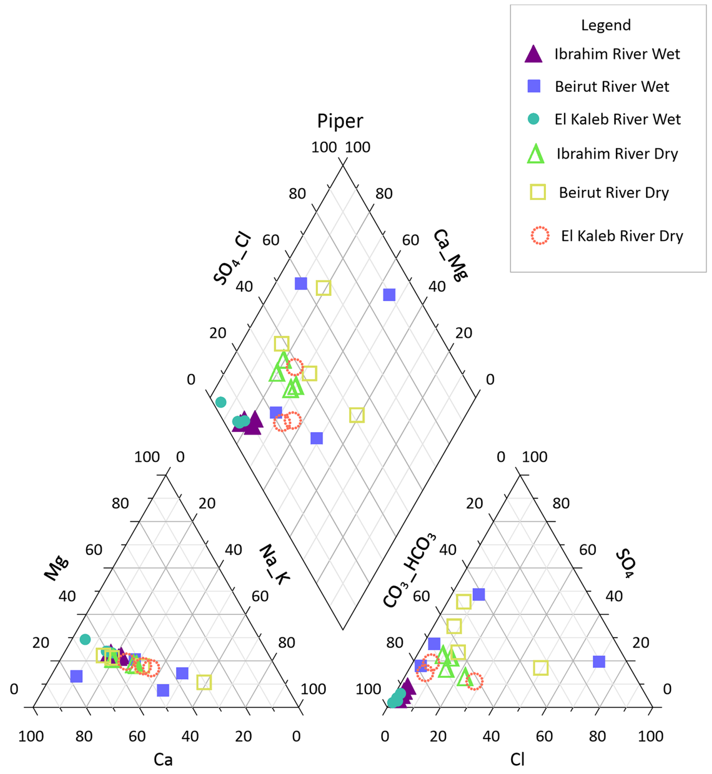

Figure 3. Chemical facies of the surface waters of the Beirut, Kaleb and Ibrahim Rivers in the dry and wet seasons.

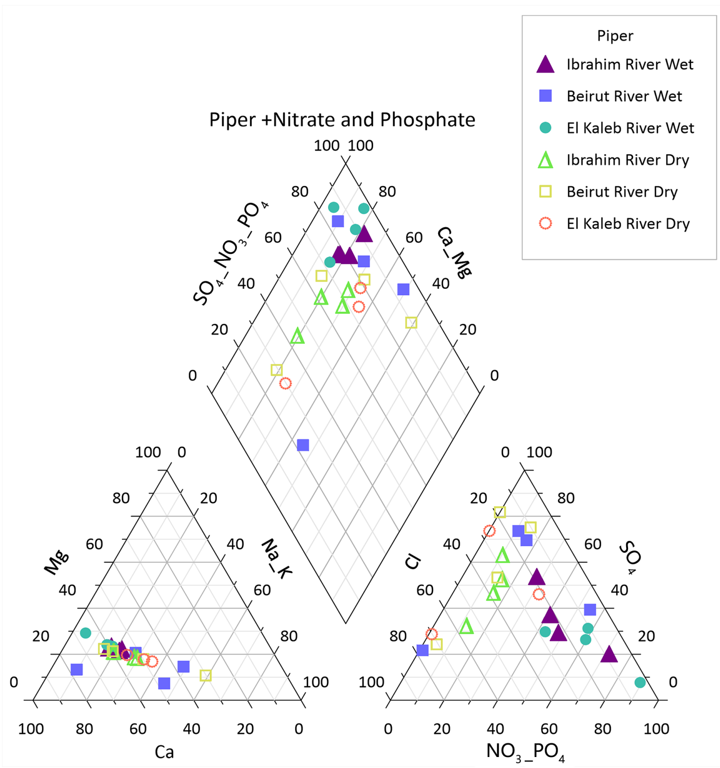

Figure 4. Non-bi-carbonate chemical facies of the surface waters of Beirut, Kaleb and Ibrahim in the dry and wet seasons.

region of Beirut, Kaleb and Ibrahim are of the nitrate-phosphate type during the wet sampling period. For the same period, the Beirut surface water has different anionic facies, which are sulfated types.

For the dry period, water samples are scattered in the anionic facies. The global facies indicate that the majority of these waters are of mixed type during the dry period. This could be a clear indication of the variability in surface water composition due to the impact of different anthropogenic inputs in the streams.

3.3. Behavior of Metals

Surface-water metallic component routing into the Mediterranean Sea is also studied to assess the impact of anthropogenic activities in high-populated Mediterranean subbasins (**Figure 5**). The concentrations of the studied total and dissolved metals (Zn, Pb, Cu, Cr and Cd) and DOC are shown for the three rivers Beirut, Kaleb and Ibrahim. To be able to compare the three rivers within the same scale, the DOC of Beirut and Kaleb was divided by 1000, that of the Ibrahim River was divided by 10, and the total cadmium concentration of the Ibrahim River was multiplied by 100. The DOC shows an increasing pattern in the three rivers from source to outlet, with the highest DOC in the Beirut River (**Figure 5(a)**), specifically at the outlet of the river, which was accompanied by increasing concentrations of total and dissolved zinc, copper and cadmium. An opposite pattern was observed for chromium, which showed a spatial decrease from the source to the outlet of the Beirut River, while Pb decreased between the source and site 2 and increased again at the outlet. It is clear that the Beirut River has pronounced concentrations of different metals, and this is obviously manifested in **Figure 6**, where the river is strongly correlated with all total and dissolved metals. Additionally, the DOC is strongly correlated with total and dissolved zinc, which are relatively more abundant in the course of this river.

When comparing the Kaleb River (**Figure 5(b)**) to the Beirut River, the chromium and copper elements clearly join the metal-increasing concentration pattern from source to outlet. **Figure 6** confirms that Kaleb River sites are strongly expressed by the increasing concentrations of chromium and dissolved copper. Zn is also enriched in water between the source at site 2 but decreased at the outlet. Similar to the Beirut River, the total lead shows a decrease with the increase in DOC. This pattern is coupled with a decrease in the concentration of dissolved Pb from the source to the outlet.

Finally, when comparing the Ibrahim River (**Figure 5(c)**) to Beirut and Kaleb, it is obviously shown that this river exhibits a different feature where all metals, except chromium, show an inverse variability between the total and dissolved form of each metal. **Figure 6** shows that Ibrahim sites are anti-correlated with total and dissolved chromium and, to a lesser extent, anti-correlated with dissolved copper. In **Figure 5(c)**, the decrease in the concentration of the total metal fraction is coupled with the increase in the concentration of the dissolved fraction and vice versa. This variability seems to be due to low binding properties with metals (as for organic and inorganic complexes), as the Ibrahim River has the lowest alkalinity and DOC from the source to the outlet.

The total and dissolved metal concentrations in the three rivers are clearly affected by urbanization where Beirut River (highly impacted by urbanization) showed high lead and zinc concentrations whereas Kaleb showed high lead and chromium concentrations.

4. Discussion

The water typology of the three rivers indicates the presence of organic and inorganic complexing potentials that subsequently influence the speciation and behavior of metallic elements at a given pH.

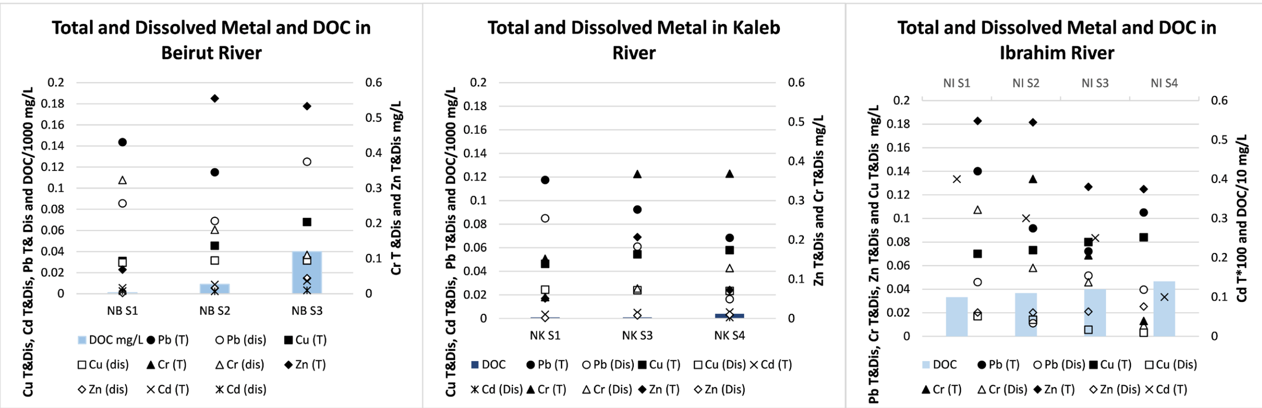

Figure 5. Total and dissolved metal (Cu, Zn, Pb, Cr and Cd) concentration (mg/L) and DOC (mg/L) at all sites of the three studied rivers: Beirut River, Kaleb River, and Ibrahim River in the dry season.

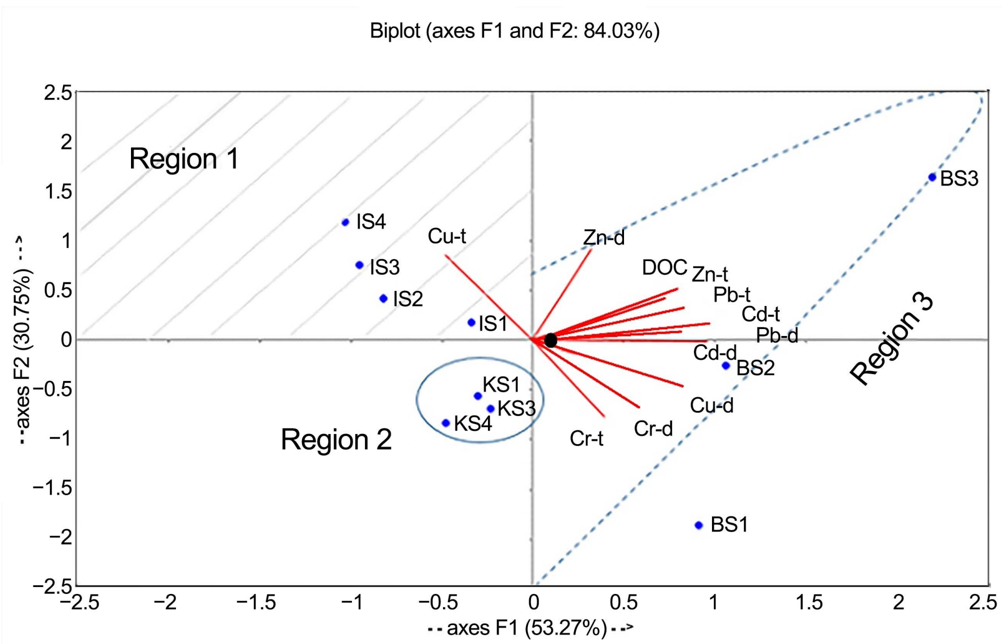

Figure 6. Principle component analysis (PCA) of total and dissolved metals (Cu, Zn, Pb, Cr and Cd) and DOC in the three Lebanese rivers Beirut, Kaleb and Ibrahim in the dry season.

Biplot analysis separated the results into 3 regions (**Figure 6**). Total copper, dispatched in Region 1, shows its own specific variability in all three rivers. In fact, it is the only element with quasi-increasing variability in the river course from upstream to downstream. The different water types (nitrate-phosphate type for both Kaleb and Ibrahim versus sulfate type for the Beirut River course) do not affect the behavior of total Cu in water. It is well known that Cu undergoes solvation in water to form copper hydrate, which is a stable form in addition to the other forms of copper chemical species at pH 7 due to inorganic complexation (mainly copper carbonate [44]-[53].

All other elements constitute other end-members showing a partition between their affinities for organic and/or inorganic complexation. The total forms of Zn and Pb exhibit stronger chemical speciation with organic complexation specifically in the Beirut River (**Figure 6**). This is confirmed in **Figure 5(a)**, where Zn-t and Pb-t are the highest with DOC values. The decreasing order of stability for metal-organic matter complexes, Pb > Zn > Cd [54], helps to explain the alignment of the distribution of total metals with respect to the DOC parameter in region 3 of **Figure 6**. The high levels of zinc can be explained by anthropogenic activities that affect our sites by urban runoff, waste incineration and electrical industries [55]. It is also known that in almost neutral pH water rivers, 21% of zinc occurs in a sorbed form [5]. This can explain why the highest concentration of total zinc was observed in our samples. The high concentration of lead is correlated with anthropogenic sources such as automobile exhaust and electroplating [56].

The dissolved fraction of metals shows a different pattern from the total fraction (**Figure 6**). This behavior is highlighted in the Kaleb and Ibrahim streams, which are characterized by lower alkalinity and OM content compared to the Beirut River. Cr is the most abundant element in the Kaleb stream and the only element that has a different feature in the Ibrahim River. The dispatching of Cr behavior relative to other elements could be related to two reasons. The first is that both dissolved and total fractions in the Ibrahim River decrease in the same percentage from upstream to downstream, indicating that the particulate fraction is negligible. The second reason is related to prevailing inorganic complexation in water with any possible anionic ligand.

From the distribution of the three river courses in **Figure 6**, we can conclude that the chemical speciation of metals is dominated by inorganic complexation for Kaleb and Ibrahim. However, the formation of metal-OM complexes is prevalent in the Beirut River.

Population growth, combined with increased exploitation of water resources to meet urban, agricultural, and industrial needs, is highly manifested, especially in the capital city of Beirut compared to its northern suburbs [34]. Urbanization in Lebanon and specifically in the Beirut region has greatly exceeded the levels; thus, water resources are highly threatened due to noticeable pollution [57]. Currently, refugees and displaced persons account for approximately 30 percent of the Lebanese population, and their influx is estimated to have increased national water demand by 8 to 12 percent and the wastewater generation rate by 8 to 14 percent without any infrastructural adjustments [3]. This explains the high content of organic matter in sewage water that is directly disposed of in the course of the Beirut River. For this reason, the impact of organic matter is highly revealed in the Beirut River and shows preferable binding to the metals existing in this course.

5. Conclusion

Based on the geochemical and metal analysis, two behaviors of preferable metal complexation were deduced: metal with organic matter in the Beirut River and metal with inorganic species in the Kaleb and Ibrahim Rivers. This difference is attributed to the water composition that was severely affected by urbanization along the Beirut River, thus resulting in anthropogenic intervention that is rich in organic matter. The Beirut River was shown to be rich in sulfates that led to the leaching of calcium into water streams, unlike the Kaleb and Ibrahim Rivers, which were both rich in nitrates and phosphates in the wet season. This composition differed in the dry season where waters were of mixed types due to the impact of different anthropogenic activities and inputs into the stream. The flux of heavy metals into the Mediterranean Sea and the particulate concentration fraction of each calculated heavy metal were directly proportional. The flux for the sampling points located at the river outlet into the Mediterranean showed that tons of metals are disposed of yearly at Beirut (131 kg of Pb, 133 kg of Cr and 1531 kg of Zn), Kaleb (1515 kg of Cr and 770 kg of Cu) and Ibrahim (568 kg of Cr).

Statements and Declarations

All authors have read, understood, and have complied as applicable with the statement on "Ethical responsibilities of Authors" as found in the Instructions for Authors.

Conflicts of Interest

The authors declare that they have no conflicts of interest.

Funding Declaration

No funding was received to assist with the preparation of this manuscript. All authors certify that they have no affiliations with or involvement in any organization or entity with any financial interest or non-financial interest in the subject matter or materials discussed in this manuscript.

Author Contribution

All authors contributed equally and extensively to this work. Nour Abboud (N.A.), Elias Maatouk (E.M.) and Zeinab Matar (Z.M.) performed all the field work. E.M., Z.M. and Veronique Kazpard (V.K.) developed the analytical tools. N.A. analyzed the data and wrote the paper. E.M., Z.M. and V.K. jointly supervised the work. All authors discussed the results and implications and commented on the manuscript at all stages.

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Data Availability

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

Article Highlights

- The Ibrahim, Kaleb and Beirut watersheds are located in a semiarid region east of the Mediterranean Sea and are impacted by urban effluents and agricultural soil leachates that are considered calcium bicarbonate water types.
- The Beirut watershed, which is a sulfate type in the wet season, shows a preferable complexation behavior with organic matter, while the Kaleb and Ibrahim watersheds show a similar nitrate phosphate water type with a preferable complexation behavior with inorganic matter.
- Remarkable calcium concentration increases at the outlet of Beirut River reflecting the anthropogenic intervention that is accompanied by high sulfate concentration that leads to leaching of calcium into the water.

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