Surface water processes in coping with anthropogenic impact in a coastal Eastern Mediterranean region

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Research Article

Keywords: anions, cations, metals, DOC, complexation, coastal rivers, spatio-temporal variability

Posted Date: October 13th, 2023

DOI: https://doi.org/10.21203/rs.3.rs-3426582/v1

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Additional Declarations: No competing interests reported.
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 season from different sampling sites along the river from the source to the outlet that represent a gradient of increased urbanization. The spatio-temporal variability of the physiochemical properties, heavy metals (Zn, Pb, Cu, Cr and Cd) and organic matter (DOC) were statistically analyzed to better understand the contribution of point and non-point 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 Beirut River has a different behavioral characteristic where the water is of 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 specially copper that has a consistent behavior in both type of waters. This difference is attributed to the urbanization effect highly impacting Beirut River.

Highlights

- Ibrahim, Kaleb and Beirut watersheds are located in a semiarid region at the East of the Mediterranean Sea, impacted by urban effluents and agricultural soil leachates that are considered of a calcium bicarbonate water type
- Beirut watershed which is of a sulfate type in the wet season shows a preferable complexation behavior with organic matter while 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’s accompanied by high sulfate concentration that leads to leaching of calcium into the water

Introduction

Anthropogenic activities are increasingly modifying nutrient cycles in freshwater bodies. Lebanon generated a volume that varies between 275 and 328 Mm³ of wastewater of which 80% was domestic and 20% industrial (Eid-Sabbagh et al., 2022). Only 8% of 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 in rivers, streams and cesspits (Houri and El Jeblawi, 2007). Add to that, overexploitation of water resources due to excessive drilling and pumping, is mainly concentrated in the coastal areas, and saltwater intrusion affects a large stretch of the aquifers along the
Lebanese coastline (UNDP, 2021). 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 (Khadra and Stuyfzand, 2014).

On the other hand, rivers become enriched in metal after leaching from agricultural land that is affected by use of fertilizers and discharging of industrial wastewater. The behavior of these metals are highly affected by pH and organic content where their adsorption and bioavailability differ (Gundersen and Steinnes, 2003). Also alkalinity may have an effect on the behavior of metals where major cations such as calcium might compete with metals (Verweij et al., 1992). Also, the pH can affect the bioavailability of metals in freshwater. So as the pH decreases, the free metal ion concentration might increase which lead to metal desorption from colloidal and particulate matter and also to dissociation of some inorganic and organic metal complexes (Galceran et al., 2021). Furthermore, organic matter OM is well known for its ability to interact with metallic micropollutants affecting their transport and their fate in the aquatic environment (Buffle et al. 1990; Soares-Pereira 2016; Chávez-Mejía et al. 2019), but also their bioavailability, their biodegradation, and their toxicity towards organisms (Tessier and Turner 1995; Matar et al. 2015; Wang et al. 2020). The metal affinities to anthropogenic OM is larger than natural OM which is relevant for environmental conditions. Organic Matter quality and quantity have almost the same impact on trace metal mobilization (Baken et al., 2011). Based on Chang 2005, when comparing Zn complexation properties of natural OM from different surface waters, they found that at same pH and ionic strength, natural OM from different surface water sources are similar in complexation to Zn with 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 (Chang, 2005). According to (Shafer et al., 1999), 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. Concerning copper, it has a high affinity for binding to OM (Matar et al., 2015). When studying Parisian aquatic system (Pernet-Coudrier, 2011), they have 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 concentration 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. Whereas 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. Besides, in surface water and ground water, lead carbonate complexes will dominate the lead hydroxy species formed in 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 of free lead concentration and the lability of lead complexes (Pernet-Coudrier et al., 2011). As for Chromium, its adsorption and complex formation are highly dependent on the presence of natural organic ligands such as fulvic acids and on pH that affects the oxidation state of chromium (Andjelkovic et al., 2012).
This work will focus on the hydrogeochemical composition of coastal rivers in Eastern Mediterranean region to show the demographic impact. Spatial variability of organic and metallic micropollutants will be highlighted from upstream (source) to downstream (Mediterranean Sea) of three adjacent rivers: Ibrahim River, Kaleb River (both located north to the capital city) and Beirut River. These rivers are located in three cities in coastal part of Mount Lebanon (Lebanon Water Project, 2019). Many sites along each river have been analyzed to be able to compare and understand the difference of pollution impact, nature and effect of urban discharges on water quality (a) on 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.

Materials and Methods

1.1. Study Area

Along with Lebanon's small surface (10,452 km²) 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: 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) (Table 1a). The studies showed that human activities have a great impact on water resources in this area quantitatively and qualitatively. A summary of water chemistry along Ibrahim River is shown in Table 1a.

- 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 are described in Table 1b.

- 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 as it is shown in Table 1c.

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. The third site IS3 was taken at Jannah Dam (800m) and the fourth site IS4 at the outlet of the river. 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-Name (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. 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. 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). The second site BS2 was at Kanater Zbeidy (150m 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 is joining the main river creating an additional flow. The calculation of the flow at this site was done as by (Maatouk, 2014). Two sampling campaigns were conducted during two seasons: the wet season in May 2020 and the dry season in October 2021.


Table 1
Nature of activities at the three watersheds and the elements emitted to water and soil based on literature
(a) Ibrahim River (b) Kaleb River and (c) Beirut River

<table>
<thead>
<tr>
<th>Rivers</th>
<th>Surface (Km²)</th>
<th>Length (Km)</th>
<th>Nature of Activity in the Basin</th>
<th>Elements released in water based on bibliography</th>
<th>Elements released in sediments based on bibliography</th>
</tr>
</thead>
<tbody>
<tr>
<td>a- Ibrahim</td>
<td>330</td>
<td>30</td>
<td>Agricultural Land</td>
<td>nitrogenous fertilizers and chlorinated pesticides (Daou et al., 2013), Downstream contamination with nitrates (El Samrani et al., 2008)</td>
<td>Fe, Mn, Zn and Pb (El Samrani et al., 2008)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Industrial facilities (Leung, 2001)</td>
<td>Caries high concentration of Cd and Hg to the sea (Korfali, 2005).</td>
<td>Cd, Cr, Cu, Ni, Pb and Zn (Khawli, 2002)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Heritage Sites (Saab et al., 2007)</td>
<td>Solid effluents (Saab et al., 2007), Domestic wastewater (Daou et al., 2013)</td>
<td>Fe (Jurdi et al., 2002)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Residential Areas</td>
<td>Domestic and waste water discharge</td>
<td></td>
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<tr>
<td></td>
<td></td>
<td></td>
<td>Vehicle Exhaust Fume</td>
<td>High Pb deposition due to leaded petrol usage (Jurdi et al., 2002)</td>
<td></td>
</tr>
<tr>
<td>b-Kaleb</td>
<td>257</td>
<td>31</td>
<td>Urban Activities</td>
<td>Domestic and waste water discharge</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Touristic sites</td>
<td>Solid wastes</td>
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<td></td>
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<td></td>
<td>Agricultural activities</td>
<td>Nitrogenous fertilizers and chlorinated pesticides (Daou et al., 2013)</td>
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<td></td>
<td>Downstream contamination with nitrates (El Samrani et al., 2008)</td>
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<tr>
<td></td>
<td></td>
<td></td>
<td>Animal farms and quarries</td>
<td>Organic waste water discharge (Joanna et al., 2018)</td>
<td></td>
</tr>
<tr>
<td>c-Beirut</td>
<td>217</td>
<td>25</td>
<td>Urbanization and high population (Shaban, 2021)</td>
<td>Domestic and wastewater discharges</td>
<td>Rich in Cd, Pb and Hg (Nakhle, 2003)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Industrial activities</td>
<td>Chemical effluent, solid waste from construction material and fabrication (Stephenson, 1997)</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Agricultural activities (Frem, 2009)</td>
<td>Nitrate and phosphates</td>
<td></td>
</tr>
</tbody>
</table>
### 1.2. Physico-chemical properties

The parameters measured for each water sample are the following: major cations (K$^+$, Ca$^{2+}$, Na$^+$), major anions ($\text{H}_2\text{PO}_4^-$, 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, sulphate, nitrate, and phosphate were analyzed as stated by the standard guidelines of water sampling and physicochemical parameters evaluation (Reasoner 2004). Mg$^{2+}$ and Ca$^{2+}$ were analyzed by atomic absorption spectroscopy (AAS-Rayleigh WFX-210; Shimadzu, China); while a 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 the acidification of these samples at pH. using 1% HNO$_3$ (grade). Cl$^-$, NO$_3^-$, SO$_4^{2-}$, and HPO$_4^{2-}$ were measured in no acidified water samples by using ion chromatography technique (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.L$^{-1}$).

### 1.3. 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 is complete, the sample is filtered using a Teflon filter (PTFE) of 0.45µm. To determine the concentration of the dissolved fraction [D], a similar protocol is applied by filtration on 0.45µm cellulose acetate membrane to remove the total suspended solids. The analysis of heavy metals is performed on the filtrate by AAS. Finally, the particulate fraction of heavy metals [P] was determined by difference between total and dissolved metals noted respectively [T] and [D]. The heavy metals content is also determined for each fraction in mg/kg, according to the formula below. For the particulate fraction [P*], i.e:

\[ [P^*] \text{(mg/kg)} = \{10^3 \times [P \text{ (µg /l)}]\} / [TSS] \text{(mg/L)} \text{(Maatouk, 2014)}. \]

The flux of heavy metals into the Mediterranean Sea is calculated for the sampling points located at the river's outlet into the Mediterranean according to the formula: Flux (kg/year) = \( Q \text{ (m}^3\text{/year)} \times [P] \text{ (kg/m}^3\) \) with Q is the flow at the studied site and P is the particulate concentration fraction of each heavy metal.

Results

2.1. Calcium Flux

The assessment of naturally weathered limestone outcrops in the study area and the resultant input into the Mediterranean Sea is referred to 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 the carbonate rocks (Holland, 2005; Gaillard et al., 1999; Tipper et al., 2010). 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 (Shaban, 2020). Calcium and carbonate alkalinity shows a similar behavior along the three rivers which indicates that they are controlled by almost identical factors as of carbonate mineral weathering which gives \( \text{CaCO}_3 \) 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 (Fig. 2) except for Ibrahim River where Calcium concentration didn't vary much throughout its pathway. It is known that Ibrahim River has Ca\(^{2+}\) in both sources Afqa and Roueiss and the seasonal comparison shows that the samples taken in dry season are Ca\(^{2+}\) depleted (Hanna et al., 2018). This aligns with the results of our study where the concentration of calcium is lower at these sites in the dry season. In the other two rivers, Beirut and Kaleb, calcium concentration at the outlet was almost three times and two times that at the source of Beirut River and Kaleb River respectively. Also, there was an important difference between the outlet site and the site just before it specifically for Beirut River (Fig. 2) where calcium concentration was 50.7 mg/L and 185 mg/L at BS2 and BS3 respectively.

These values shows the intervention of anthropogenic effect at these sites and the impact of human activities at the lower part of the river. Moreover, at Beirut River, the high concentration of calcium at the outlet was accompanied by a very high concentration of sulfate (215mg/L). According to Weyhenmeyer
et al., 2019, sulfate can lead to a quickened calcium leaching from soils into the water. This also explains the obvious perturbation at the outlets and specifically at Beirut.

2.2. River water chemical facies

The three rivers are studied for their cationic and anionic chemical facies (Fig. 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 bicarbonate nature. The three rivers are calcium bi/carbonate type. This hydrochemical composition reflects the calcareous geological nature of the sampling areas (Nader, 2014; Basson and Edgell, 1971). Moreover, the mean pH values in both season is around 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 the nitrate and phosphate components on the anionic composition of the water (Fig. 4). The cationic parameters being unchanged, the cationic facies in Fig. 4 remains the same as the previous one. However, the anionic facies shows a separation of the typology according to the sampling periods (dry and wet). The waters at the North region of Beirut, Kaleb and Ibrahim, are of the nitrate-phosphate type at the wet sampling period. For the same period, Beirut surface water has different anionic facies which is sulfated type.

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 to the streams.

2.3. 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 sub-basins (Fig. 5). The concentration 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 between the three rivers within the same scale, the DOC of Beirut and Kaleb was divided by 1000 and that of Ibrahim River was divided by 10 and total cadmium concentration of Ibrahim River was multiplied by 100. The DOC shows an increasing pattern in the three rivers from source to outlet with the highest DOC at Beirut River (Fig. 5a) specifically at the outlet of the river which was accompanied with an increasing concentration of total and dissolved zinc, copper and cadmium. An opposite pattern was observed for chromium that showed a spacial decrease from the source to the outlet of Beirut river while Pb decreased between the source and site 2 and reincreased at the outlet. It is clear that Beirut River has pronounced concentration of different metals
and this is obviously manifested in Fig. 6 where the river is strongly correlated with all total and dissolved metals. Also, the DOC is strongly correlated to total and dissolved zinc which are relatively more abundant in the course of this river.

When comparing Kaleb River (Fig. 5b) to 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. Similarly to Beirut River, the total lead shows a decrease with the increase of DOC. This pattern is coupled with a decrease in the concentration of dissolved Pb from the source to the outlet.

Finally, when comparing Ibrahim River (Fig. 5c) 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 in a lesser extent anti-correlated with dissolved copper. In Fig. 5c, the decrease in the concentration of the total metal fraction is coupled with the increase of concentration of the dissolved fraction and vice versa. This variability seems to be addressed to low binding properties with metals (as for organic and inorganic complexes) as Ibrahim river has lowest alcalinity and DOC from the source to the outlet.

Discussion

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

Biplot analysis separates the results into 3 regions (Fig. 6). Total copper, dispatched in region 1, shows its own specific variability in all three rivers. In fact, it is the only element with a 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 Beirut river course) do not affect the behavior of total Cu in water. It is well known that Cu undergoes a phenomenon of 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 (Byrne and Miller, 1985; Conry, 2005; Constantino et al., 2017; Gulens et al., 1984; Klučáková, 2012; Rader et al., 2019; Shank et al., 2004; Sunda and Hanson, 1979; Van Den Berg, 1984).

All other elements constitute another end-members showing a partition between their affinity 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 (Fig. 6). This is confirmed in Fig. 5a, 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 (Dykyjová, 1983; Förstner and Wittman, 1983), helps to explain the alignment of the distribution of total metals with respect to the DOC parameter in region 3 of Fig. 6. The high levels of zinc can be explained by the anthropogenic activities that affect our sites either by urban runoffs, waste
incineration and electrical industries (Andarani et al., 2020). It also known that in near neutral pH water rivers, 21% of zinc occur in a sorbed form (Gundersen and Steinnes, 2003). This can explain the highest concentration for total zinc in our samples. The high concentration of lead is correlated to anthropogenic source such as automobile exhaust and electroplating (Ahmed et al., 2020).

The dissolved fraction of metals shows a different pattem from the total fraction (Fig. 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 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 Ibrahim River decrease in the same percentage from upstream to downstream, indicating that the particulate fraction is negligible. The second reason is related to a prevailing inorganic complexation in water with any possible anionic ligand.

From the distribution of the three rivers courses in Fig. 6, we can conclude that the chemical speciation of metals is dominated by inorganic complexation for Kaleb and Ibrahim. Whereas 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 specially in the capital city of Beirut compared to its northern suburbs (Maatouk, 2014). Urbanization in Lebanon and specifically in Beirut region has highly exceeded the levels thus water resources are highly threatened due to noticeable pollution (Khatib et al., 2018). 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 wastewater generation rate by 8 to 14 percent without any infrastructural adjustments (UNDP, 2021). This explains the high content of organic matter of sewage water that is directly disposed to the course of Beirut River. For this reason, the impact of organic matter is highly revealed in Beirut River and shows a preferable binding to the metals existing in this course.

**Conclusion**

Based on the geochemical and metal analysis, two behaviors of preferable metal complexation were deduced: metal with organic matter at Beirut River and metal with inorganic species at Kaleb and Ibrahim River. This difference is attributed to the water composition that was severely affected by urbanization along Beirut River and thus resulting in anthropogenic intervention that is rich in organic matter. Beirut River was shown to be rich in sulfates that leads to leaching of calcium into water streams, unlike Kaleb and Ibrahim River where they both were 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 heavy metal that were calculated were directly proportional. The flux for the sampling points located at the river's outlet into the Mediterranean showed
that tons of metals are disposed 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).

Declarations

Acknowledgment

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.

Conflict of Interest

The authors declare that they have no conflict of interest.

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Figures
Figure 1

(a) Ibrahim River Watershed (b) Kaleb River Watershed (c) Beirut River Watershed
Figure 2

Calcium concentration in mg/L at all sites of Ibrahim, Kaleb and Beirut Rivers in dry and wet season.
Figure 3

Chemical facies of the surface waters of Beirut, Kaleb and Ibrahim Rivers in dry and wet season
Figure 4

Non bi-carbonate chemical facies of the surface waters of Beirut, Kaleb and Ibrahim in dry and wet season
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: a- Beirut River b- Kaleb River c- Ibrahim River in the dry season

Biplot (axes F1 and F2: 84.03 %)

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