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Heavy Metals Content in Water and Sediments in the Upper Litani River Basin, Lebanon

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Abstract

Surface water quality is largely influenced by both natural processes and anthropogenic inputs. This study involves the characterization of the concentration of heavy metals of Cd, Cr, Cu, Fe, Mn, Ni, Pb, and Zn, and the sources of pollution in water and sediment of the Upper Litani River Basin (ULRB) in Lebanon. The investigation was performed during three seasons of rainy, mid-rainy spring and wet periods for two years during different flow rates. Sediments were characterized by a set of chemical analyses, cation exchange capacity (CEC), mineralogy of the sediments, X-ray diffraction (XRD), and Fourier transformed infrared spectroscopy (FTIR). To assess metal contamination in sediment, Consensus-Based Sediment Quality Guidelines of Wisconsin (CBSQG) were applied. The metals contamination in the sediments was also evaluated by contamination factor (*Cf*). The test results showed that the effect of seasonal variations was significant in the Upper Litani River Basin. Principal Compound Analysis (PCA) and Pearson's correlation were also performed in this study to compare and determine the correlation between metals in water and sediments. The concentrations of Pb, Cd, Cu, Cr and Zn in all sediment samples are above the norms in winter, while Fe was increased in summer. The results showed that the importance of monitoring of changes of heavy metals values and physico-chemical characterization of different parameters could represent the possibility of a comprehensive assessment of negative pressures on the water and soil ecosystem of Litani River Basin during different seasons.

1. Introduction

The solid particulate materials that are included in water of ponds, lakes, springs, streams, and other aquatic systems are called sediments (Kabata-Pendias & Pendias, 1992; ASTM, 2001). Sediments in surface water are most vulnerable to various pollution aspects including heavy metals due to their ease of access for the disposal of urban and industrial processes, which occupy untreated waste water, municipal sewage effluent and surface run-off. Toxicity appears after exceeding level of indispensability (Kabata-Pendias & Pendias, 1992; Radha et al., 1997; Li et al., 2004; Li, 2000; Casas et al., 2003; Yang et al., 2007).

The mineralogical properties of sediments reflect the geological history of weathering, erosion, transporting and sorting process. Many studies showed that the investigation of sediments by the absorption of infrared rays has attracted considerable interest (Fysh & Fredericks, 1983; Davies & Abowei, 2009). Heavy metals are among the most persistent of pollutants in the ecosystem such as water and sediments because of their resistance to decomposition under natural conditions (e.g. changing climate). Metals have low solubility in water, get adsorbed and accumulated on bottom sediments (Jain et al., 2008). In fact, the bioavailability of heavy metals in soil depends on many factors such as pH, cation exchange capacity, and the type of the metals. In addition, the different mineralogical composition between the sources affects the mobility of heavy metals (Filipinski & Grupe, 1990), and consequently the availability of heavy metals to soil micro-organisms (Giller et al., 1998).

The study of river sediments is becoming more important internationally and in Lebanon, there are 14 rivers, but there are few data concerning the concentration of heavy metals in the sediment of the river (Korfali & Davies, 2005; Nehme et al., 2012; Diaba et al., 2014; Nehmeh et al., 2019; Nehmeh et al., 2020; Darwish et al., 2021). The Litani River is the longest river in Lebanon, with a length of 172 km and largest basin area of about 2180 km^2. The river basin extends between latitudes: 33˚50'N and 34˚50'N, and longitudes 35˚15'E and 36˚25'E. Geologically, the Litani River Basin (LRB) was formed due to the pre-existence of the median depression, which diverted water streams to join and flow together. It is located between the Mont Lebanon and the Anti-Lebanon mountain chains. This perennial river originates primarily from Al Oulaik Spring of the Bekaa Plain, and flows southward parallel to the two adjacent mountain chains. It deviates to the west in a deep V-shaped valley southwest of Marjaayoun, and then to discharge finally into the Mediterranean Sea at Qasmieh area, 7 km north of Tyr (Sour).

The LRB can be hydrologically classified into two major units, the Upper and

Lower units, that are separated by the Qar'aoun Reservoir, an artificial reservoir constructed in 1956. Therefore, this study focuses on the Upper Litani River Basin (ULRB). The two adjacent mountain chains of the ULRB are geologically composed largely of carbonate rocks, which are dated to the Jurassic, Cretaceous, Tertiary and Quaternary periods. Most of these rocks are of karstified, dominated by fractured limestone and dolomitic limestone. Most of the lithologies exhibit high permeability and are subjected to erosion caused by flowing water (Shaban & Hamzé, 2017; Nehme et al., 2020). The river supplies water to many domestic and agricultural purposes in the ULRB.

Hence, the main objective of this study is to: 1) Analyze the mineralogical and geochemical characteristics of the sediments and water of the ULRB; 2) Calculate the contamination Factor (C*f*) and the degree of contamination (Cd) in order to know the relative distribution and accumulation of major metals in sediment contamination; and 3) Assess the influence of the mineralogical, geochemical of the sediment and water using multivariate statistical analysis.

2. Materials and Methods

2.1. Sampling

Seven sampling sites were selected along the ULRB. **Figure 1** shows the geographic distribution of these sites. The characteristics for each sampling site can be described as follows:

Site 1: Oulaik spring (Roads with high traffic density; farms and industry for dairy products).

Site 2: Houch El Rafika village.

Site 3: Bedanyl village (Intensify agricultural land: potatoes and wheat; farms; industries for slaughter of poultry; coffee shops and tourist activities).

Site 4: Bednayl 1 village (Electricity power station; water industry above 400 m).

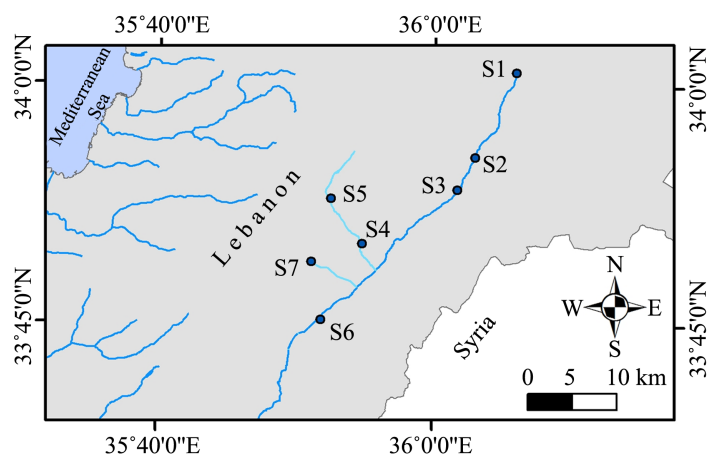Site 5: Berdawnil 2 (Industries; tourist activities and restaurant; in front Lebanese France hospital).

Figure 1. Location of the selected samples at the ULRB/Lebanon.

Site 6: Dair Zanoun village (End of intensive agricultural land; potatoes and wheat; farm; road with high traffic density (Lebanon-Damascus); paper mills; tanneries).

Site 7: Massabiki village (Road with intensive traffic density; Massabiki hotels).

The selection of these sites was based, firstly, on the practicability of collecting sediments; especially accessibility, and secondly their location with respect to typical activities of industries like dairy and poultry farms, tanneries, paper mills, wheat and potatoes, tourist and high vehicle movements located around the ULRB and their effect in the reject direct of pollutants.

Sediments were collected during the rainy (February), mid rainy (May) and dry seasons (September) over two years. During winter the ULRB carries huge loads of suspended sediments which result turbid water, whereas in the dry season the river runs off with low energy and least turbidity appears. During this study the average annual discharge of the ULRB is 17.19 m^3/sec; while the average discharge for the wet season is 22.29 m^3/sec and that of the dry season is 8.81 m^3/sec (Shaban & Hamze, 2017).

Approximately 2 kg of sediment were collected from each of the sampling points at the sediment-water interface (i.e. surface river bed sediments) using a polyethylene bags. Water samples were collected simultaneously with sediments at each sampling site using two 1 L polyethylene bottles. Each bottle was supplied by 2% of nitric acid to acidified (pH < 2) and stored in portable coolers before transport them to the laboratory.

The pH, Electrical Conductivity (EC) and Total Dissolved Solids (TDS) were determined in-situ, and water samples subsequently filtered through 0.45 μm membrane in the laboratory. Sediment samples were dried at room temperature and sieved; where the sediment size less than <65 μm size was retained.

2.2. Sediment Total Metal Digestion

The concentrations of Pb, Cd, Fe, Mn, Cr, Cu, and Zn were measured using the Inductively Coupled Plasma-Optical Emission Spectrometry (ICP-OES) with Ultra Sonic Nebulizer (USN) (Model: Perkin Elmer Optima 3000). The samples were filtered by filtration system through membrane filter with pore size 0.45 μm before the analysis using Standard Methods (APHA, 1992). Sediment samples were digested using microwave digestion techniques as reported by Littlejohn et al. (1991) in which 0.5 mg of sample was placed in Teflon vessel with 5 ml HNO_3 (65%), 2 ml HF (40%) and 2 ml H_2O_2 (30%) by using Microwave digestion system (model: MILESTONE mls-1200 mega). An aliquot of the filtration of the samples was taken (i.e. about 100 ml). Digestion solutions were measured for the total heavy metals using ICP-OES (APHA, 1995). Digestion extracts were used to analyze the total metal concentrations by Atomic Absorption Spectrophotometer (AAS). Blanks containing all the components except sediments were analyzed to determine background interferences. All measurements were performed in triplicate and average values were reported.

2.3. Sediment pH, TDS and EC Analysis

Approximately 10 g of air-dried sediments was suspended in 50 mL of deionized water and manually agitated for 5 min. The suspension was allowed to rest for about 1 hour with occasional shaking until the pH, TDS and EC were measured.

2.4. CEC, XRD and FTIR Measurements

Cation Exchange Capacity (CEC) was measured after it was exchanged with cobalt hexamine ($Co(NH_3)_6Cl_3$) and dosage of its residual concentration in the equilibrium solution (Morel, 1957; Mantin & Glaeser, 1969). About 1.5 g of sample was dispersed and shaken during two hours at 30°C in 30 mL of cobaltihexamine solution (16.6×10^{-3} mol/L). Samples were then centrifuged for one hour at 46.251 g. Supernatants analyzed on a UV–Visible Spectrophotometer, using cobalt absorption band at 472 nm to derive CEC from residual concentration in cobaltihexamine. Measurements were always carried out in duplicate to check for further reproducibility.

Sediment samples were analyzed by X-Ray Diffraction (XRD) using 1 g of randomly oriented sediment powder, that put on a rotating sample holder and leveled with a glass slice to obtain a flat surface. XRD was also acquired using zincite (ZnO) as internal standard. In this latter case, samples were first mixed with 0.111 g of ZnO and ground in an agate mortar for 5 minutes. XRD patterns were collected on a D8 Advance Bruker AXS Diffractometer equipped with a Lynx Eye fast linear detector using Cobalt K radiation (k = 0.17903 nm) at 35 kV and 45 mA. Intensities were recorded from 3° to 64° with a 0.035° step using a 3-second counting time per step. In the presence of standard, intensity was recorded from 4° to 80° with a 0.02° step using a 3-second counting time per step. Data reduction and analysis were performed with the *EVA* software (DIFFRAC plus from Bruker) and diffraction peaks were determined by comparison with powder diffraction files.

FTIR spectra were collected on bulk samples powder mixed with KBr ($KbrO_3$) as a transparent matrix. Diffuse reflectance FTIR were recorded on a Bruker IFS-55 Spectrometer in the range from 4000 to 600 cm^{-1} with a resolution of 2 cm^{-1}. Spectra were obtained from the average of 200 scans collected during 2 minutes. Data reduction and analysis were performed using *OPUS* program from Farmer (1974), Marel and Beutelspacher (1976) and Russell and Fraser (1994).

2.5. Statistical Analysis of Sediments

Multivariate statistical analyses, including Pearson's Correlation Analysis (PCA), Cluster Analysis (CA) and Factor Analysis (FA) were performed in this study to reflect the degree of dispersion distribution of the different metals. PCA was carried out by using SPSS16 of 2007. CA is a multivariate technique, whose primary purpose is to classify the objects of the system into categories or clusters based on their similarities, while, FA was carried out to assess the relationship between

3. Results and Discussion

3.1. Concentration of Heavy Metals in Water

The resulted pH values of the ULRB range between 7.7 and 8.5, which is due to the intensive agricultural activities and the excessive use of fertilizers such as ammonium phosphates. The conductivity and total dissolved solids were found within the permissible limits: 384 - 1484 μs/cm and 159 - 321 mg/l, but only in sites S3 and S6 (1688 and 1780 μs/cm), were high and this could be due to the presence of intensives industrials activities that often release wastes directly into the river without treatment. The total concentration and the mean values of element concentration in the water samples of the three seasons for two years are shown in Table 1.

The heavy metals were differently distributed in all the selected sites, and this due to the presence of different aspects of activities such as industries, intensify agriculture urbanism and tourist, and thus are mainly responsible for elevated levels of the measured elements in ULRB. Mean concentration of heavy metals were ranging as follows: Mn: 0.49 - 1.17 mg/l; Fe: 0.23 - 1.78 mg/l; Zn: 0.28 - 0.54 mg/l; Pb: 0.11 - 0.91 mg/l; Cr: 0.03 - 0.54 mg/l; Cd: 0.04 - 0.05 mg/l; Cu: 0.10 - 0.20 mg/l; and this allowing to arrange the metals from higher to lower mean content in this area as: Mn > Fe > Zn > Pb > Cr > Cd > Cu.

Figure 2 shows that metals concentration was varied between different seasons. Thus, Pb, Mn, Cu and Cr were high in concentration in dry season (class 3). Fe and Cd, were important in rainy season (class 1), while the Zn was observed in high concentration in mid rainy (class 2).
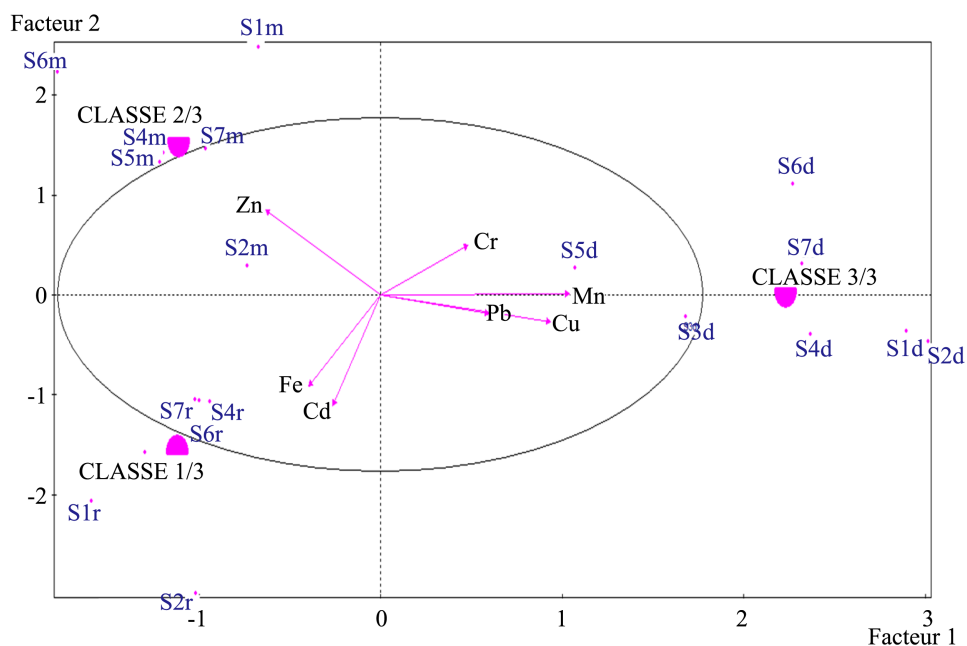

Figure 2. Seasonal distribution of heavy metals in water of ULRB.

Table 1. Concentration of heavy metals in water samples of ULRB.

Heavy Metals in water mg/l	Season	S1	S2	S3	S4	S5	S6	S7	Norms (WHO, 2006)
Pb	Rainy (r)	0.101	0.762	0.05	0.048	0.05	0.11	0.09	
	Mid rainy (m)	0.145	0.953	0.15	0.09	0.09	0.13	0.12	0.01
	Dry (d)	0.43	1.02	0.30	0. 45	0.21	0.43	0.78	
	Mean	0.22	0.91	0.16	0.069	0.11	0.22	0.33	
Cd	Rainy (r)	0.1	0.1	0.1	0.1	0.1	0.1	0.1	
	Mid rainy (m)	0.017	0.081	0.009	0.016	0.016	0.01	0.01	0.003
	Dry (d)	0.051	0.045	0. 034	0.035	0.025	0.02	0.035	
	Mean	0.05	0.07	0.05	0.05	0.04	0.04	0.04	
Fe	Rainy (r)	5	7	2.9	0.7	1	1	1	
	Mid rainy (m)	0.315	0.007	0.009	0.016	0.01	0.01	0.01	<0.3
	Dry (d)	0.04	0	0.03	0	0	0.01	0	
	Mean	1.78	2.33	0.98	0.23	0.33	0.34	0.33	
Mn	Rainy (r)	0	0	0	0	0	0	0	
	Mid rainy (m)	0.02	0.09	0.1	0.06	0	0.01	0.02	<0.05
	Dry (d)	3.49	2.32	2.43	1.62	1.47	2.06	2.15	
	Mean	1.17	0.80	0.84	0.56	0.49	0.69	0.72	
Cr	Rainy (r)	0.80	0.1	0.80	0.1	0.1	0.1	0.1	
	Mid rainy (m)	0.84	0.04	0.84	0.04	0.005	0.00	0.01	<0.05
	Dry (d)	0.299	0.309	0.22	0.044	0.19	1.44	0.73	
	Mean	0.54	0.12	0.10	0.03	0.07	0.48	0.25	
Cu	Rainy (r)	0.02	0.02	0.02	0.02	0.02	0.02	0.02	
	Mid rainy (m)	0.041	0.059	0.02	0.068	0.06	0.05	0.11	1
	Dry (d)	0.299	0.309	0.22	0.44	0.19	0.17	0.18	
	Mean	0.14	0.15	0.11	0.20	0.12	0.10	0.13	
Zn	Rainy (r)	0.15	0.2	0.2	0.1	0.1	0.2	0.2	
	Mid rainy (m)	0.11	0.976	0.68	0.761	0.70	1.34	0.78	5
	Dry (d)	0.20	0.029	0.10	0.053	0.04	0.10	0.06	
	Mean	0.43	0.40	0.32	0.30	0.28	0.54	0.34	
pH	Mean	7.8	8.2	8.4	7.7	7.8	8.5	8.01	6.5 - 8.5
EC	Mean	345	1134	923	319	574	1484	860	<500
TDS	Mean	171	687	456	159	273	884	520	Max. 1500 μs/cm

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According to Suresh et al. (2011), if the correlation coefficient between the metals is high, then metals have common sources, mutual dependence and identical behavior during their transportation. The absence of correlation among the other metals suggests that the contents of these metals are not controlled by a single factor during three seasons. However, it could be controlled by a combination of geochemical support phases and their mixed associations. In the present study, Pearson's Correlation Coefficient (PCC), matrix among the selected heavy metals is shown in Table 2. The highly significant positive correlation (r = 0.612) between the concentrations of Fe and Cd suggests that the association of the two elements originates from a common source of input, and also during transportation or deposition processes and this also confirm with what present in Figure 2.

Significant positive correlations between the contaminants Mn and Cu (r = 0.791), indicates the same source of input. Figure 2 confirms that these metals are associated and concentrated in the dry season.

The concentrations of Zn during the winter closure period were lower than those after the mid rainy period (Table 1). This is attributed to the increased consumption of this element by the others compound present in water. The negative correlation between Cu and Zn concentrations ($r = -0.617$) it could be a result of precipitation of the elements as hydrous metal oxides (El-Sayed & El-Sayed, 1980), whereas the concentrations of Zn increase in mid rainy season and Cu more concentrated during the winter closure period. The major sources of Zn are the liquid and solid domestic and municipal wastes followed by dumping and atmospheric deposition (Issa et al., 1996).

The relationship between EC and TDS varies with the concentration of salts in the water and the proportions of various present salts, while the correlation between TDS and EC (r = 0 .988) was positive and significant.

Table 2. Correlation matrix of heavy metals in water of the ULRB.

	Pb	Cd	Fe	Mn	Cu	Cr	Zn	pH	TDS	EC
Pb	1									
Cd	0.035	1								
Fe	0.073	0.612*	1							
Mn	0.422	−0.335	−0.339	1						
Cu	0.021	−0.137	−0.202	0.791**	1					
Cr	0.028	−0.330	−0.233	0.379	0.079	1				
Zn	−0.119	−0.387	−0.19	−0.542*	−0.617**	−0.048	1			
pH	−0.123	−0.088	0.120	0.138	0.−116	0.341	0.129	1		
TDS	0.316	−0.066	0.037	−0.021	−0.167	0.142	0.146	0.207	1	
EC	0.392	0.010	0.003	−0.019	−0.171	0.101	0.133	0.192	0.988**	1

*.correlation is significant at the level (2-tailed); **.correlation is significant at the 0.05 level (2-tailed).

3.2. Sediment Analysis

Measured of pH in sediments was shown to be higher than that in the water, which is ranged between 7.00 up to 8.45, it is slightly alkaline and this could be partly contributing to the increased concentration of heavy metal ions in the sediments due to precipitation of dissolved metals. EC and TDS are related together and they were increased. EC was ranged from 319 to 1484 um/cm and TDS varies from 171 to 884 mg/l (Table 3).

3.2.1. Capacity of Exchange Cations

CEC of a soil represents the total amount of exchangeable cations that the soil can absorb. The actual CEC of the soil depends on the pH of the soil, a neutral soil (pH ~ 7) has higher CEC. The CEC of a soil with pH dependent charge will increase with an increase of pH (Figure 3). The CEC ranges from 3.72 to 29.12 meq·100 g^{-1}.

River sediments are usually composed of fine grains of minerals with high cation exchange capacity (CEC), such as clay minerals and iron oxides. In general, the more clay and clay loams in the soil, the higher the CEC 20 - 50 meq·100 g^{-1} (Heiny & Tate, 1997).

The CEC and the pH of sites 4 and 5 are low. According to the results of CEC, clay minerals and loamy soil were predominant in all the sites of the ULRB while the sand effluents are abundant.

3.2.2. XRD Analysis

Sediment are mostly formed of loose sands, clay, silt and other soil particles that
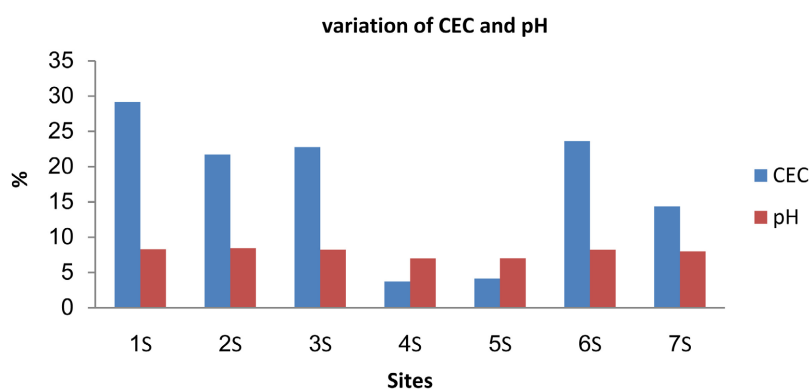

Figure 3. Relationship between CEC and pH in the sediments of ULRB.

Table 3. Physical parameters of sediments and CEC in the ULRB.

Sites	S1	S2	S3	S4	S5	S6	S7
pH	8.30	8.45	8.25	7.00	7.03	8.23	8
TDS mg/l	171	565	456	159	273	884	597
EC 1500 μs/cm	345	1134	923	319	574	1484	1023
CEC meq/100g	29.12	21.71	22.76	3.72	4.13	23.59	14.37

settle at the bottom of water body (Davies & Abowei, 2009). The accumulation and distribution of elements depend mainly on the characteristics of the rock lithology as the parent rock, such as mineral species and grain sizes (Taylor, 2007).

The major components in the inorganic phase of ULRB sediments were formed of quartz (SiO_2), calcite ($CaCO_3$), dolomite ($CaMg(CO_3)_2$) and Koalonite $Al_2Si_2O_5(OH)_4$ (**Figure 4**). Most of the visible coarse materials in the stream bed are limestone and dolomitic limestone. Calcite content was decreased from the first two sites (i.e. S1 and S2) in downstream of the river, while the percentage of quartz was increased. This is due to the leaching of $CaCO_3$ by the soil. The concentration of $CaCO_3$ in water during the two years of the study was increased from 200 to 570 mg/l from the S1 till S7 (Haydar et al., 2014). XRD indicated also the presence of minerals Anorthoclase ((Na, K)$AlSi_3O_8$) in sites 1 and 3; hematite Fe_2O_3 and orthoclase $KAISi_3O_8$ in site 2 and goethite: $Fe^{3+}(OH)$ in site 4 (**Figure 4**).

3.2.3 Granulometric Analysis

Granulometric analysis has been carried out to determine the sediments texture (i.e. percentage of sand, silt and clay). The grain size distribution in the samples indicates that clay is the main component with mean value of 39%. The average silt content is 36%, while the least constituents is sand (i.e. averaging 25%). The obtained results show that the characteristics of sediments of the ULRB are mainly loamy clay. In sites 4 and 5 (i.e. the effluents) the average of fine sand (<50 μm fraction) content in sediment samples is 46%, which is the most constituent of these sites, while the average content of silt is 34% and clay is 20%, which means that these sediment are mainly loamy soil.

3.2.4. FTIR Analysis Frequencies

The major minerals of quartz, calcite, kaolinite, dolomite and other secondary minerals such as anorthoclase, hematite, orthoclase and goethite are identified by comparing the observed wave numbers with available literature (Russell, 1987; Ramasamy et al., 2009, Littlejohn et al., 1991). The relative distribution of major minerals can be quantified by calculating the extinction coefficient for the identified peaks of quartz and kaolinite at around 464 cm^{-1} and 1032 cm^{-1}; respectively, and for calcite at 1430.92 cm^{-1}.
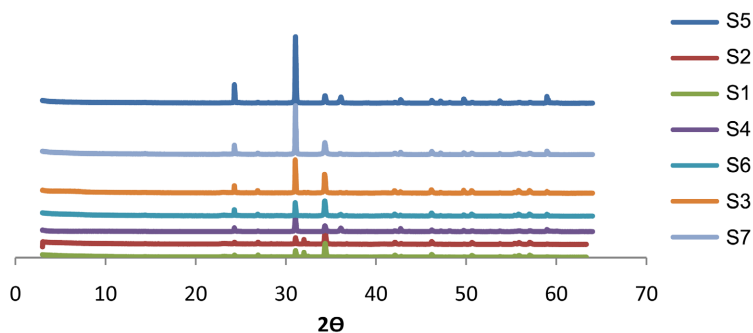

Figure 4. Distribution of minerals in the investigated sites in the ULRB as tested by XRD.

It can be noticed that the amount of montmorillonite is less than kaolinite, quartz and calcite. The result of FTIR confirms with the result of XRD (Table 4).

3.2.5. Heavy Metals in Sediments

Sediment analysis plays an important role in assessing the pollution status of the environment. Analysis of heavy metals levels in sediment samples helps in the interpretation of water quality and contamination sources (Heiny & Tate, 1997; Casas et al., 2003). The distribution of heavy metals in sediments is dependent on the samples location along the river course and is found to be not uniform. Descriptive statistics, including mean, standard deviation are performed after analysis and present in Table 5.

The contamination of the sediment by metals was evaluated by comparison the mean with the sediment quality guideline proposed by Consensus-Based Sediment Quality Guidelines of Wisconsin (CBSQG) by Wisconsin Department of

Table 4. Observed absorption wave numbers and corresponding minerals from FTIR spectra of the ULRB.

Mineral	Site No.	Observed wave (cm^{-1})
Quartz	S1-S4-S5-S6-S7	464.4; 692.3
	S2-S3-S7	460.5; 793.5; 520.4
	S6	466.6
Kaolinite	S1-S3-S7	1032
	S2-S6-S7	3693.9; 3620.7; 3622.6
Calcite	S1-S2-S3-S4-S5-S6	1430.92
	S7	1035.7; 1421
Montmorillonite	S1	872
	S3-S4-S6	874.5; 877
Feldspar	S6	535.1

Table 5. Heavy metals values over three different seasons of the ULRB.

	Pb	Cd	Fe	Mn	Cu	Cr	Zn
Rainy Mean	72.4	1.4	14,583	434.8	65.7	103	207
Mid Rainy Mean	11.65	2.6	9587	140	98.9	28	168
Dry Mean	36.5	2.5	23,037	362.4	227.1	87	72
Std. Dev.	36.55	10.26	9092	158.2	47.9	64.2	93.1
Limestone	2.82	0.007	3651	-	23.5	-	-
GBSQG	36	0.99	20,000	460	32	43	120

All concentrations are in mg/kg, dry weight; Std. Dev: standard deviation; a GBSQG (Wisconsin Department of Natural Resources, 2003); b Limestone values adapted from Abdel-Rahman and Nader (2002) and Li (2000).

Natural Resources (2003). The mean of metal concentrations in the sediments was present in different forms. There was decrease in the order of Fe > Mn > Zn > Cr > Pb > Cu > Cd in rainy season, while in mid rainy the variation was: Fe > Zn > Mn > Cu > Cr > Pb > Cd, and in wet season: Fe > Mn > Cu > Cr > Zn > Pb > Cd. The mean of dry season of Fe content is 6 times than the calicite reference value, similarly the wet season ratio which is 4. While, Pb values exceed the limestone reference value (2.82) in all season and at all sites. According to CBSQG, the mean of Pb in rainy season is classified as heavily polluted. The Pb in mid rainy and dry season are classified as not polluted. According to the two references, the sediments are therefore regarded as Copper-Cadmium contaminated.

It can be argued that the mean concentration of Zn is lower than the normal according to CBSQG (Table 5) in the low flow rate, but the contamination appears in rainy and mid rainy seasons. Downstream dilution from this source can adequately explain the dry season progressive decline. It was noticed also that the concentration of Mn is lower that the normal according to CBSQG, while the river is not contaminated by this metal. The contamination of Cr doesn't exceed the norm during the mid rainy season, but it appears in the rainy and dry seasons as well.

3.2.6. Assessment of Heavy Metals Using Contamination Factor (C_f)

In order to assess the degree of contamination in the ULRB, contamination factor (C_f) or enrichment ratio (ER) and the degree of contamination (Cd) were used. C_f can be used to differentiate between the metals originating from anthropogenic activities and those from natural processes, and to assess the degree of anthropogenic influence. The resulted calculation of contamination Factor (C_f) for the heavy metals in sediments in the rainy, mid rainy and dry seasons are shown in Tables 6-8; respectively. The contamination factors are calculated according to the following formula:

Table 6. Contamination factor (C_f) of heavy metals in sediment during the rainy season of the ULRB.

C_f	Pb	Cd	Fe	Mn	Cu	Cr	Zn	Cd
S1	2.45	1.33	1.13	0.9	0.9	5.84	1.87	14.42
S2	1.46	1.39	0.52	1.35	1.35	2.27	1.29	9.63
S3	2	2.2	0.47	0.76	0.76	0.44	0.74	7.37
S4	0.49	1.34	0.69	0.84	0.84	0.8	1.1	6.1
S5	0.85	1.26	0.69	0.91	0.91	1.16	1.2	6.98
S6	3.08	1.28	0.87	1	1	2.52	2.76	12.51
S7	3.76	1.28	1	0.82	0.82	3.81	3.1	14.59
Mean	2	1.44	0.76	0.94	0.94	2.4	1.72	10.22
Background value	36	0.99	20.000	460	32	43	120	

Table 7. Contamination factor (C_f) of heavy metals in sediment during the mid rainy season of the ULRB.

C_f	Pb	Cd	Fe	Mn	Cu	Cr	Zn	Cd
S1	5.6	3.43	0.31	0.1	8.02	2	1.6	21.15
S2	5.1	1.6	0.76	0.03	0.25	0.27	0.64	8.65
S3	4.2	1.8	0.62	0.63	5.1	10.2	1.62	24.17
S4	0.27	3.2	0.09	0.26	2.66	0.23	1.13	17.57
S5	0.27	2.2	0.1	0.3	2.55	0.3	1.26	6.98
S6	6.5	3.8	0.86	0.76	0.76	0.25	2.24	15.17
S7	0.5	2.6	0.52	0.05	1.34	0.53	1.31	6.85
Mean	3.2	2.66	0.46	0.3	3	2	1.4	14.42

Table 8. Contamination factor (C_f) of heavy metals in sediment during the dry season of the ULRB.

C_f	Pb	Cd	Fe	Mn	Cu	Cr	Zn	Cd
S1	8.05	2.5	0.58	0.69	0	4.3	0.28	16.4
S2	7.77	2.3	0.71	0.73	0	1.6	0.36	13.47
S3	13.8	2.4	1.99	0.59	2.5	0.43	0.3	22.01
S4	0	3	0.93	0.92	0.9	0.93	0.71	7.39
S5	0.7	3.2	0.96	0.85	0.93	1.4	1.03	9.07
S6	8	2.4	1.6	0.91	1	2.28	1.3	17.49
S7	8	2.3	1.71	0.79	1.87	3.09	0.21	17.97
Mean	6.6	2.5	1.2	0.7	1.02	2	0.59	14.8

$$C_f = \text{Measured concentration/background concentration}$$

where, background value of the metal = Metal Consensus Based Sediment Value (mg/kg dry) as it is given by Wisconsin Departmental of Natural Resources (2003). The degree of contamination (Cd) was defined as the sum of all contamination factors (Figure 5).

In this study, the contamination factors were calculated from the concentrations of heavy metals in the sampling points at the study area. Contamination Factor (C_f) of heavy metals in sediments clearly indicates the effect of seasonal variations was important: The C_f values were higher in the dry season than in the wet season for Pb, Cd and Cu. Normally, as the C_f values increase the contributions of the anthropogenic origins also increases.

In rainy season, the maximum contamination was found in sites S1 and S7, where the degree of contamination is 14.42 and 14.59; respectively. The classification of level of contamination of Cf was done according to Hakanson (1980). The low contamination factors appears when $Cf < 1$ and this is present in all
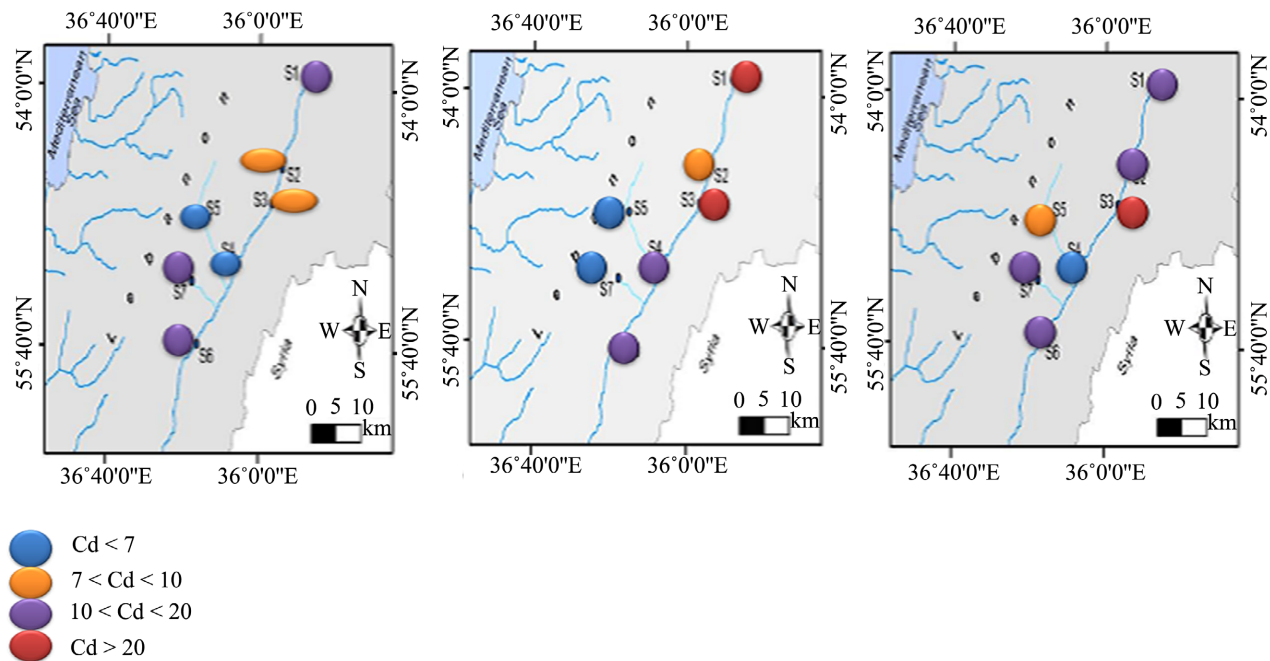
Figure 5. Levels of degree of contamination (Cd) in the three investigated seasons in the ULRB.

sites for Cu and Mn (mean = 0.94); Fe (mean = 0.76) and for Pb in sites S4 and S5. When Cf is between $1 > Cf > 2$, it is considered as moderate pollution, and this is the case of Pb, Cd and Zn. When Cf is between $3 > Cf < 6$, the contamination is considerable and this is the case of Cr (Mean = 2.4).

In mid rainy season, the level of contamination increases, and this appears in all sites where the degree of contamination is 24.17 in site S3. According to Hakanson (1980), Nehme et al. (2020), the low contamination factors appears when $Cf < 1$, for Fe and Mn in the entire sites. In site S1, there are all forms of contamination: moderate pollution for Cr and Zn; considerable pollution for Pb, Cd, and severe pollution for Cu. The pollution of Pb is classified as considerable to sever S6 ($Cf > 6$); except in sites S4 and S5, Cd (except S1), whereas Zn and Cu exist as moderate pollution in all investigated sites.

In dry season, the degree of contamination is 22.01 in site S3. Pb is classified as a severe contamination in all investigated sites, except in sites S4 and S5. No variation in the mean of level of contamination of Cd and Mn (in the entire sites). All sites show that the degree of contamination of Zn and Cu showing a decreasing in C_f. In sites S3, S6 and S7 Fe showing a moderate pollution $Cf > 1$.

4. Multivariate Statistical Methods

The multivariate statistical analyses such as Pearson's correlation, Cluster and Factor analysis have been carried out to find out the interrelation among the parameters obtained from elemental and mineralogical analysis.

4.1. Pearson's Correlation Analysis

Pearson's Correlation Coefficient matrix among the selected heavy metals, phys-

ical parameters such as EC, TDS, PH, and CEC; and the concentration of relative distribution of Quartz (Q), Calcite (C), Dolomite (D) and kaolinite (K) are shown in Table 9. Pb tends to remain tightly bound to sediments under oxidizing conditions. Positive correlation coefficients are observed among the metals Pb and Mn (r = 0.549), and this is normal, because, the Pb in sediments is primarily found in association with manganese hydroxide (Nehmeh et al., 2019). There is significant correlations between the contaminants of Pb and Cu (r = 0.796), Cr (r = 0.848), Zn (r = 0.562); and TDS (r = 0.449); and this is due to the same source of contamination, such as wastewater, industrial and agricultural activities residues. Cd and Cr (r = 0.445); Mn and Cu (r = 0.582); Cu and Cr (r = 0.721); Cu and Zn (r = 0.649); TDS and EC (r = 0.988).

The major minerals of quartz, calcite, dolomite and koalonite are poorly correlated with the studied metals. However, sand mineral (i.e. quartz) has positive correlation with EC (r = 0 .450) and TDS (r = 0.506); CEC and pH (r = 0.848) have positive correlation and significant, and this was observed in all sites. CEC and dolomite are positively correlated (r = 0.515), and this is due to the competition between Ca^{2+} and Mg^{2+} as cation substitution to incorporated in CEC. Calcite and dolomite are significant positively correlated (r = 0.775), because the majority of rock lithologies in Lebanon is principally formed from carbonate rocks (limestone and dolomite).

Table 9. Correlations matrices of sediments of the ULRB.

	Pb	Cd	Fe	Mn	Cu	Cr	Zn	CEC	pH	TDS	EC	Q	K	C	D
Pb	1														
Cd	0.292	1													
Fe	0.292	0.257	1												
Mn	0.549	0.412	0.351	1											
Cu	0.796	0.127	0.251	0.491	1										
Cr	0.614	0.445	0.309	0.582	0.721	1									
Zn	0.562	−0.148	−0.224	−0.007	0.064	0.194	1								
CEC	0.404	0.339	0.166	−0.015	0.114	0.343	0.104	1							
pH	0. 380	0.339	0.162	−0.064	0.112	0.254	0.175	0.848	1						
TDS	0.449	−0.033	0.264	0.066	0.149	0.055	0.344	0.369	0.207	1					
EC	0.421	0.033	0.256	0.067	0.094	−0.042	0.276	0.384	0.192	0.988	1				
Q	0.162	−0.135	0.023	0.089	−0.067	−0.180	0.288	0.065	0.137	0.506	0.450	1			
K	0.289	0.375	−0.018	0.507	0.101	0.381	0.076	0.865	0.611	0.294	0.317	0.092	1		
C	0.042	0.337	−0.139	0.114	−0.091	0.127	0.118	0.515	0.097	0.206	0.262	0.221	0.775	1	
D	−0.248	−0.230	−0.203	0.017	−0.093	−0.165	0.049	−0.482	−0.262	0.379	−0.463	0.524	−0.437	−0.181	1

Q = Quartz; C = Calcite; D = Dolomite; K = Kaolinite.

4.2. Principal Compound Analysis (PCA)

Factor analysis (FA) is carried out on the data set (16 variables as in the above analyses). FA yielded three factors with explaining 63.44% of the total variance (Table 10). The first factor accounted for 30.44 % of the total variance, and it is mainly characterized by positive loading of concentrations of Pb, Cr, Cu, Mg, CEC, pH, TDS, EC quartz, kaolinite and calcite.

Factor 2 accounted for 18.29% of the total variance, which mainly consists of positive loading of Fe, Mn, and dolomite mineral, whereas factor 3 accounted for 14.71% of total variance and showed positive loading of Cd. From the overall factor analysis, it was found that calcite is the major factor and quartz is the least important factors to increase the heavy metals concentrations.

Figure 6 allows distinguishing that the factor of seasonal variations is not important, because there is combination between the sampling sites.

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The first class (Class 1/3) has found in the positive right side of the axis F1 and F2, and it contains the sites of S1r, S6r and S7r during rainy season. This class characterized by the presence of heavy metals of Pb, Cu and Zn. The third class (Class 3/3) corresponds to spring (mid rainy) and has found in the positive side of C1 and C2. This means that no variation occurs between two seasons. The

Table 10. Loading factor of variables of the analyzed sediments in the ULRB.

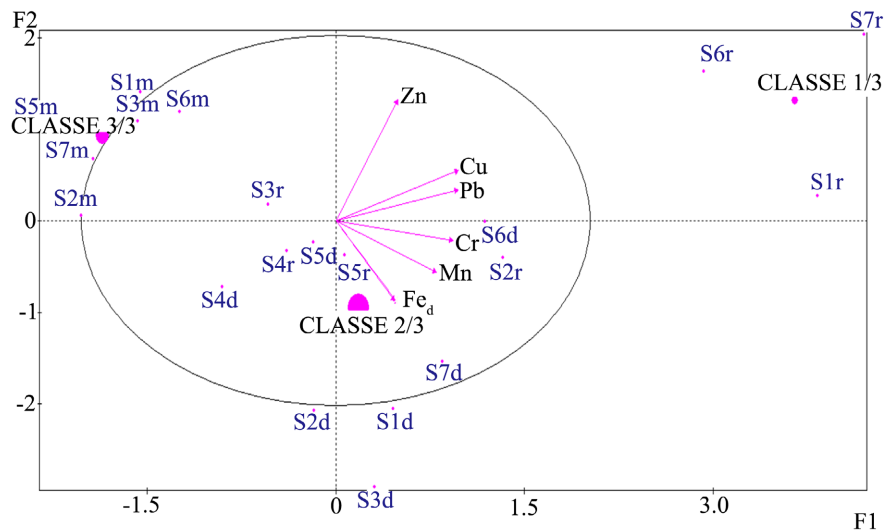| Variables	Factor 1	Factor 2	Factor 3
Pb	0.84		
Cd			0.60
Fe		0.43	
Mn		0.32	
Cu	0.64		
Cr	0.65		
Zn	0.37		
CEC	0.65		
pH	0.68		
TDS	0.65		
EC	0.64		
Q	0.19		
K	0.57		
Calcite	0.40		
Dolomite		0.29	
Variability %	30.4	18.2	14.7
Cumulative %	30.4	48.6	63.44

Figure 6. Circle of correlation of metals in F1 and F2 for sediments of the ULRB (r: rainy season; m: mid rainy; d: dry rainy).

second (Class 2/3) corresponds to mixed of samples in summer season, whereas the samples during rainy season has found in negatives side of the axis C1 and C2 and have the influence of the metals Cr, Mn and Fe.

5. Conclusion

Likewise, several Lebanese rivers, the Litani River became contaminated by a spectrum of deterioration aspects including microbiological and chemical pollutants. This has occurred lately due to a number of factors including mainly the lack of monitoring approaches, and it was exacerbated by the challenging climatic conditions and population growth and the related agricultural practices. Few concerns are given to this issue; while the deterioration of river water and sediments has become intolerant, and this was reflected by the existing diseases appearing in many localities in the river basin.

As a major aspect of pollution in water and sediments, heavy metals with their severe impact on human life were investigated over different seasons for two investigated years in the upper tributaries of the Litani River. It can be noticed that there was a clear seasonal variation in heavy metals content over these seasons, and thus dry periods show much more contamination ratio due to the low flow rate and capacity.

The results showed the importance of monitoring of heavy metals values and physic-chemical characterization of different parameters that could represent the possibility of a comprehensive assessment of negative pressures on the water and soil ecosystem of ULRB during different seasons. To mitigate such negative pressure this needs elimination of those sources that required serious implementations which are lacking from different institutional and parties in the country as the absence of the required implementations (e.g., infrastructures, landfills, treatments plants, channels etc.) to mitigate or decrease pollution.

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Conflicts of Interest

The authors declare no conflicts of interest regarding the publication of this paper.

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