

Assessment of Heavy Metal Pollution in the Sediments of the Lower Litani River Basin, Lebanon

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Abstract

Concentrations of eight heavy metals (Cu, Fe, Cd, Mn, Cr, Zn, Ni, and Pb) were determined in this study to evaluate their levels and spatial distribution in sediments from the Lower Litani River Basin (LLRB) in six sites, during the dry seasons for the period from 2011 to 2012. Consensus-based sediments quality guidelines of Wisconsin Department of Natural Resources were applied to assess metal contamination in these sediments. The range of the measured concentrations in the total sediments were determined for dry weights to the total sediments. The samples were characterized by a set of cation exchange capacity, granulometric, X-Ray diffraction (XRD) and Fourier Transformed Infrared Spectroscopy (FTIR). Pearson's correlation was also performed in this study to compare and determine the correlation between heavy metals in these sediments. Geo-accumulation (Igeo) index, Contamination Factor (Cf), and contamination degree (Cd) were also applied to assess the level of contamination in these sites. The results of this study show that the concentrations of Pb and Fe are high in the sites S5 and S6, and the values of Cr and Ni are high in site S6. All of the investigated sites are characterized by a moderate to a highly-polluted range of contamination, with the degree of contamination increasing during the dry season.

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1. Introduction

Heavy metals in the environment may accumulate to toxic levels without visible signs. The accumulation of the trace metals occurs in the upper sediments of an aquatic environment by biological and geochemical mechanisms. They can become toxic to the sediments, organisms and fish, resulting in death, reduced growth, or in impaired reproduction and lower species diversity (Praveena et al., 2007). This may occur naturally from normal geological processes such as weathering and the leaching of rocks or due to increased urban and industrial activities, agricultural practices, exploration and exploitation of natural resources (Ajayi and Osibanjo, 1981). Hence, trace metals may be used as sensitive indicators for the monitoring of the changes in the water environment (Iwashita and Shimamura, 2003).

The anthropogenic sources are mainly associated with industrial and domestic effluents, urban storm, runoff, landfills, the mining of coal, atmospheric sources and inputs from rural areas (Biney et al., 1994). The nutrition requirements of heavy elements differ substantially among species or elements, and the optimum ranges of concentrations are generally narrow given the fact that heavy elements exhibit extreme toxicity even at trace levels (Nicolau et al., 2006). Exposure to heavy metals has been linked to several human diseases such as development retardation or malformation, kidney damage, cancer, abortion. It also has been said to have effects on intelligence and behavior, and may even lead to death in cases of exposure to very high concentrations. The degree of particulate heavy-metal pollution can be evaluated in terms of the geochemical background of the element value in a

drainage network, normally obtained in the headwater region without anthropogenic influences, according to Salomons and Forstner (1984), using an Igeo-accumulation index (Müller 1979; Simonovski et al., 2003; Audry et al., 2004; Yan et al. 2007).

2. Study Area

2.1. Description of the Study Area

The discharge of the Lower Litani River varies across seasons, and also according to different localities, where the average annual discharge is about 360 million m³ (LRA, 1999). There are eighteen measuring stations along the lower Litani river course. In this study, four stations are included along the investigated river course. They are situated from north to south as: Qelia, Gandourieh, Khardali and Qasmieh. The average discharge from these stations is 31.7, 224.2, 227.5 and 176.3 Mm³, respectively.

In addition to water pollution by nutrients and bacteria, the heavy-metal content in sediments has become one of the most important problems, because of its toxic effect even at minor concentrations. This is the case in the Litani River, the largest of its type in Lebanon with a basin area of about 2180 km² and a length exceeding 174 km.

The Litani River is divided into two sub-basins with its upper basin stretching from the north of the Bekaa plain to the Qaraaoun dam, where a lake (8km²) exists. Its lower sub-basin extends from the dam along Qelia Village down to the Qasmieh where it outlets into the sea north to Tyre city (Fig. 1-A and Fig. 1-B). The river water in the lower basin is used mainly for irrigation purposes, particularly in highly agricultural areas (Khoury et al., 2006).

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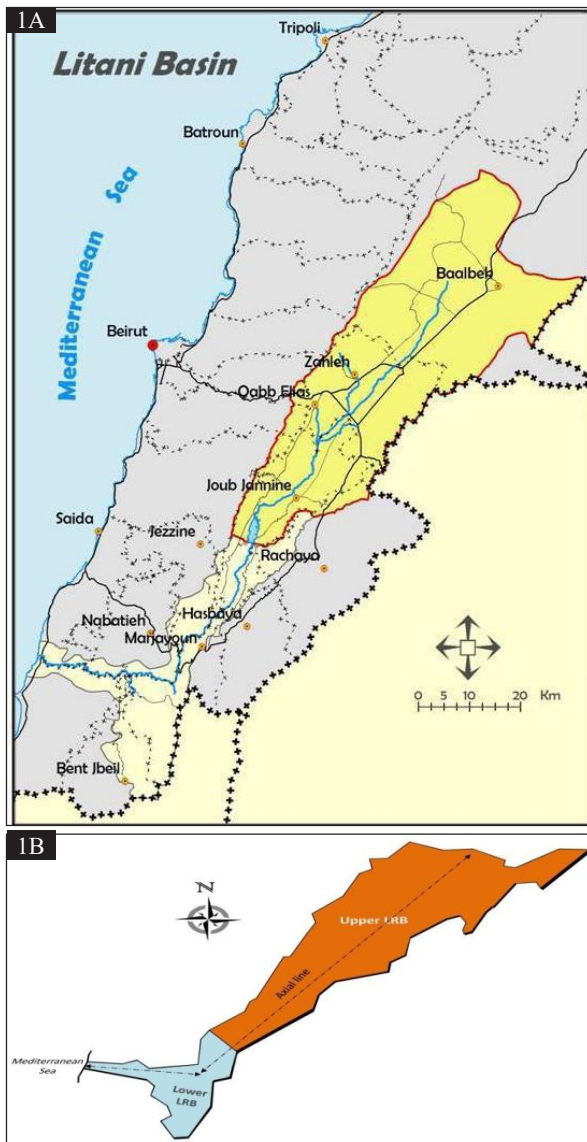


Figure 1. A: Map of Litani river basin location in Lebanon (BAMAS, 2005). B: Schematic figure for the LRB with its axial line (Shaban et al., 2018).

According to Beydoun (1988), the eastern Mediterranean basin, including Lebanon, represents a terrain mass for the unstable tectonic shelf of the Middle East Region, which is affected by plate tectonic movements of the Dead Sea Rift System, and has its extension forming the Bekaa Plain. Therefore, the folded mountain ranges with uplifted blocks created the three elongated and parallel physiographic units of Lebanon (Mount-Lebanon, Anti-Lebanon, and Bekaa Plain).

The Bekaa depression (wide plain), where the LRB is extended, is almost a graben structure located between the two uplifted mountain chains. The western side of the graben structure is marked by a well-defined fault boundary (i.e., Yammouneh Fault). Beydoun (1972) described the eastern side of this graben as a sharp flexure, in place, partly formed by en-echelon faults. The exposed stratigraphic rock sequence among the LRB is similar to the one representing the entire sequence of Lebanon. It reveals rocks from Middle Jurassic up to the quaternary deposits. This stratigraphic rock sequence shows sedimentation in a marine environment until the Middle Eocene, with carbonate rocks building up the largest part of the stratigraphic column separated by continental clastic rocks

at the Lower Cretaceous and some intercalated volcanic rocks up to the Pliocene.

Several aspects of rock deformations exist in the LRB. They are considered as complicated as the geological structures, notably because the area of concern is affected by the presence of the Yammouneh Fault, which is characterized by lateral displacement, accompanied by diagonal sliding of the adjacent rock formations. The orientation of the LRB is mainly controlled by the presence of the extension of the Yammouneh Fault and the Serghaya Fault along the western and eastern sides of the Bekaa Plain, respectively (Fig. 2). As a result of these two major faults, however, several secondary fault systems, with different scales and magnitude, are developed and sometimes with diagonal/or lateral displacement. However, the existing faults, among the LRB in the southern part are different from those in the Bekaa area, and they are often of the wrench type. These faults cut for several tens of kilometers from outside the Litani catchment and almost terminate into the sea (Shaban et al., 2018). In the LRB, there are many other aspects of rock deformation, including small and moderate-scale faults, folding flexures structures, which are often accompanied by intensive fissuring and jointing systems. Additionally, sharp dips of bedding planes exist in several localities (Shaban et al., 2018). Karstification is well pronounced among the carbonate rocks in the LRB. These are on surface karsts, with special emphasis on sinkholes. In addition, subsurface karst is well-developed, including the cavities, conduits, and galleries, which are characterized by water transport for long distances and water that creates many karstic springs, such as the springs of Berdaouni, Anjar, Yammouneh and Khrayzat (Shaban et al., 2018).

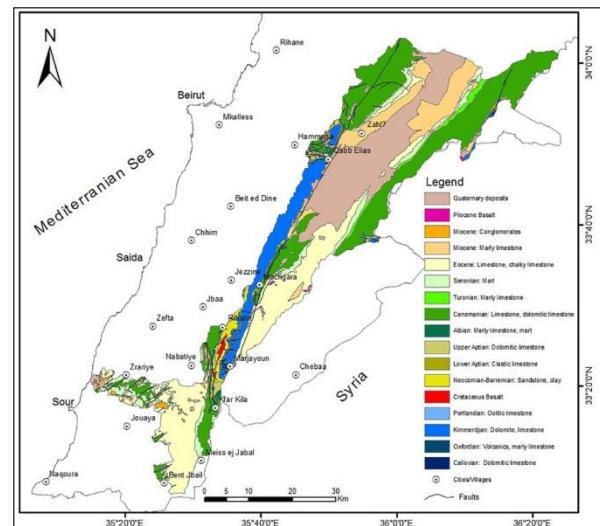


Figure 2. Geological map of Litani River Basin (Shaban et al., 2018).

The heavy metals were investigated during the dry seasons for the period from 2011 to 2012. During this study, the estimation focuses on how much the sediments are impacted (naturally and anthropogenic) by heavy metals. Pollution levels will be measured as the ratio of the sample metal enrichment above the concentration present in the reference station or materials (Abraham and Parker, 2008; Mediolla et al., 2008).

In this study, the influence of minerals and geochemical characteristics on the natural radiation level of the sediments

were considered; the contamination factor (Cf) or enrichment ratio (ER) and the degree of contamination (Cd) have been used to determine the contamination status of the sediments. The Igeo – accumulation index (Igeo) is used to evaluate the heavy-metal pollution in the sediments and to measure the degree of metal contamination or pollution in terrestrial, aquatic and marine environments (Tijani and Onodera, 2009). The Igeo of a metal in sediments can be calculated by the formula obtained by Mediolla et al., (2008) and Asaah and Abimbola (2005).

The main objective of this study is to analyze heavy- metal concentrations in sediments, and thus to assess their geochemical characteristics in the LLRB by calculating the geo – accumulation index (Igeo) and (Cf) in order to detect their relative distribution and to know the influence of mineral content using XRD and FTIR on the geochemical characterization and the level of contamination in the river using multivariate analysis.

3. Sampling and Analytical Techniques

3.1. Sample Collection

The sediment samples were collected from six sites along the LLRB as shown in Figure 3. Coordinates and the distribution of the main activity for each site are illustrated in Table 1. Approximately 2 kg of sediment were collected from

each site at the sediment – water interface (i.e. surface river sediments) using polyethylene bags. The bed sediments from the LLRB were collected by scooping up 10 cm of the bed sediments, 10 m away from the riverbank at the point, where the water samples were taken, using anti-rust scoops. The sediments were naturally dried at room temperature (25°C± 2) in the laboratory prior to analysis.

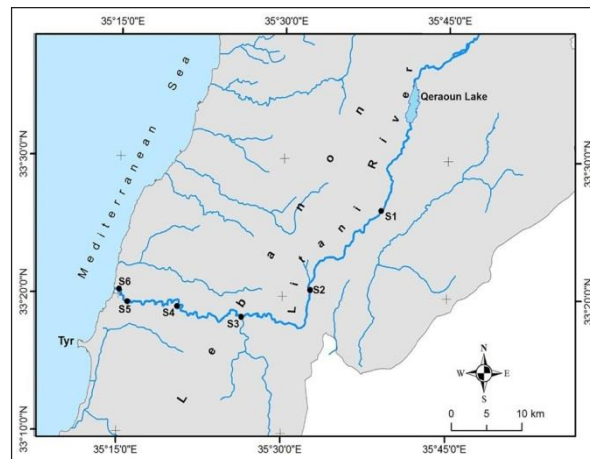


Figure 3. The Lower Litani River Basin (LLRB) shows the sample locations.

Table 1. Location of the sediment samples in the LLRB.

Sampling site	Latitude	Longitude	Other activities
S1= Qelia	33°26' 21" N	35°38' 55" E	Quarry site and Touristic zones. There are many pumping stations.
S2= Kardali	33°20' 34" N	33°32' 34" E	Agriculture and touristic zones.
S3=Kaekaeayat eljisr	33°18' 31" N	35°26' 18" E	Interfered touristic and agricultural zones, near small village
S4=Tair filsaiy	33°19' 00" N	35°20' 27" E	Touristic zone.
S5=Abouabdellah	33°19' 26" N	35°15' 50" E	Vegetated sites with citrus trees
S6= Qasmieh	33°20' 22" N	35°15' 04" E	Road with high traffic is in the proximity of the site. There is an irrigation canal and an agricultural land of banana.

3.2. Sediments' Metal Digestion

The concentrations of Pb, Cd, Fe, Mn, Cr, Cu, Ni, 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 a membrane filter of a pore size of 0.45µm before analyses using Standard Methods (APHA, 1995). The samples were digested using microwave digestion techniques (Siaka et al., 1998) in which 0.5 g of each sample was placed in Teflon vessel with 5ml HNO₃ (65 %), 2ml HF (40 %), and 2ml H₂O₂ (30 %) using a microwave digestion system (model: MILESTONE mls-1200 mega). An aliquot of the filtration of the samples was taken (about100ml). Digestion solutions were measured for the total heavy metals using ICP-OES (APHA, 1995). The extraction method was used to analyze the total metal concentrations by atomic absorption Spectrophotometer. Blanks containing all the components except sediments were analyzed to determine background interferences. All of the measurements were performed in triplicate and their average values were reported.

3.3. pH, TDS and EC Analysis

Approximately 10g of the air-dried sediments was suspended in 50mL of deionized water and manually agitated

for five minutes. The suspension was allowed to rest for about one hour with occasional shaking until the pH, TDS and EC were measured.

3.4. CEC, XDR and FTIR Measurements

Cation-Exchange Capacity was measured after exchange with cobalt hexamine (Co(NH₃)₆ Cl₃) and the dosage of its residual concentration in the equilibrium solution (Mantin, 1969; Morel, 1957). An amount of 1.5g of the samples was dispersed and shaken during two hours at 30°C in a 30mL of cobalt hexamine solution. The samples were then centrifuged for one hour at 46.251g. The supernatants were analyzed on a UV–Visible spectrophotometer, using a Cobalt absorption band at 472nm to derive CEC from the residual concentrations in Cobalt hexamine. Measurements were always carried out in duplicate to check for reproducibility.

The sediment samples were analyzed by XRD using 1g of a randomly-oriented powder, put on a rotating sample holder, and leveled with a glass slice to obtain a flat surface. XRD were also acquired using Zincite (ZnO) as internal standard. In the latter case, the samples were first mixed with 0.111g of ZnO and ground in an agate mortar for five minutes. XRD patterns were collected on a D8 Advance Bruker AXS diffractometer equipped with a Lynx Eye fast

linear detector using Cobalt K radiation ($R=0.17903$ nm) at 35 kV and 45 mA. Intensities were recorded from 3 to 64° with a 0.035° using a three-second counting time per step. Data reduction and analysis were performed with the EVA software (DIFFRAC plus from Bruker) and diffraction peaks were identified by comparing them with the powder diffraction files.

FTIR spectra were collected on the bulk powder samples mixed with KBr as a transparent matrix. Diffuse reflectance Fourier transform infrared spectra were recorded on a Bruker IFS-55 spectrometer in the range from 4,000 to 600 cm^{-1} with a resolution of 2 cm^{-1} . Spectra were obtained from the average of 200 scans collected over two minutes. Data reduction and analysis were performed using OPUS program (Russel, 1987).

3.5. Chemical and Statistical Analysis

The concentrations of Cu, Fe, Cd, Mg, Zn, Pb, Al, Ba, Ni, Mn, Ag, and Cr were measured using the Atomic Absorption Spectrophotometric method, (Spectrophotometer (RAYLEICH – MFX-210) with an air/acetylene flame and background correction and a deuterium lamp to remove any solid impurities before testing (AOAC 974.27). The samples were filtered through a membrane filter of a pore size of 0.45 μm before analyses using Standard Methods (APHA, 1992).

Bed sediment samples were digested using microwave digestion techniques as reported by Made Siaka et al. (1998), where 0.25gm of the samples was placed in a Teflon vessel with 5 ml HNO_3 (65 %), 2ml HF (40 %) and 2ml H_2O_2 (30 %) using the Microwave digestion system (model: MILESTONE mls- 200mega). An aliquot of the filtration of the samples was taken (about 100 ml). Digestion solutions were measured for the total heavy metals using ICP-OES (APHA, 1995). Correlation coefficients were calculated between all pairs of measured elements' concentrations.

Multivariate statistical analyses such as Pearson Correlation Analysis, the degree of dispersion distribution of different metals were performed. Pearson's correlation analysis was carried out using SPSS, 2007. Cluster analysis (CA) is a multivariate technique, whose primary purpose is to classify the objects of the system into categories or clusters based on their similarities.

3.6. Granulometric Analysis:

The samples were also tested to measure their granulometric fractions, such as the content of the sand, silt and clay using an ASTM sieve. About 100g of the sediments were taken for separation of sand, silt and clay fractions by wet sieving.

4. Results and Discussion

4.1. Physical Parameters and CEC Analysis of the Sediments

The tested sediments of LLRB have pH values ranging between 7.4 and 8.09, which is slightly alkaline (Table2), the alkaline nature is mainly pronounced in sediments in LLRB during the dry season, and this can be attributed to heavy metal enrichment, EC and TDS are related together and they increased, EC ranged from 204 to 707 $\mu\text{s}/\text{cm}$, and TDS varies between 94 and 352 mg/l.

4.2. CEC (Cation Exchange Capacity)

The CEC is defined as the ability of a particle to change its positive bases with the environment in which the particle interacts (Huu et al., 2010). Cations have the ability to be exchanged for another positively-charged ion from the surfaces of clay minerals and organic matter.

Knowledge of the CEC in the soil can be of great importance in order to characterize the soil content of ionic elements, concentration of clay and mud, texture, degree of compaction, levels of porosity and permeability. It also provides information about possible needs for fertilizers and correction of the soil acidity. CEC is an important soil property, and the high CEC may indicate clay content, low permeability and internal drainage, due to the high soil compaction. Low levels of CEC may indicate a soil texture ranging from clayey-sandy to sandy, with variable grain sizes and high permeability. Soils with low CEC can be attributed to the higher content of clay minerals and organic matter.

Table 2 shows that the CEC is decreased in the sites as this order ($S_6>S_2>S_1>S_5>S_3>S_4$), and this identifies the agricultural activity present substantially in the sites S_6 , S_2 and S_5 . Generally, soils with high CEC have a color ranging from dark brown to black, due to the high lignin content of the organic matter. Soil with a high organic matter content are not necessarily productive in agriculture.

Table 2. Physical parameters of sediments and CEC

Sites	S1	S2	S3	S4	S5	S6
pH	4.7	7.8	8.09	8.04	8.04	7.4
TDS (mg/l)	183	155	94	104	150	352
EC 1500 ($\mu\text{s}/\text{cm}$)	364	313	186	204	300	707
CEC (meq/100g)	13.54	16.94	4.11	3.56	11.38	17.32

4.3. Heavy Metal Distribution in Sediments

The results obtained from the total metal concentrations for each sample are shown in Tables 3 and 4. Metal content ranged according to the following intervals, whereas 1.5-17.5 mg/kg for Cu; 890-40477 mg/kg for Fe; 5-37.5 mg/kg for Cd; 5-90 mg/kg for Zn; 2.5-45 mg/kg for Pb; 4-24.5 mg/kg for Ni; 3.5-55 mg/kg; Cr and 4-451 mg/kg for Mn. This allows for the arrangement of the metals from the higher to lower mean content in this area as follow: $\text{Fe} > \text{Zn} > \text{Cr} > \text{Pb} > \text{Cd} > \text{Ni} > \text{Cu}$.

The results show that the concentration of Cd is higher in all sediments, whereas the contents of Fe, Pb, Ni were higher in the sites 5 and 6 due to the steep slopping and deposition of pollutants in these sites. The sediments are contaminated with Cd, Fe, Zn, Cr, Pb, Ni and Cr exceeding the standard levels.

Standard (CBSQG), is considered harmful for farming and human health, and commonly, Cd is believed to affect human health. The retention of alarming exchangeable levels of cadmium may be related to the leaching of soil particles containing certain types of fungicides employed through agricultural practices. This argument is valid, because the sediments containing cadmium were collected during the rainy seasons, a period in which erosion and leaching processes are often observed.

Table 3. Concentration of heavy metals in the investigated sites (mg /Kg dry weight)

Site	Concentration of heavy metals							
	Cu	Fe	Cd	Mn	Cr	Zn	Ni	Pb
1	16	890	5	416	3.5	90	4	17
2	2.5	8049	16	4	12.5	47	4	3.5
3	1.5	17559	36	190	12.5	5	4.5	23.5
4	2.5	11460	26	39	26.5	43	11	2.5
5	3.5	35070	32	261	25	13.5	7	45
6	17.5	40477	37.5	451	55	71.5	24.5	143
Range	1.5-17.5	890-40477	5-37.5	4-451	3.5-55	5-90	4-24.5	2.5- 45
Minmum	1.5	890	5	4	3.5	5	4	2.5
Maximum	17.5	40477	37.5	451	55	90	24.5	45
Average	9.5	40.9	21.2	227.5	29.2	50	14.2	25

Table 4. Consensus-Based Sediment Quality Guidelines of Wisconsin (CBSQG, 2003)

Metal	Consensus-Based Sediment Value (mg/kg)
Cu	32
Fe	20000
Cd	0.99
Mn	460
Cr	43
Zn	120
Ni	23
Pb	36

Pearson’s correlation coefficient matrix among the selected heavy metals is presented in Table 5. Significant correlations between the contaminants of Cu and Zn ($r = 0.84$), Cd and Cr ($r = 0.68$), Zn and Cu ($r = 0.84$), Pb and Mn ($r = 0.71$), Cr and Fe ($r = 0.83$), Ni and Cr ($r = 0.96$), almost

indicate the similar source of the inputs. Fe and Cr ($r=0.83$), presumed that the association of the two elements originates from a common source and also during the transportation or deposition processes, and this also confirms the results in Table 5.

The major source of Zn is the domestic and municipal wastes followed by dumping and atmospheric deposition. The positive correlation in Cd and Cr may be attributed to the industrial origin of these metals. According to the samples’ location, the elevated levels of “urban” elements Cu, Zn, Mn, Pb and Ni are associated with the direct supply of untreated urban and industrial wastes. Thus, it can be concluded that the anthropogenic inputs resulted in the exceeding levels of Cu, and Zn. These metals were also positively-correlated with the percentage of quartz, dolomite, calcite and kaolinite in these sediments. Calcite and dolomite were significant positively correlated ($r = 0.98$), because they represent the widespread rocks nearby the study area.

Table 5. Correlation matrix between heavy metals in the sediment samples of the LLRB

Matrix	Cu	Fe	Cd	Zn	Pb	Ni	Mn	Cr	pH	Ec	TDS	CEC	Q	K	C	D
Cu	1.00															
Fe	0.17	1.00														
Cd	-0.21	0.82	1.00													
Zn	0.84	-0.27	-0.60	1.00												
Pb	0.37	0.87	0.58	-0.15	1.00											
Ni	0.55	0.70	0.55	0.32	0.47	1.00										
Mn	0.87	0.40	0.06	0.49	0.71	0.45	1.00									
Cr	0.36	0.83	0.68	0.10	0.55	0.96	0.33	1.00								
pH	-0.78	-0.38	-0.05	-0.68	-0.31	-0.76	-0.54	-0.65	1.00							
EC	0.82	0.56	0.18	0.60	0.54	0.82	0.69	0.74	-0.96	1.00						
TDS	0.83	0.56	0.18	0.60	0.55	0.82	0.70	0.74	-0.96	1.00	1.00					
CEC	0.59	0.20	-0.28	0.58	0.27	0.29	0.40	0.25	-0.79	0.74	0.74	1.00				
Q	0.77	-0.06	-0.58	0.77	0.24	0.12	0.65	0.00	-0.43	0.49	0.49	0.60	1.00			
K	0.94	0.30	-0.18	0.73	0.55	0.50	0.90	0.37	-0.68	0.79	0.79	0.62	0.87	1.00		
C	0.90	0.46	-0.03	0.61	0.69	0.55	0.92	0.46	-0.68	0.82	0.82	0.62	0.80	0.98	1.00	
D	0.89	0.50	0.03	0.58	0.71	0.59	0.93	0.50	-0.69	0.84	0.84	0.60	0.77	0.97	1.00	1.00

Q = quartz; C = calcite; D = dolomite; K = kaolinite

4.4. Mineralogical characterization

4.4.1. XRD Analysis

Six samples were performed by using XRD. The results show that the major minerals are quartz and calcite, whereas kaolinite and dolomite are secondary minerals (Fig. 4).

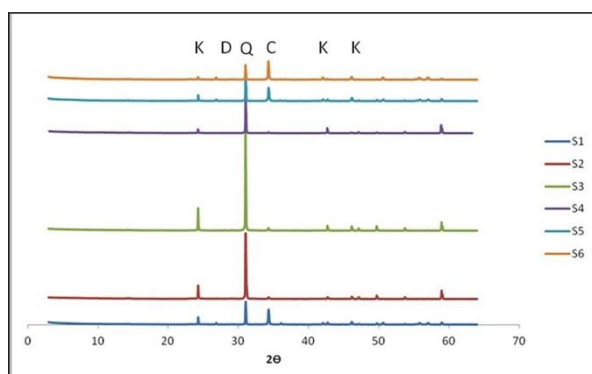


Figure 4. XRD results of major and secondary minerals of the sediments in LLRB. (Q=Quartz, C=Calcite, K=Kaolinite, D=Dolomite)

According to Figure 4, quartz is the dominant mineral in all of the tested sites particularly in site S3; while calcite occurs in site S1, and then leached in water and again reappears in sites S5 and S6. Calcite is decreased from the first two sites in the downstream of the river and the percentage of quartz is increased. This is due to the leaching of CaCO_3 by the agricultural soils. This soil is originated from sandy deposits, justifying the expressive contents of quartz in the sediments. The presence of kaolinite could be explained by the chemical weathering of primary minerals such as feldspar (KAISi_3O_8), which makes up the solid phase of all soils as described in Figure 4. Dolomite is present with low concentrations and occurs as a result of small leaching processes.

4.4.2. Granulometric Analysis

Granulometric analysis has been carried out for the sake of this study. The contents of sand, silt, and clay are shown in

Figure 5. The particle size distribution in the samples indicated that sand is the main constituent in all of the samples with an average of 66.5 %, whereas the average of silt content is 16.3 %, and clay reaches up to 17 %. The particle size constituent in the samples is sand; the least important constituent is clay except in site S6. The results show that the content of sand is important, and the content of silt and clay are gradually increased in sites S1, S5 and S6. Hence, this figure shows that the important content of the clay is present in site S6 with a high value of CEC due to the high clay content.

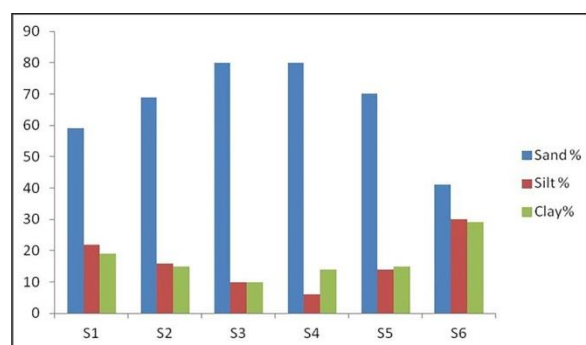


Figure 5. Sand, silt and clay contents in the investigated sites of the LLRB.

4.4.3. FTIR Analysis Frequencies

Minerals of quartz, calcite, kaolinite, dolomite and other components such as feldspar, organic compound are identified by comparing the observed wave numbers with the available literature (Ramasamy et al., 2009; Russell, 1987; Farmer, 1974). The relative distribution of major minerals can be quantified by calculating the extinction coefficient for the characteristic peaks of quartz and kaolinite at around 464cm^{-1} and 1032cm^{-1} , respectively, and for calcite at 1428cm^{-1} . In general, the amount of montmorillonite is less than kaolinite and less than quartz and calcite. The results of FTIR show the presence of montmorillonite and feldspar and some organic compounds (Table 6).

Table 6. Observed absorption wave numbers and corresponding minerals from FTIR spectra.

Mineral	Site	Observed wave (cm-1)
Quartz: SiO_2	S1- S2 S3- S4- S5-S6	468.6 -790-465.7-784 461.8-690.4 -463.7-691.4-1081 469.5-707-790
Kaolinite: $\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$	S1-S2- S3 S4- S5- S6	3694-3620- 3695-3621
Calcite: CaCO_3	S1-S2-S3-S4-S5-S6	1424-1425-1426-1427- 1428-1429
Montmorillonite $(\text{Na, Ca})_{0.3}(\text{Al, Mg})_2\text{Si}_4\text{O}_{10}(\text{OH})_2 \cdot n\text{H}_2\text{O}$	S1,S4,S5,S4	875.5-877.4-873.6-873.6
Feldspar $(\text{KAISi}_3\text{O}_8)$	S1,S2,S6	536-533-536
Organic compounds	S1,S5	2872.4-2514.7-2872.4

5. Assessment of Heavy Metal Contamination

5.1. Contamination Factor (Cf)

In this study, the Contamination Factor (Cf) or enrichment ratio (ER) and the degree of contamination (Cd) were used to determine the contamination level of the sediments by applying the following equations:

$$CF = \frac{(Cn)\text{Concentration of the heavy metal in the soil sample}}{(Bn)\text{Background concentration of the same metal}}$$

Or $CF = C_{\text{metal}}/C_{\text{background}}$

$EF = (\text{Metal}/RE)_{\text{Soil}} / (\text{Metal}/RE)_{\text{Background}}$

The maximum contamination factor was found in site S3, where the degree of contaminations is 38.88. The contamination factor $CF > 6$ indicates a very high contamination found in all sites: Site 3 by Cd, S5 by Cd, Fe, Ni, Pb and S6 by Cd, Pb, Fe and Mn. In all stations, the contamination factor was $(Cf) > 6$ for all of the tested heavy metals. The mean values of Cf are found: Cd: 25.67 (high contamination); Ni: 3.7 (Low contamination). On the basis of the mean values of

Cf sediments are enriched with metals in the following order: Cd> Pb >Fe > Ni (Table 7).

Table 7. Contamination factor (Cf) values for the sediments of the LLRB

Sample site	Cf									Contamination factor and level of contamination (Hakanson, 1980)	
	(Cu)	(Fe)	(Cd)	(Mn)	(Cr)	(Zn)	(Ni)	(Pb)	Cf	Contamination fact	Contamination Level
S1	0.5	0.045	5.05	0.90	0.08	0.75	0.17	0.47	7.42	Cf < 1	low
S2	0.08	0.4	16.17	0.86	0.29	0.39	0.17	0.1	17.20	1 ≤ Cf < 3	moderate
S3	0.05	0.88	36.37	0.41	0.29	0.04	0.19	0.65	38.88	3 ≤ Cf < 6	Considerable
S4	0.08	0.57	26.26	0.08	0.62	0.36	0.48	0.07	28.52	Cf > 6	Very high
S5	0.11	1.75	32.32	0.57	0.58	0.11	0.30	1.25	36.99		
S6	0.55	2.02	37.88	0.98	1.28	0.59	1.06	3.97	48.33		
Mean	0.23	0.94	25.67	0.49	0.52	0.37	3.7	1.08	29.55		

5.2. Assessment of Sediments According to Geoaccumulation index (I_{geo})

A common criterion to evaluate the heavy metal pollution in the sediments is the geo-accumulation index (I_{geo}), which was originally defined by Müller (1979). It is applied to determine metal contamination in the sediments by comparing current concentrations with pre-industrial levels and can be calculated by the following equation (Müller, 1979):

$$I_{geo} = \text{Log}2 = [C_n / 1.5B_n]$$

where C_n is the concentration of element 'n' and B_n is the geochemical background value. In this study, it was

considered that B_n=world surface rock average given by Martin and Meybeck (1979). The factor 1.5 is incorporated in the relationship to account for possible variation in the background data due to lithologic effects. The geo-accumulation index (I_{geo}) scale consists of seven grades (0-6) ranging from unpolluted to highly-polluted (Table 8). According to the Müller scale, the calculated results of I_{geo} values indicate that the Cd sediment quality is reported as very strongly polluted, I_{geo} is strongly to very strongly polluted in the sites: S3, S4, S5 and S6 (I_{geo}>6) for all stations, while as for the sites S1 and S2, sediment quality was recorded as moderately polluted (I_{geo}>2).

Table 8. I_{geo} –accumulation index values for the sediment samples of the LLRB.

Sample site	I _{geo}									Grade standards for I _{geo} (Rahman et al., 2012)		
	Cu	Fe	Cd	Mn	Cr	Zn	Ni	Pb	I _{geo}	I _{geo}	Class	Sediment quality
S1	0.10	8.9 ⁻³ ₁₀	1.01	0.18	0.01	0.15	0.03	0.09	1.58	<0	0	Practically Uncontaminated
S2	0.01	0.08	3.24	1.74 ⁻³ ₁₀	0.06	0.08	0.03	0.02	3.52	>0-1	1	Uncontaminated to moderate
S3	9.40.10 ⁻³	0.18	7.23	0.08	0.06	8.36 ⁻³ ₁₀	0.04	0.13	7.73	>1-2	2	Moderate
S4	0.02	0.12	5.27	0.02	0.12	0.07	0.09	0.01	5.72	>2-3	3	Moderate to strong
S5	0.02	0.35	6.49	0.11	0.12	0.02	0.06	0.25	7.42	>3-4	4	Strong
S6	0.11	0.41	7.60	0.19	0.26	0.12	0.21	0.78	9.68	>4-6	6	Strong to very strong

6. Conclusions

Heavy metal contamination in the Litani river sediments was assessed in this study. The results reveal significant information about heavy metal contents and physical characteristics of sediments from different sampling sites of the LLRB. The characteristics of quality sediment show that the sediments of LLRB have pH ranging between 7.4 and 8.09, which is slightly alkaline. EC ranged from 204 to 707µs/cm, while TDS varies from 94 to 352 mg/l.

The CEC is decreased in the sites in the following order (S6>S2>S1>S5>S3>S4), which indicates that agricultural

activities are present substantially in sites S6, S2 and S5.

The results obtained from the sediment analysis regarding the total metal concentrations for each site allowing for the arrangement of metals from a higher to a lower mean content as follows: Fe > Mn > Zn>Cr>Pb>Ni>Cr. The results show that the concentration of Cd was higher in all sediments which can affect human health and the environment as well, whereas the Fe, Pb and Ni were higher in sites 5 and 6 due to the higher slopping and deposition of pollutants in the tested sites as a result of waste water infiltration into the soil.

In order to evaluate the minerals in the sediments for the

collected samples, X-ray diffraction was carried out. XRD revealed that quartz and calcite are major minerals, whereas kaolinite and dolomite are minor minerals. Quartz is dominant in all of the selected sites, particularly in site S3, while calcite is present in site S1, and then leached in water and reappears again in sites S5 and S6. Calcite is decreased in the first two sites in the downstream of the river; the percentage of quartz is also increased. This can be attributed to the leaching of CaCO_3 by the agricultural soils.

The FTIR analysis shows that the amount of montmorillonite is less than that of kaolinite and is lesser than quartz and calcite. The results of FTIR shows the presence of montmorillonite and feldspar and some organic compounds. The presence of the solid minerals is related to weathering processes, while the organic materials are related to agricultural additives.

Heavy metal contamination of the sediments was assessed with respect to metal pollution load contamination factor of heavy metal concentration and Igeo-accumulated risk. Based upon the used indices, a proposed priority index (Pindex) was used to rank the utmost contaminated sites.

In the present study, the maximum contamination factor was found in site S3, where the degree of contamination is 38.88. Contamination factor, $C_f > 6$ indicates very high contamination for all sites (S3 with Cd, S5 with Cd, Fe, Ni and Pb and S6 with Cd, Pb, Fe, Mn). In all of the tested sites, there are a contamination factor (C_f) >6 for all of the tested heavy metals. The mean values of the C_f was found as: Cd: 25.67 (high contamination); Ni: 3.7 (low contamination). On the basis of the mean values of C_f , sediments are enriched by metals in the following order: $\text{Cd} > \text{Pb} > \text{Fe} > \text{Ni}$.

The calculated results of Igeo values indicate that Cd sediments are strongly polluted, Igeo is strongly to very strongly polluted in sites S3, S4, S5 and S6 (i.e. $\text{Igeo} > 6$) for all stations, while as for sites S1 and S2, the sediments' quality were recorded as moderately polluted (i.e. $\text{Igeo} > 2$). It can be argued that the high concentrations of heavy metals across different sites can be related to the industrial waste and agricultural additives. In can be concluded that in addition to the problem of water pollution by nutrients and bacteria, the heavy metal content in the sediments has become one of the most serious problems as well, because of heavy metal toxic effects even at minor concentrations.

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