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Assessing contamination Level of Heavy Metals in the Lake of Qaraaoun. Lebanon

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Abstract

Water pollution in the Lake of Qaraaoun became a common criterion and it has been exaggerated in the last few decades as a result of population growth and the changing climatic conditions. The Qaraaoun Lake is the largest artificial reservoir in Lebanon, which is located along the Litani River. It represents the connecting point between the Upper and Lower Litani River Basins. The study aimed at assessing the levels of heavy metals concentration of and their sources in the sediment of the Qaraaoun Lake at three representative sites during dry season of the year 2012.

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1. Introduction

With the over-expanding population in the Upper Litani River Basin in Lebanon, there is the urgency for proper conservation and efficient utilization of freshwater bodies for sustainable development. The population pressures in the basin caused an acceleration of the progressive deterioration of water quality, because of the increased domestic, municipal, agricultural and industrial activities, and effluent being discharged into water bodies and increase in environmental degradation resulting from urbanization.

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An impounded reservoir along the Litani River, the largest river in Lebanon, the Qaraaoun Lake (photo 1) exists to represent an important source of water supply for the downstream regions. The major environmental concerns are erosion, siltation and pollution of the river, garbage and human wastes and excreta disposal, effluents from industries, activities. In addition, agricultural activities in the basin have caused considerable damage to the environment and polluted the river. Human contact and use of the water for bathing, washing, swimming, irrigation and gardening are also intense in the basin.



Photo 1: Quarroun lake

Industrial wastes from agricultural processing factories and other industries are discharged into the river. This paper aims at assessing the present water quality of the upper Litani River at the Qaraaoun Lake in relation to agricultural and other activities in the basin.

2-Materials and methods

2.1- Sample collection

Six sampling sites were chosen (Table 1) along the lake. The selection of these sites was based, firstly, on the practicability of collecting sediments (especially accessibility) and secondly to describe the main activities of industries like dairy and poultry farms, tanneries, paper mills, wheat and potatoes plants, tourist and high vehicle movements located around the lakes. Table 1 summarized the characteristics for each of the sampling sites.

Table 1: Characteristics of sampling point.

Sites	Latitude	longitude	Possible pollution sources
Q1	33° 35' 32"	35° 41' 44"	Connection between the Litani River and Quaraaoun Lake
Q2	33° 34' 15"	35° 41' 00"	Site facing herbaceous vegetation, vineyards and olive tree
Q3	33° 33' 01"	35° 41' 02"	Near the equipment and industrial site
Q4	33° 32' 51"	35° 41' 50"	Opposite to the fruits, horticulture, olives tree and to the forest
Q5	33° 34' 06"	35° 42' 25"	Site facing horticulture, fruits and few little urban
Q6	33° 35' 43"	35° 42' 11"	Site facing to vineyards and Horticulture

Sediments were collected during dry season (July, august and September) of the year 2012. Approximately 2 kg of sediments were collected at each of the sampling sites at the sediment– water interface (surface river sediments) using a polyethylene bags. Sediment samples were dried at room temperature and sieved; the sediment size <65µm size was retained.

2.2- Sediment total metal digestion

The concentrations of heavy metals 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 of pore size 0.45µm before analyses using Standard Methods [1]. Sediment samples were digested using microwave digestion techniques as reported by Littlejohn et al (1991) in which 0.5mg of the sample was placed in Teflon vessel with 5ml HNO₃ (65%), 2ml HF (40%) and 2ml H₂O₂ (30%) by using Microwave digestion system (Model: MILESTONE mls-1200 mega). An aliquot of the filtration of the samples was taken (about 100 ml). Digestion solutions were measured for total heavy metals using ICP-OES [2].

Digestion extracts were used to analyze the total metal concentrations by AAS. Blanks containing all the components except sediment were analyzed to determine background interferences. All measurements were performed in triplicate and average values reported.

2.3 - Multivariate statistical method

The multivariate statistical analyses such as excel and Pearson's correlation, which was carried out by using SPSS16 of 2007, have been carried out to find out the interrelation among the parameters obtained from elemental and mineralogical analysis.

3- Result and discussion

3.1-Heavy metals in sediments

Sediment analysis plays an important role in assessing the pollution status, in terms of heavy metals content, of the environment [3]. The total metal concentrations for each sampling site found in sediments in this study are shown in Table 2. Heavy metals contents were ranging over following interval: Pb: 25.3-62.4 mg/kg; Cd: 0.99 - 2.8 mg/kg; Fe: 4.97- 9.73; Mn: 0.0234-0.0891 mg/kg; Cu: 36.1-77.4 mg/kg; Zn: 129.1-232.8 mg/kg; Cr: 132 -205mg/kg; Al: 8.56-12.3 mg/kg; Ca: 33.9- 59.8mg/kg; Ni:45-107 mg/kg; Mg: 1.12-1.44mg/kg dry weights, allowing to arrange the heavy metals from higher to lower mean

content in the study area as: Zn> Cr> Ni> Cu> Ca> Pb> Al> Fe> Cd> Mg> Mn. Figure 1 shows the major distribution of metals in sites.

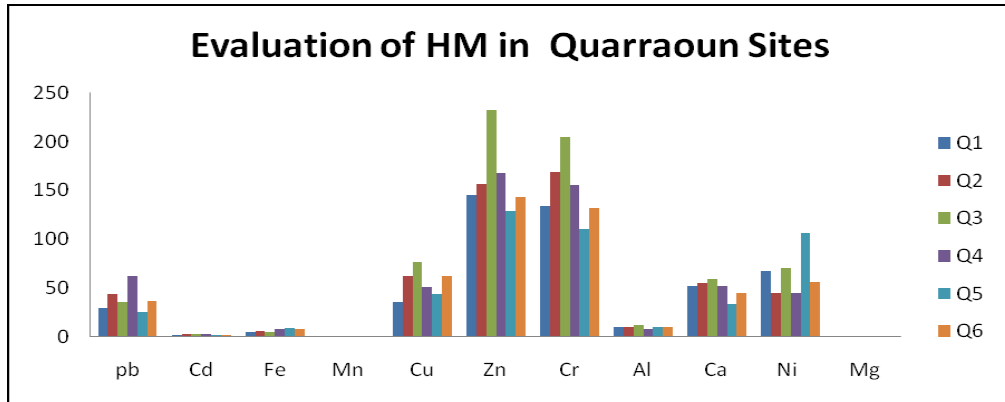


Figure 1: Distribution of metals in sediments.

It is clear that Pb content is more concentrated in the Q4, Fe in the Q5, Cu, Zn, Cr, Al, and Ca in the Q3 and Ni in the Q5.

Table 2: The Concentration of Metals

	Pb	Cd	Fe	Mn	Cu	Zn	Cr	Al	Ca	Ni	Mg
Q1	29.7	1.9	5.19	0.087	36.1	145.2	134	9.86	52.5	68	1.44
Q2	44.5	2.7	5.99	0.089	62.1	156.7	169	9.92	55.3	45.1	1.4
Q3	35.5	2.8	4.97	0.075	77.4	232.8	205	12.3	59.8	71	1.32
Q4	62.4	2.7	8.42	0.068	51.2	168.2	156	8.56	51.9	45	1.12
Q5	25.3	2.3	9.73	0.025	43.7	129.1	111	9.8	33.9	107	1.24
Q6	36.7	2.5	7.71	0.023	62.1	143.1	132	10.1	45.3	56	1.42
Mean	39.0	2.4	7	0.06	55.4	162.5	151	10.9	49.7	65.3	1.3
GBSQG*	36	0.99	20.0	460	32	120	43	-	-	23	-

* GBSQG = (Wisconsin Department of Natural Resources, 2003).

The contamination of sediment by heavy metals was evaluated by comparison their mean with the sediment quality guideline proposed by Consensus-Based Sediment Quality Guidelines of Wisconsin [4]. According to United States Environmental Protection Agency (USEPA), the resulted data from this study was compared accordingly to figure out the status of heavy metal contents (Table 3).

Table 3: EPA Guidelines for sediments (Mg/kg dry weights)

Metals	Not polluted	Moderately polluted	Heavily pollutes	Present study
Pb	<40	40-60	>60	25.3 -62.4
Cd	-	-	>6	0.99 – 2.8
Cr	<25	25-75	>75	132 – 205
Cu	<25	25-50	>50	36.1- 77.4
Zn	<90	90-200	>200	129.1- 232.8
Ni	11	-	57	45- 107

Thus, the chemical contaminations in the sediments were evaluated by comparison with the sediment quality guideline proposed by USEPA (Table 3).

The present study shows that all investigated sites are characterized by moderate to heavily pollute by Pb and Zn, heavily for Cr and Ni and Cu and Zn are moderately polluted to heavily.

3.2 - Assessment of heavy metals contamination by Index of geo-accumulation (Igeo)

In order to assess the degree of contamination in the Quarsaoun Lake; however, the geo-accumulation (Igeo) are used. It is a common criterion to evaluate the heavy metal pollution in sediments, which was originally defined by to determine metals contamination in sediments, by comparing current concentrations with pre-industrial levels and can be calculated by the following equation [5].

$$I_{geo} = \text{Log } 2(C_n/1.5B_n)$$

Where, C_n is the concentration of element 'n' and B_n is the geochemical background value [In this study we considered B_n =world surface rock average given by [6] The coefficient 1.5 is incorporated in the relationship to account for possible variation in background data due to lithogenic effect. The geo-accumulation index (Igeo) scale consists of seven grades (0-6) ranging from unpolluted to highly pollute (as shown in Table 4).

In the present study, the Igeo were calculated from the concentrations of the heavy metals in the sampling points in the study area.

According to the Muller scale, the calculated results of Igeo values (as shown in Table 5) indicated that all the selected sites are considered as unpolluted to moderately pollute. The heavy metals (i.e. Pb, Cd, Fe, Mn, Cu, Zn, Cr, Ni) content presented in sediments of Qaraaoun was recorded as unpolluted for all stations because $0 < I_{geo} < 1$.

Table 4: Muller's Classification for the GEO-Accumulation index.

Igeo Value	Class	Sediment Quality
<0	0	Unpolluted
0-1	1	From unpolluted to moderate polluted
1-2	2	Moderately polluted
2-3	3	Moderately to strongly polluted
3-4	4	Strongly polluted
4-5	5	Strongly to extremely polluted
>6	6	Extremely polluted

Table 5: Geo-Accumulation Index Values for the sediments samples of the Qaraaoun Lake.

Site	Igeo Index									
	Pb	Cd	Fe	Mn	Cu	Zn	Cr	Al	Ca	Ni
Q1	0.16	0.38	0.05	0.00	0.22	0.24	0.62	-	-	0.88
Q2	0.24	0.54	0.08	0.00	0.58	0.39	1.18	-	-	0.59
Q3	0.19	0.56	0.07	0.00	0.72	0.58	1.43	-	-	0.92
Q4	0.34	0.81	0.08	0.00	0.47	0.42	1.08	-	-	0.58
Q5	0.14	0.69	0.09	0.00	0.40	0.32	0.77	-	-	1.40
Q6	0.20	0.50	0.07	0.0	0.58	0.27	0.92	-	-	0.79

3.3- Correlation Coefficient

Pearson's correlation coefficient matrix among the selected site for investigating heavy metals is presented in the Table 6. Significant correlations between the contaminants of Cd and Cu ($r=0.84$), Cd and Cr ($r=0.70$), Mn and Ca ($r=0.83$), Cu and Zn ($r=0.79$), Cu and Cr ($r=0.79$), Cu and Al ($r=0.69$), Zn and Cr ($r=0.93$), Zn and Al ($r=0.72$), Zn and Ca ($r=0.75$), Cr and Ca ($r=0.88$), could indicate the same or similar source inputs.

4. Conclusion

The results of this study provide valuable information about heavy metal contents and the physical characteristics of sediments from different sampling sites of the Qaraaoun Lake. The order of the mean concentrations of tested heavy metals were: Zn > Cr > Ni > Cu > Ca > Pb > Al > Fe > Cd > Mg > Mn, and this conducted to conclude that Pb are more concentrated in the Q4, Fe in the Q5, Cu, Zn, Cr, Al, and Ca in the Q3, Ni in the Q5. The correlations between metals indicate that the same source of pollution which is anthropogenic (human activities and agricultural).

According to USEPA: all the sites are moderate to heavily polluted for Pb and Zn, heavily polluted for Cr and Ni and moderately polluted to heavily for Cu. All the sites are ranges over no-polluted to moderately polluted condition. According to the analyze of *Igeo* present between 0 and 1 this meaning that all the sites of Qaraaoun lakes are consider as unpolluted to moderately polluted.

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