Metal concentrations in river water and bed sediments of the Lower Litani River Bassin, Lebanon

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ABSTRACT

The distribution of pollutants in the Litani River is almost severe. It resulted from domestic, sewage, agricultural and industrial sources. In this study, the distribution of metals (Cu, Fe, Cd, Mg, Zn, Pb , Al, Ba, Ni, Mn, Ag and Cr) were measured in river water and the bed sediments of the Lower Litani River Basin (LLRB). The impacts of metals on the water quality were monitored during the rainy, mid rainy and dry season in the year 2012. The objectives of this study were first to identify possible sources of metals (i.e. geological and/or anthropogenic) and then to characterize the chemical behavior of these metals in water and bed sediments. Water and bed load sediments were sampled at six sites along the LLRB main watercourse, The metal concentrations in the river sediments were remarkably high, but varied between different sampling sites, and the concentrations in water were mainly within the permissible limits. The metal contents in bed sediment were highest during closure of summer period. By applying the principal component analysis applied to total and extractable metal contents as a tool for studying metal pollution in the LLRB, it was useful to distinguish between anthropogenic and natural sources.

Keywords

Litani River; water; sediment; zinc; contamination; seasonal variations.

Academic Discipline And Sub-Disciplines

Physical chemistry, sediment, river water, pollution;

TYPE (METHOD/APPROACH)

Physico-chemical properties of river water

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INTRODUCTION

Most environmental regulations have established limitations for the total heavy metal concentration in water, thus they must not exceed some quality criteria for the protection of the environment and human life Sediments act as a major source of heavy metals [1] and also as a source of Contaminants.Thus, the determination of the extent of pollution by a given heavy metal requires that the pollutant metal concentration must be compared with an unpolluted reference material. Lebanese rivers are subjected to pollution from many sources [2] and development of an effective water usage strategy requires effective pollution remediation and, in turn, better information on the geochemical properties of the rivers and their capacities for self Purification.

The Litani River drains nearly one fifth of the waters of Lebanon and has a 2170 km^2 watershed that extends between latitudes $33^0 50'$ N and longitudes $35^0 15'$ E. Geomorphologically, the Litani River Basin is divided into two sub-basins (Figure 1), with the upper one stretching from the Bekaa plain to the Qaraoun dam and the lower part extended from the Qaraoun dam to reach the coast [3].
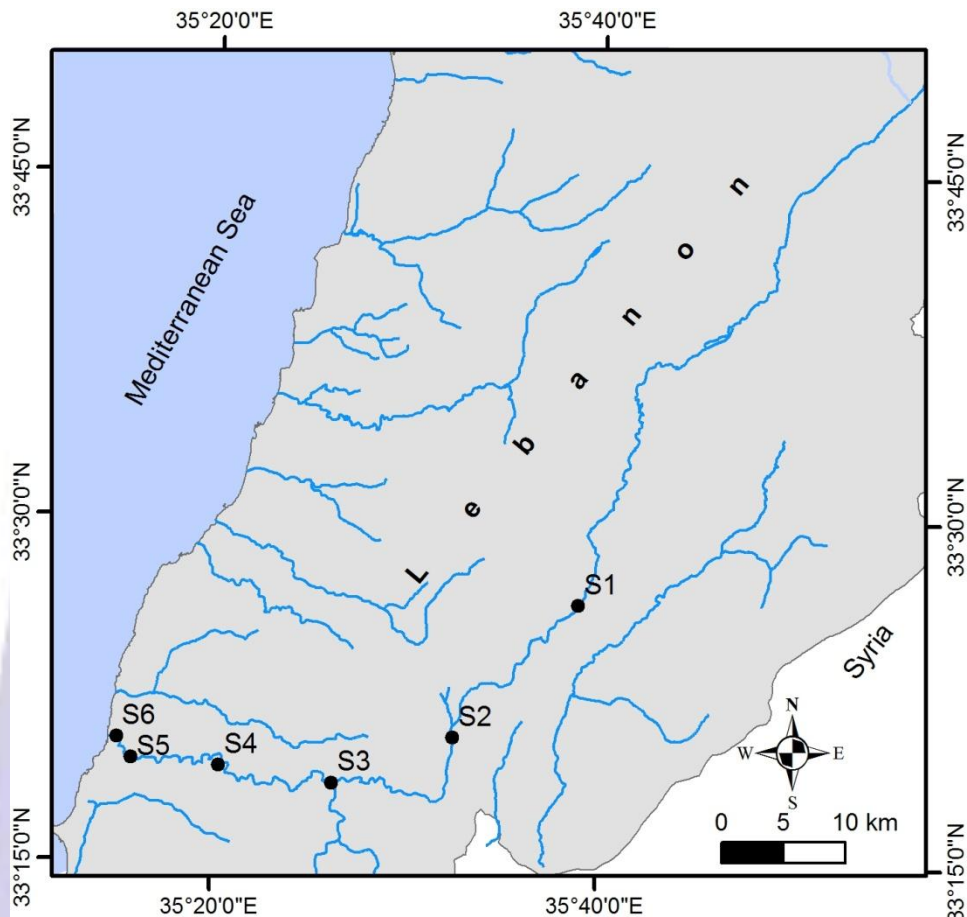

Fig. 1: The study area of the Lower Litani River Basin(LLRB).

The LLRB consists of one primary river course and eight secondary branches; It encompasses eight districts or administrative Caza hosting a population of about 133,000 persons [4]. Previous research in our laboratory showed that The major sources of pollutants are local anthropogenic activities, agricultural runoff due to a high level of NO_2^-, Fe and $CaCO_3$ [5].

For much of the year pollutants enter the fluvial system will be incorporated into bed sediments by precipitation and sorption over the surface layer of static bed sediments.

Sediments are a habitat and major nutrient source for aquatic organisms. Sediment analysis is

important in evaluating qualities of total ecosystem of a body of water, in addition to water sample analysis practiced for many years because it reflects the long term quality situation independent of the current inputs [6].

Heavy metals are among the most common environmental pollutants, and their occurrence in water and sediments indicates the presence of natural or anthropogenic sources. The main natural sources of metals in waters are chemical weathering of minerals in rocks and soil leaching. The anthropogenic sources are associated mainly with industrial and domestic effluents, urban storm, water runoff, landfill, atmospheric sources and inputs rural areas [7-9].

The aim of the current study is to clarify the spatial and temporal variations in heavy metal concentrations including Copper (Cu), Iron (Fe), Cadmium (Cd), zinc (Zn), Plomb (Pb),Magnesium (Mg) ,Aluminum (Al), Barium (Ba), Nickel (Ni), Manganese (Mn), Silver (Ag), Chrome (Cr), in surface water and bed sediment in LLRB in Lebanon. Furthermore, the role of

pollution sources in the LLRBL on the water quality was assessed as well as the relationships between metal concentrations was analyzed.

MATERIALS AND METHODS

The study area

For water and bed sediments sampling, six sampling sites were selected along the LLRB (Table 1) describe the major activities. This was done during the rainy, mid rainy, dry seasons of 2012.

Table 1. Location and description of the study sites in LLRB

Sampling site	Symboles	Latitude	Longitude	Major activities
Qelia	S1	$33^{o}26'21"$ N	$35^{o}38''55'E$	Quarry site and Touristic zones pumping stations.
Kardali	S2	$33^{o}20'$ 34'N	$33^{o}32'34"$ E	Agriculture and touristic zone.
Kaekaeyat eljisr	S3	$33^{o}18'$ 31'N	$35^{o}26'18"$ E	Touristic and agriculture zone small village
Tair flsaiy	S4	$33^{o}19'10N$	$35^{o}20'27'$ E	Touristic zone.
Abou abdellah	S5	$33^{o}19'26"$ N	$35^{o}15'50'$ E	Vegetated sites with citrus tree
Qasmieh	S6	$33^{o}20'$ 22"N	$35^{o}15'04"E$	Road with high traffic density, irrigation canal and agricultural zone with banana.

These sites were selected because they receive considerable amounts of waste water from the surrounding industrial areas, as well as from intensively cultivated agricultural areas and domestic wastes from towns and villages.

Water and bed sediment sampling, chemical and statistical analysis

Six water and bed sediment samples were collected once in three times before, during rainy, mid rainy, dry periods from February to September 2012. For the water, six water samples were collected in a 1-l polyethylene bottles soaked overnight with 10% (v/v) nitric acid was used for water sampling collection. The samples were filtered by filtration system through membrane filter of pore size 0.45 μm before analyses using Standard Methods [10].

The method of sampling and collection are in accordance with Standard Methods APHA, AWWA, WPCF [10]. The samples were transported to the laboratory in portable coolers. Thus, pH, electrical Conductivity and Total Dissolve Solid were estimated directly at the sampling sites. While the other nutrients parameters were measured in the laboratory.

Samples were analyzed for water quality indicators including: pH, total dissolved solids (TDS), conductivity (EC),

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 solid impurities before testing (AOAC 974.27).

Bed sediment samples were digested using microwave digestion techniques as reported by [11] in which 0.25 gm of each 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- 200 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 [12].

Correlation coefficients were calculated between all pairs of the measured element concentrations. Multivariate statistical analyses such as Pearson correlation analysis, Factor analysis (FA) were performed to reflect the degree of dispersion distribution of different metals Pearson's correlation analysis was carried out by using SPSS16 2007.

RESULTS AND DISCUSSION

Metals in water

The means of element concentrations in the water samples are presented in Table 2. The results showed that, most of the heavy metal concentrations are in surface water of LLRB. The mean values of the elements at different sites showed that Fe is the most abundant element in all points followed by Pb, Cd, Cr, Ag, and Ni. The concentrations of Ba, Ni, Al, Zn, Mg, Cu are within the norms (Table 2).

Table 2. The element concentrations measured from the water samples (mg/L).

Heavy metal	Period	S1	S2	S3	S4	S5	S6	WHO (2006)	Libnor (1999)
Cu	RS	0.02	0.2	0.2	0.2	0.2	0.2		
	MRS	0.03	0.05	0.1	0.05	0.02	0.2		
	DS	0.05	0.05	0.05	0.05	0.05	0.05		
	Mean	0.03	0.10	0.12	0.10	0.09	0.15	1 mg/L	1 mg/L
Fe	RS	1	6	3	2	7	6		
	MRS	1	11	1	1	2	2		
	DS	0.02	0.08	0.09	0.04	0.04	0.08		
	Mean	0.67	5.69	1.36	1.01	3.01	2.69	0.3 mg/L	0.3 mg/L
Cd	RS	0	0.1	0.1	0.1	0.1	**0.1**		
	MRS	0.01	0	0	0.01	0.02	0.02		
	DS	0.01	0.02	0.02	0.02	0.02	0.02		
	Mean	0.01	0.04	0.04	0.04	0.05	0.05	0.005 mg/L	0.005 mg/L
Mg	RS	1	1	1	1	1	**1**		
	MRS	1	1	1	1	1	1		
	DS	2.02	2.87	1.62	3.26	11.37	12.19		
	Mean	1.34	1.62	1.21	1.75	4.46	4.73	50 mg/L	50 mg/L
Zn	RS	0.5	0.3	0.2	0.2	0.2	0.2		
	MRS	0.5	0.3	0.3	0.2	0.2	0.2		
	DS	0	0.02	0.03	0.03	0.02	0		
	Mean	0.33	0.21	0.18	0.14	0.14	0.13	5 mg/L	5 mg/L
Pb	RS	0.1	0.07	0.09	0.1	0.07	0.1		
	MRS	0.1	0.07	0.09	0.1	0.07	0.1		
	DS	0.01	0.07	0.06	0.05	0.21	0.05		
	Mean	0.07	0.07	0.08	0.08	0.12	0.08	0.01 mg/L	0.01 mg/L
Al	RS	0.02	0.03	0.04	0.05	0.05	0.05		
	MRS	0.02	0.03	0.04	0.05	0.05	0.05		
	DS	0.05	0.08	0.07	0.05	0.01	0.01		
	Mean	0.03	0.05	0.05	0.05	0.04	0.04	0.2 mg/L	0.2 mg/L
Ba	RS	0.05	0.05	0.03	0.03	0.02	0.08		
	MRS	0.05	0.05	0.03	0.03	0.02	0.08		
	DS	0.06	0.03	0.03	0.04	0.08	0.12		
	Mean	0.05	0.04	0.03	0.03	0.04	0.09	0.5 mg/L	0.5 mg/L
Ni	RS	0.02	0.02	0.01	0.01	0.01	0.01		
	MRS	0.02	0.02	0.01	0.01	0.01	0.01		
	DS	0	0.01	0.02	0.01	0.01	0.01		
	Mean	0.01	0.02	0.01	0.01	0.01	0.01	0.02 mg/L	0.02 mg/L
Mn	RS	0	0	0.01	0	0	0.01		
	MRS	0	0	0.01	0	0	0.01		
	DS	0	0.01	0.01	0	0.01	0.01		
	Mean	0.00	0.00	0.01	0.00	0.00	0.01	0.05 mg/L	0.05 mg/L
Ag	RS	0.02	0.02	0.02	0.02	0.02	0.02		
	MRS	0.02	0.02	0.02	0.02	0.02	0.02		
	DS	0.02	0.02	0.02	0.02	0.02	0.02		
	Mean	0.02	0.02	0.02	0.02	0.02	0.02	0.01 mg/L	0.01 mg/L
Cr	RS	0.1	0.1	0.1	0.1	0.1	0.1		
	MRS	0.3	0.1	0.15	0.02	0	0.01		
	DS	0	0.01	0.01	0.01	0.01	0.01		
	Mean	0.13	0.07	0.09	0.04	0.04	0.04	0.05 mg/L	0.05 mg/L
PH	**Mean**	8.1	8.2	8.4	8.5	8.4	7.8	6.5-8.5	6.5-8.5
TDS	**Mean**	299	233.6	279.75	272.5	335	300.7	500 mg/L	500mg/L
Ec	**Mean**	587.5	446.1	473.7	475.5	627.5	561.2	1500 µs/cm	1500 µs/cm

(RS): Rainy season; (MRS): Mid rainy season; (DS) Dry season.

Metals such as Ba, Ni, Al, Zn, Mg, Cu were found within the permissible limits according to WHO [13] and Libnor. It was found that agricultural and industrial activities are mainly responsible for high levels of the measured elements in river water. The Fe concentrations were highest at the sites of (S2) and (S5) because of the presence of cultivated land and wastes water.*.*

Generally, given heavy metals concentrations were higher during summer closure period, which is due to lower

discharging rates of water and the elements adsorb and precipitate on the sediment particles resulting from low pH values and microbial activity [14].

Table 3 shows that the concentrations of Mg and Zn during the rainy season were higher than those after the dry period, because of the increased consumption of this element by the phytoplankton [15].

Much correlation occurs during this study, Cd was significantly positively correlated with Cu (r=0.85) and Fe (r=0.45) (Table 3) and this is due to the same source origin of contamination. The major sources of these elements in fresh water include atmospheric deposition, manufacturing processes related to chemicals and metals, is the discharges of municipal waste and domestic wastes and atmospheric deposition.

Table 3. Correlation coefficient matrix for metals of water during the period of 2012

	Cu	Fe	Cd	Mg	Zn	Pb	Al	Ba	Ni	Mn	Ag	Cr
Cu	1.00											
Fe	0.29	1.00										
Cd	**0.85**	0.45	1.00									
Mg	0.46	0.22	**0.64**	1.00								
Zn	-0.83	**-0.20**	-0.95	**-0.59**	1.00							
Pb	0.09	-0.05	0.54	**0.65**	-0.51	1.00						
Al	**0.58**	0.34	0.55	-0.27	-0.57	-0.09	1.00					
Ba	0.37	0.10	0.16	**0.65**	-0.11	-0.11	-0.47	1.00				
Ni	0.02	**0.87**	0.66	-0.27	0.14	-0.35	0.40	-0.15	1.00			
Mn	**0.64**	-0.34	0.39	0.23	-0.59	-0.18	0.30	0.36	-0.40	1.00		
Ag	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	
Cr	-0.69	-0.32	**0.90**	-0.67	**0.94**	-0.52	-0.45	-0.18	0.02	-0.54	0.00	1.00

The correlation was positively between Fe and Zn (0.34); Mg and Mn (r = 0.40); Ba and Mn (r = 0.39). The negative correlation between Mg and Zn concentrations because they are not from the same sources of pollution (*r* = –0.53) is may be a result of precipitation of the elements as hydrous metal oxides [16].

Principal component analysis

Despite that the pollution at some sites being explained, multivariate analysis must be applied so as to unambiguously describe the pollution sources for each metal. By applying of the multivariate technique of principal components analysis to the matrix of 12 features (total concentration of Cd, Cr, Ni, Pb and Cu…) and 6 samples of the LLRB, four components were extracted describing approximately 97.53 % of the common variance (Table 4).

Table 4. Factor loadings of elements data in the water samples

Variables	F1	F2	F3	F4
Cu	-0.87	0.11	0.24	**0.28**
Fe	-0.33	**0.72**	-0.56	0.24
Cd	-0.97	0.15	-0.08	-0.11
Mg	-0.70	-0.46	-0.53	**0.10**
Zn	**0.97**	-0.01	-0.15	0.17
Pb	-0.47	-0.29	-0.48	-0.68
Al	-0.48	**0.70**	0.49	-0.18
Ba	-0.30	-0.48	-0.28	**0.78**
Ni	0.06	**0.90**	-0.29	0.29
Mn	-0.56	-0.32	**0.66**	0.31
Ag	0.00	0.00	0.00	0.00
Cr	**0.94**	-0.02	0.03	0.11
Eigenvalues	**5.00**	**2.48**	**1.75**	1.47
%Variance	**45.54**	**22.59**	**15.96**	13.44
% cumulative	**45.54**	**68.12**	**84.08**	97.53

Table 4. shows that F1 describe 45.54 % of the common variance and is highly loaded by Zn, Cr, Ni and is the negatively correlated with Mn and Mg. F2 describes 22.59% of the common variance and is highly loaded by the elements Fe, Al, Cu and Cd. F2 is negatively correlated with Pb , Mn, Ag and Ba. The third factor F3 describes 15.98 % of the common

variances of data and positively correlated with Mn, F4 describes 13.44% of the common variances of data and positively correlated with Ba, Mn, Fe, Mg and Cu.

The results in the Figure 2 show that the classification by seasons is not important and this appear in the Figure 2, for examples the class1\3 contains S2 RS, S2 MR, S1 RS and S3 MRS and not all the selected sites of winter selection. This class1\3 was found in positive side of the axis of F11 and have the same character.

The class 3\3 opposite to F1 and F2 was found in the negative site and the class 1\3 and class2\3 are in the positive site of F1 and F2 , the effect of parameters varies by seasons due to the variation in temperature as well as the rainfall periods and the different source of pollution.
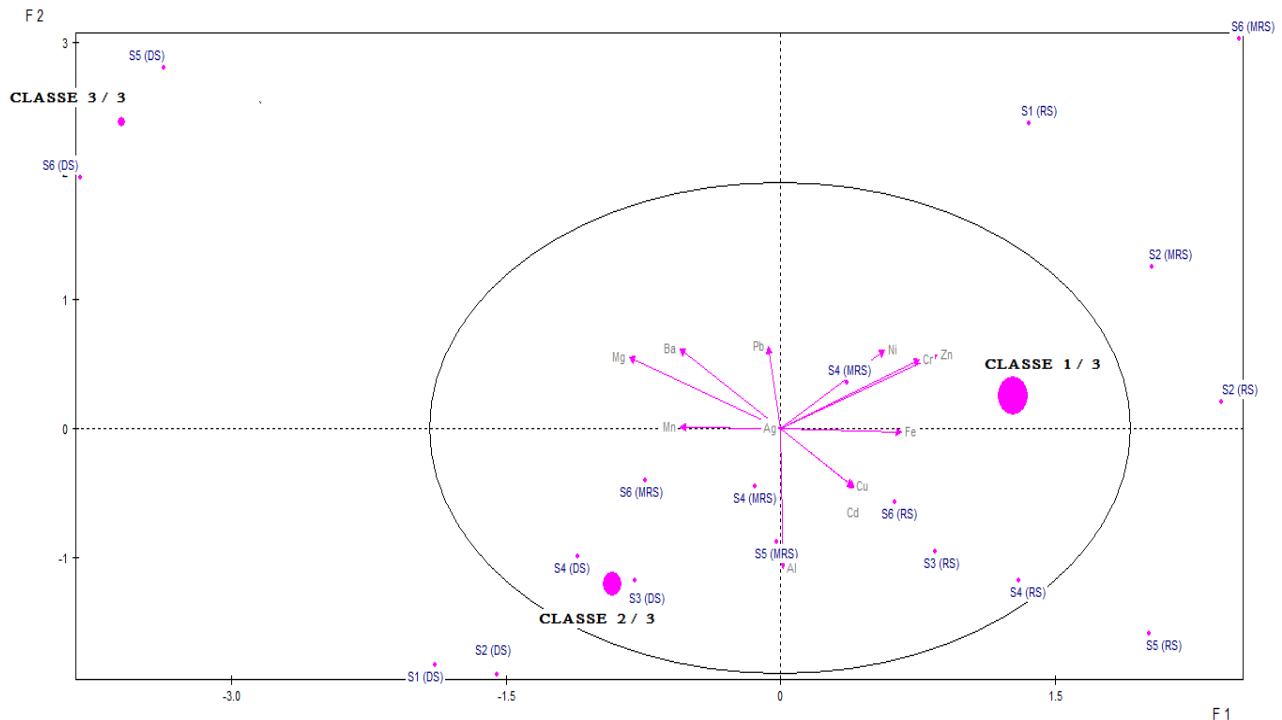

Fig. 2: Factorial F1, F2 classification by season.

Figure 2 shows that the distribution in the first class is characterize by the presence of Zn, Cr, and Ni is characterized by the presence of many industries and the reject of waste water without recycling (Cr),

In the third class were found in the positive site of F2 and negative site of the axis of F1 and which are characterize by the presence of Pb, Mn, Mg and Bawhich are the main natural characteristics of the water in the site S4,S5,S6.

Site S1 is characterized by the presence of Zn and Cr, than the site S2 and S3 has the main source of pollution Ni in the opposite site S4, S5 and S6 is characterize by the presence of Pb, Mn, Mg and Ba.

Fe, Cu⁻, Cd and Al , is present in the S6, S3 and S4, this is normal in the sites because all around villages reject their waste without any treatment.

HEAVY METALS IN SEDIMENTS

Sediment analysis plays an important role in assessing the pollution status of the environment [17] the analysis of heavy metals levels in sediment samples helps in the interpretation of water quality [18].

Many heavy metals concentrations in sediment; especially in the fine grained sediments which act as a transport agent in the water column, are at least three orders of magnitude higher than the same metals in surrounding water [8].

Resulted data from sediments can provide information on the impact of distant human activity on the wider ecosystem. The composition of sediment sequences provides the best natural archives of recent environmental changes.

Determination and speciation of heavy metals pollution is one of a primary target in environmental research [19, 20].

Therefore, the analysis of heavy metals in sediments enables the detection of pollution deteriorating water quality and provides information about the "critical sites" of the water system [21, 22].

Variations in the contents of studied elements in the river bed sediment were observed to be as following: Cu:0-44 mg kg–1, Fe: 980-26000mg kg^{-1} , Cd: 2-18 mg, Mg: 600-5366 mg kg^{-1},Zn :2-224 mg kg^{-1}, pb:0-106 mg kg^{-1}, Al: 3200–35962m g kg–1, Ba: 10–680 mg kg^{-1}, Ni: 4–24 mg kg^{-1}, Mn: 30-760 mg kg^{-1}, Ag: 10–34mg kg^{-1}, Cr: 2–60. mg kg^{-1}, respectively, in each time period (Table 5).

Table 5. The element contents in bed sediment samples along LLRB (mg kg⁻¹, dry weight). RS: Rainy season, MRS: mid-rainy season, DS: dry season: After winter period, ISQGs: Interim freshwater sediment quality guidelines, No guideline available: *):

Heavy metal	Period	S1	S2	S3	S4	S5	S6	CBSQG, Mg Kg⁻¹	ISQG, Mg Kg⁻¹
Cu	RS	10	40	20	40	0	0		
	MRS	14	42	100	30	134	60		
	DR	14	0	0	0	0	14		
	Mean	12	28	40	24	44	24	32	35.7
Fe	RS	980	1636	1200	7000	12000	4800		
	MRS	980	14000	20000	10000	20000	26000		
	DS	980	15118	22398	10920	20040	30954		
	Mean	980	10252	14532	9306	17346	20584	*	20000
Cd	RS	2	10	10	10	10	10		
	MRS	2	6	4	10	6	8		
	DS	2	14	32	22	34	36		
	Mean	2	10	16	14	16	18	0.99	0.6
Mg	RS	1000	1000	600	800	4000	1800		
	MRS	600	800	800	800	4000	4600		
	DR	600	776	1068	666	4566	5366		
	Mean	734	858	822	756	4188	3922	*	*
Zn	RS	80	224	200	60	60	40		
	MRS	80	10	10	6	20	6		
	DS	80	54	2	26	12	68		
	Mean	80	96	70	30	30	38	120	123
Pb	RS	14	88	100	20	100	100		
	MRS	14	0	20	0	20	80		
	DR	14	0	22	0	40	136		
	Mean	14	30	48	6	54	106	35	35
Al	RS	4000	3600	4000	3200	6000	28000		
	MRS	8000	3400	10000	4800	15400	20000		
	DR	8000	3536	10976	5528	15418	35962		
	Mean	6666	3512	8326	4510	12272	27988	*	*
Ba	RS	20	230	60	100	40	40		
	MRS	32	10	24	10	98	680		
	DR	32	28	38	14	98	670		
	Mean	28	90	40	24	78	464	500	750
Ni	RS	4	4	4	4	4	4		
	MRS	4	4	4	10	6	24		
	DR	4	4	4	10	6	24		
	Mean	4	4	4	8	6	18	23	*
Mn	RS	432	760	400	200	400	600		
	MRS	200	324.16	294.06	698.44	486.34	464.1		
	DR	432	30	180	38	272	452		
	Mean	354	372	292	312	386	506	460	*
Ag	RS	10	26	10	10	10	10		
	MRS	10	10	10	20	10	10		
	DR	14	34	14	20	14	14		
	Mean	12	24	12	16	12	12	*	*
Cr	RS	2	10	10	10	20	40		
	MRS	36	8	38	46	44	60		
	DR	2	10	10	28	20	60		
	Mean	14	10	20	28	28	54	43	37.3

(RS): Rainy season; (MRS): Mid rainy season; (DS) Dry season

The mean concentrations of the heavy metals in sediment in rainy, mid-rainy and dry season were higher than the values recommended in Consensus-Based Sediment Quality Guidelines of Wisconsin (CBSQG) [23] and ISQGs: Interim freshwater sediments quality guidelines as shown in Table 5.

The mean concentrations of Cd, Mg, Al, Ba, Ni and Ag were higher in the dry season than in the wet season probably due to the dilution by rainwater which influences concentration and heavy metal mobility.

However, it has been reported that mobility of heavy metals depends not only on the total concentration in the soil and sediments but also on the soil or sediment properties themselves, metal properties and environmental factors.

According to the Table 5, the concentration of iron in Site 1 was not varied during the 3 sampling, but we showed that the effect of season is important because the concentration of Fe increase during the dry season, and thus conduct to conclude that the presence of Fe in sediments is geologically derived.

The high concentrations of Fe that was found in the sediments may be mainly resulted from the natural deposits and industry, where Fe is one of the chemicals used for drilling operations.

Cd may be explained by the fact that Cd in sediments is associated with the carbonate fraction and concentrates on the suspended matter in water [24].

Domestic and industrial effluents are the major sources of the observed high level of Pb,Zn, Co, Cu, and Cr are mainly precipitated as soluble oxide [25].

It was concluded that water pH (7.8–8.5) was typical for a river located on a karstic rock exposures, that Fe in the sediments was derived from geological sources, whereas Cu, Pb and Zn were anthropogenic in their origin.

The high concentrations of the studied elements may be attributed to the effect of intrusion of water borne Fe, Mg, Cu, Zn, Pb and Cd derived from agricultural, domestic and industrial effluents, and the small grain size of the sediment facilitates the adsorption of these metals to bed sediments.

Table 6 shows that there are many metals positively correlated together and this explained by their capacity of retention by the sediment. Positive correlation coefficients are observed among the metals Cu, Fe, Cd, pb, Al and other elementals such as Zn which have very low correlation.

Table 6. Correlation coefficients for elements in the bed sediment during the three   seasons of 2012.

	Cu	Fe	Cd	Mg	Zn	Pb	Al	Ba	Ni	Mn	Ag	Cr
Cu	1.00											
Fe	**0.66**	1.00										
Cd	**0.69**	**0.93**	1.00									
Mg	0.39	**0.76**	0.57	1.00								
Zn	-0.28	-0.53	-0.64	-0.63	1.00							
Pb	0.28	**0.84**	**0.64**	**0.78**	-0.31	1.00						
Al	0.03	**0.71**	0.54	**0.79**	-0.47	**0.94**	1.00					
Ba	-0.12	**0.65**	0.47	**0.65**	-0.29	**0.89**	-0.94	1.00				
Ni	-0.17	**0.62**	0.54	0.62	-0.56	**0.77**	**0.90**	**0.93**	1.00			
Mn	**-0.17**	0.53	0.27	**0.75**	-0.26	**0.80**	**0.87**	**0.92**	0.82	1.00		
Ag	-0.09	-0.20	-0.19	-0.41	**0.52**	-0.35	-0.49	-0.18	-0.28	-0.12	0.00	
Cr	0.04	**0.72**	**0.67**	**0.73**	-0.73	**0.79**	**0.92**	**0.86**	**0.96**	0.74	- 0.47	1.00

High correlation coefficient between Cd and Fe (r = 0.93); Cd and Cu (r = 0.69); Al and Fe (r = 0.71); Cr and Fe (r = 0.72) and Fe and Mg (r = 0.76) oxides can play a role in the retention of trace metals and this explained by their origin from the same source (i.e. industry, urban origin and transport). Thus, Cd, Fe, Mg and Cu appear to be associated with to discharges from urban origin, which typically contains large amounts of organic matter.

The given elements, such as Cr, Cd and Ni have interacted with organic matter in the aqueous phase and settled resulting in a high concentration of these elements in the sediment [26, 27].

Negative correlation means that the metals do not have common sources and this might be due to the variation in the sources.

Factors analysis

The factors analysis is a tool for the recognition of variables structures and for differentiation evaluation of pollution in the sediments. Principal component analysis for the sediments of LLRB is shown in Table 7. It includes loading for the rotated component matrix, eigenvalues for each component, per cent and cumulative per cent of variance explained by each component. It indicates that the three principal components together account for 90.56% of the total variance in the data set, in which the first principal component is 62.96%, second principal component is equal to 17.43%, and the third principal component is 10.17%. The first factor is positive loaded by Zn, Ba, Ag and negatively loaded by Fe, Cd, Mg, Pb, Al, Ni, Mn and Cr.

Ni and Cr are probably associated with industrial effluents (e.g. chromium-plating). While Cd behaves different source than the other two groups. This metal appears in the most mobilisable fractions in many sampling points and a variety of pollution sources may contribute to the Cd existence in the sediments.

The results shown in the Figure 3 reveal that the classification of class (i.e. season) is not important and this appears in the Figure 2. For examples, the class1\3 contains S1 MRS, S1 DS, and not all the selected sites of winter sampling. This classes1\3 was found in positive side of the axis of F1 and has the same character.

Table 7. Factor loadings of elements data in the sediments samples

Variables	F1	F2	F3
Cu	-0.24	**0.92**	**0.23**
Fe	-0.86	**0.43**	-0.27
Cd	-0.73	**0.58**	-0.14
Mg	-0.86	0.15	0.03
Zn	**0.63**	-0.34	-0.54
Pb	-0.92	-0.04	-0.23
Al	-0.96	**0.23**	0.04
Ba	**0.89**	-0.40	-0.21
Ni	-0.89	**-0.34**	0.05
Mn	-0.81	-0.47	-0.21
Ag	**0.42**	-0.11	-0.77
Cr	-0.95	-0.11	**0.20**
Eigenvalues	**7.55**	**2.09**	**1.22**
%Variance	**62.96**	**17.43**	**10.17**
% cumulative	**62.96**	**80.39**	**90.56**

Figure 4 shows that the distribution in the first class is characterized by the presence of Ag and Zn and the second class is characterized by the presence of Cd, Cu, Fe and Mg due to many industries and the reject of waste water without recycling.

In the third class, it was found in the positive site of F2 and negative site of the axis of F1 and which are characterize by the presence of Pb, Mn, Mg and Ba.

Sites S1and S2 are characterized by the presence of Zn and Ag, then the sites S3, S4 and S5 are characterized by the presence of Cu, Cd Mg and Fe. Whichmean that they has the main source of pollution,S6 is characterize by the presence of Pb, Cr, Al, Ni, Ba and Mn.

The nutritional requirements of elements (Cu, Zn etc.) differ substantially between species or elements, and optimum ranges of concentrations are generally narrow. Given elements (Pb, Cd etc.) exhibit extreme toxicity even at trace levels [28], which are the characteristics of the sediment in the study area.
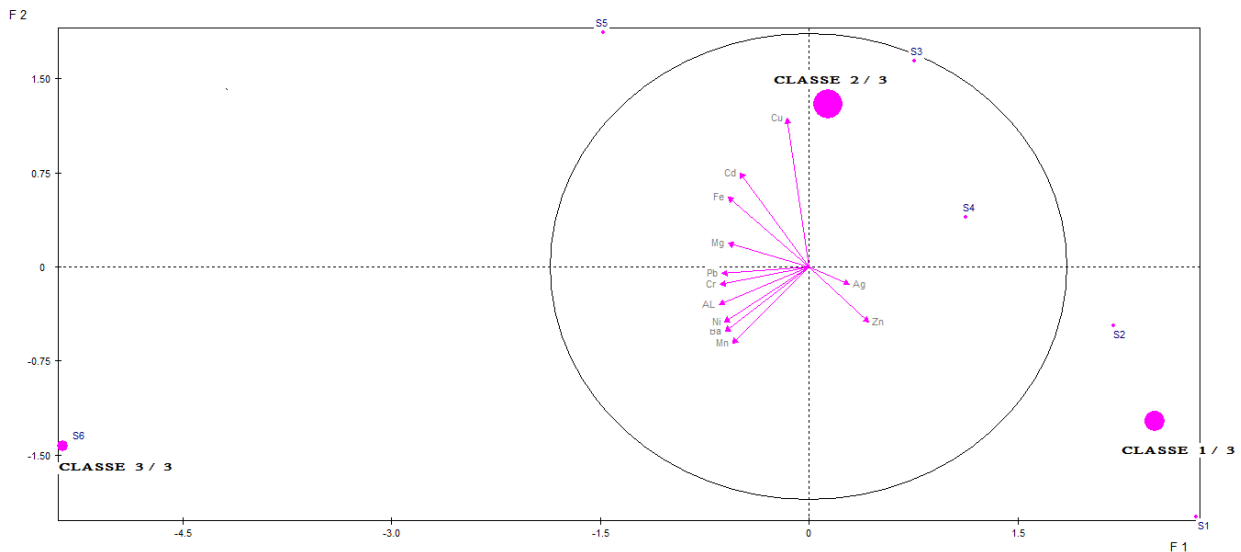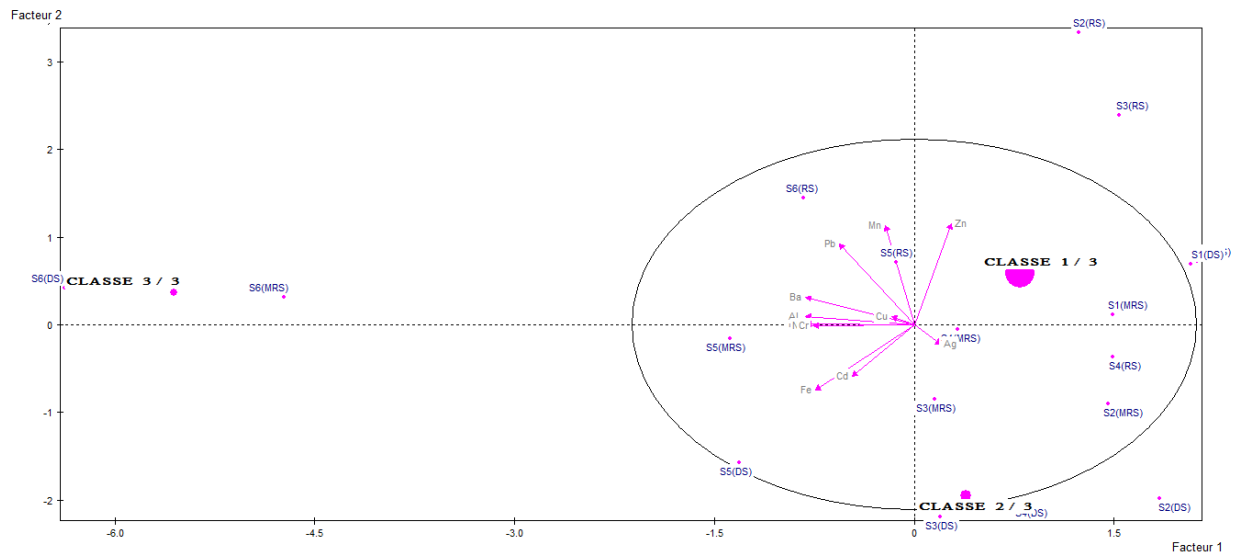

Fig. 3: Factorial F1and F2 classification by the mean.

Fig. 4: Factorial F1 and F2 classification by the seasons.

CONCLUSION

The results of water analysis of the LLRB showed that the heavy metals concentrations were mainly within the permissible limits according to the norms introduced by WHO and Libnor. However, significant local water pollution problems were found (*in S1), which are* due to the increasing swept-out effluents along different drains into the river and extensive water use, and thus the quality of river water is exposed to deterioration. In recent years, the impact of the wastes (i.e. solid and liquid) discharged on ambient water of the LLRB has been significant due to the high self-assimilation capacity of the river water.

The heavy metal concentrations in the river sediments were remarkably high, but varied among sampling sites. The results suggest that special attention must be given to the issue of element re-mobilization, because a large portion of elements in sediments are likely to release back into the water column. Special attention should be paid to mitigate pollution from these sources as their effects may become significant during seasons and years of low water flow in the river. Therefore, periodical monitoring on the LLRB river water quality is needed to record any alteration in the quality and mitigate outbreak of health disorders and the detrimental impacts on the aquatic ecosystem.

However, partitioning patterns highlighted with exception of Zn, Ag (site 1 and Site 2) and Cr,Pb,Al,Ni and Mn (Site 6), Cu, Cd, Fe and Mg (Site 5) metals were mainly associated with the residual fraction and hence, the possibility to affect the water quality is minimal. Whilst, Cd displayed the highest mobility and bioavailability, since it was largely distributed among the non-residual phases and Cd will be mobilized from sediment to water [29].

Cu is high on the (Site 5) the latter may confirm the anthropogenic origin of Cu at that point, probably as a consequence of sewage effluents (i.e. both domestics and industrials).

Ni and Cr association and its negative correlation with Cu suggest a different source. An anthropogenic origin from urban effluents may be thought in case of Cu.

Principal component analysis applied to total and extractable metal contents as a tool for studying heavy metal pollution of the LLRB, proved useful to distinguish between anthropogenic and geologic sources.By comparing the accumulation of heavy metals in water and sediments, it can be concluded that the heavy metals are highly accumulated in sediments of the LLRB than in water, since the sediments act as reservoir for all contaminants and dead organic matter descending from the ecosystem above, the total amounts of heavy metals in the six sampling sites distributed along the sediment of the LLRB course, indicate high pollution by heavy metals, according to the (CBSQG,ISQG) norms.

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