Original Article

Assessment of heavy metal contamination in surface sediment of the Darreh-Morad Beyg River

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Abstract

Background and Purpose: The heavy metal pollution and its fractionations in the surface sediments of Darreh-Morad Beyg River, Hamedan City were monitored for Cd, Cr, Cu, Fe, Ni, Pb, and Zn in 2014.

Materials and Methods: Totally 30 surface sediment samples were taken from 10 stations with three replicates. The samples subjected to bulk digestion and chemical partitioning. The concentrations of heavy metals in sediment were determined by ICP-OES. I-geo, EF, CF, and PLI were also used to assess the sediment contamination.

Results: The results of the present study showed that the proportions of residual fraction for Cu, Ni, Pb, Cd and especially Cr (93.61%) were relatively high, which implied their lower pollution risks due to low mobility characterization, while Zn was mainly associated with the anthropogenic portion of the existing pollution which meant an increase in mobility for this element. Also, on the basis of the mean, the I-geo values of metals were found in the following order: Cr>Cu>Zn>Ni>Pb>Fe>Cd. At the same time, the average EF of metals in the sediment samples was in the order of Cr>Cu>Zn>Ni>Pb>Fe>Cd. According to the calculated PLI, the pollution class of heavy metals in sediments from the Darreh-Morad Beyg River was between 1 and 2, indicating a moderately polluted degree.

Conclusion: Regarding the high Zn concentrations in sediments, it is likely that this element is a major hazard for the aquatic environment since it is mainly found in the anthropogenic portion. Also, Cu, Ni, Pb, Cd, and Cr are present in the greatest percentages in the residual fraction, which implies that these metals are strongly linked to the sediments.

Key words: Heavy Metals; I-geo; Surface Sediment; Sequential Extraction; Darreh-Morad Beyg River

1. Introduction

Rapid worldwide urban and economic growth has a negative impact on the environment, especially in terrestrial and aquatic ecosystems, which are the ultimate receiving sink for untreated industrial and agricultural effluents, and domestic sewage discharges (1, 2). Therefore, the spread of pollutants, particularly of toxic metals, to the aquatic ecosystems is increasingly worrying (3).

Riverine sediments play an important role in the overall geochemical cycle and provide a reasonable history of pollution in the river (4-7). Sediments act mainly as both carriers and sinks for contaminants in aquatic environments (8). A wide range of persistent chemicals, such as heavy metals, are adsorbed on sediment after being deposited from surface water and are regarded as serious pollutants of aquatic ecosystems, especially aquatic life, due to their toxicity, persistence, bioaccumulation, and their ability to be incorporated into food chains (9-11).

The assessment of the potential ecological risk of toxic metal contamination was proposed as a diagnostic tool for controlling the programs of water pollution as a result of the increasing content of metals in sediments and their subsequent release into the water, which could then threaten the ecological heath (12). So far, enrichment factor, geo-accumulation index, the potential ecological risk index, contamination factor, pollution load index, and sediment quality guidelines had been extensively introduced to assess pollution for heavy metals (7, 13). Therefore, geochemical approaches have been successfully used to estimate the impact of human activities on sediments. Also, the partitioning pattern of metals is considered important in altering the potential toxicity and mobility of contaminant metals (14).

Darreh-Morad Beyg River is located in the eastern slopes of the northern Zagros Mountains, and originates from Alvand Mountain in the south of Hamedan City. After passing through the city of Hamedan, this river enters the Simineh Rood River. The basin area of Darreh-Morad Beyg River is about 30 km^2, and its discharge rate is variable in different seasons. Drinking water of the Darreh-Morad Beig Valley and surrounding agricultural lands is usually provided by the river water. As a primary attempt, the present study was carried out to assess the total concern of heavy metals (Cd, Cr, Cu, Fe, Ni, Pb, and Zn) due to the discharge of agricultural effluents, human and industrial wastewater along the river (15). This research analyzed the correlation between the total organic carbon and heavy metals in Darreh-Morad Beyg River sediments, assessing the distribution of heavy metals in the surface sediments through the three steps of extraction and investigation of geochemical indexes in the sediment samples.

which are presented in Table 1. The sampling sites were obtained through the GIS.

2. Material and Methods

2.1. Sample sites

As is shown in Figure 1, in the present study, ten sites were selected along the stretch of river with 18 Km long, the geographical locations of

2.2. Sampling collection

Totally 30 surface sediment samples (upper 0-5 cm depth) were grab sampled along the river with a stainless steel container in the winter,

2013. The samples were placed into polyethylene bags and returned to the laboratory. Care was taken to avoid any contamination. Then, the samples were frozen at 4 °C prior to analysis. Each sediment sample was dried in an oven at 105 °C and sieved through a 2mm sieve (7).

2.3. Analytical methods

2.3.1. Heavy metal content analysis

For analyzing the total heavy metal content and the chemical analysis, all of the samples were powdered in Teflon tubes. One gram of each dried sediment sample was placed in a 250 mL Pyrex flask. The digestion was performed with 8 ml of aqua regia (HNO_3/HCl 1 V:3 V, HNO_3 70 %, HCl 37%) which was added to the flask and the flask was then placed on a heating plate for digestion. A small amount of HNO_3 was added intermittently to digest the sediment completely until the supernatant became clear and a brownish-colored fume was no longer generated. After the sample was nearly dried, it was taken up in 1% nitric acid, and the solution was filtered through a 0.45 ml membrane filter and was then ready for analysis (3, 16). Finally, the metal contents of the sediment samples were determined with an ICP-OES (Varian 710-ES, Australia), while the standard solutions were made from stock solutions (1000 mg/L) of all elements, which were supplied by Merck (Germany) (3, 16). All the instrumental conditions applied for Cd, Cr, Cu, Fe, Ni, Pb, and Zn content determinations were set in accordance with general recommendations (wave length for Cd, Cr, Cu, Fe, Ni, Pb, and Zn: 226.5 nm, 267.7 nm, 324.7 nm, 258.6 nm, 231.6 nm, 220.3 nm, and 206.2 nm, respectively)

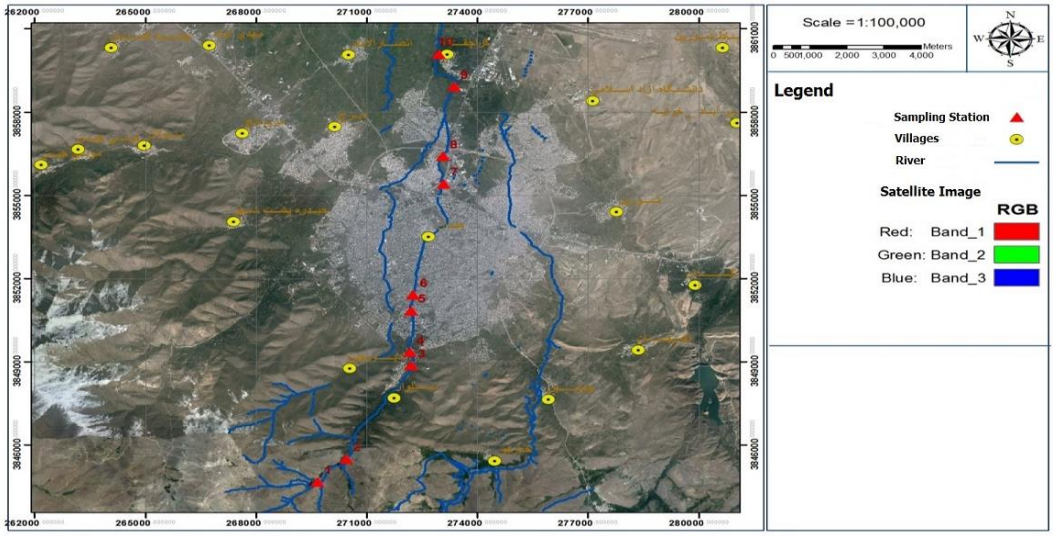

Figure 1. Location of the study site

Table 1. Geographical locations of the sampling stations

Sampling Stations	Latitude	Longitude
1	48°48′471′′ E	34°71′821′′ N
2	48°49′300′′ E	34°72′589′′ N
3	48°51′128′′ E	34°75′664′′ N
4	48°51′082′′ E	34°76′093′′ N
5	48°51′066′′ E	34°77′444′′ N
6	48°51′113′′ E	34°77′955′′ N
7	48°51′907′′ E	34°81′585′′ N
8	48°51′870′′ E	34°82′475′′ N
9	48°52′121′′ E	34°84′740′′ N
10	48°51′634′′ E	34°85′794′′ N

2.3.2. Sequential extraction

In this study, the chemical partitioning of metals was determined by means of the sequential extraction scheme proposed by Rauret et al. (1999) (17). This scheme consists of three successive extractions that make it possible to determine the association of the metals in three phases: (i) acid soluble/exchangeable fraction extraction with 0.11 M acetic acid (HOAc), (ii) reducible/ sulfidic phase extraction with 0.5 M hydroxylamine hydrochloride (NH_2 OH.HCl) at pH 1.5 and (iii) oxidisable extraction with 8.8 M H_2O_2 and with 1.0 M ammonium acetate at pH= 2. Furthermore, a fourth phase—residual or inert (fraction 4) was determined by difference of content BCR extractable fractions and the total metal content.

2.3.3. Total organic carbon (TOC)

Total organic carbon (TOC) was determined using the El Rayis (1985) modification based on the acidification of the sediment sample, and grain size distribution was analyzed by using a Fristch laser particle sizer (model ANALYSETTE 22) according to Kalman et al. (2012) in environmental pollutants monitoring and control laboratory (18).

2.3.4. Organic matter (OM)

The organic matter may provide a sink for heavy metals. Organic matter content (%) of the sediment was measured using an OM soil test kit (Model ST-OR 5010, LaMotte, USA). The acid-dichromate soil solution was titrated with 0.4 N $FeH_8N_2O_8S_2$ until color changed from dark brown to a deep green endpoint (19).

2.4. Assessment of sediment contamination

2.4.1. Geo-accumulation index (I_{geo})

The geo-accumulation index was initially introduced by Muller (1969) for assessing the degree of metal pollution in aquatic sediments. Geo-accumulation index was calculated according to the equation 1 (7):

$$I_{geo} = \frac{log_2(Cn)}{1.5(Bn)} \quad (1)$$

where Cn indicated the concentration of metals measured in sediment samples and Bn indicated the geochemical baseline concentration of the metal (n). Factor 1.5 is the lithospheric variations of trace metals. The geo-accumulation index classified to seven grades. Class 0: Igeo<0 (unpolluted); Class 1: 0 < Igeo < 1 (unpolluted to moderately polluted); Class 2: 1 < Igeo < 2 (moderately polluted); Class 3: 2 < Igeo < 3 (moderately to strongly polluted); Class 4: 3 < Igeo < 4 (strongly polluted); Class 5: 4 < Igeo < 5 (strongly to extremely polluted); Class 6: 5 < Igeo (extremely polluted) (7).

2.4.2. Enrichment factor (EF)

Enrichment factor was employed by Simex and Helz (1981), to assess the degree of contamination and to understand the distribution of the elements of anthropogenic

origin from sites by individual elements in sediments (20). The EF was calculated according to the equation 2:

$$EF = \frac{\left(\frac{Metal}{Fe}\right)Sample}{\left(\frac{Metal}{Fe}\right)Background} \quad (2)$$

The judgment standard of contamination degree by enrichment factor was classified into five grades: Class 1: EF < 2 (unpolluted to slightly polluted); Class 2: 2 < EF < 5 (moderately polluted); Class 3: 5 < EF < 20 (remarkably polluted); Class 4: 20 < EF < 40 (strongly polluted); Class 5: 40 < EF (extremely polluted) (11).

2.4.3. Contamination factor (CF)

The CF and degree of contamination are used to determine the contamination status of the sediment in the present study. The level of contamination of sediment by metal is expressed in terms of a contamination factor calculated as equation 3:

$$CF = \frac{C_{heavy\ metal}}{C_{background}} \quad (3)$$

Contamination factor values for describing the contamination level are categorized to four classes: CF < 1 indicates low contamination; 1 ≤ CF < 3 indicates moderate contamination; 3 ≤ CF<6 indicates considerable contamination; and CF > 6 indicates very high contamination (21).

2.4.4. Pollution load index (PLI)

This index assessed the level of metal pollution and was calculated according to the equation 4:

$$PLI = (CF_1 \times CF_2 \times CF_3 \times \ldots \times CF_n)^{1/n} \quad (4)$$

If PLI < 1 indicates Unpolluted; 1<PLI<2 indicates moderately polluted; 2<PLI<3 indicates Strongly polluted and PLI ≥ 1 indicates Extremely polluted (22).

2.5. Data analysis

All statistical analyses were performed using the SPSS 20.0 statistical package. Pearson correlation analysis was implemented to determine the relationship between the heavy metals and TOC. Also cluster analysis (CA) was performed to identify similarities or dissimilarities between elements and the main sources of them (5).

3. Results

3.1. Total heavy metals and organic carbon content

Heavy metal concentration and the total organic carbon content (TOC) in the sediment samples are shown in Table 2. The ranges of the metals concentration (mg/kg) were: 85-113 for Zn, 32.1-58 for Cu, 35-52 for Ni, 22-35 for Pb, 0.22-0.43 for Cd, 73-114 for Cr, 29020-32700 for Fe, respectively, and they display the following order: Fe> Zn> Cr> Ni> Cu> Pb> Cd. The results were compared with other rivers and the comparison of these results with sediment quality guidelines proposed by USEPA revealed that Zn, Cu, Ni have moderately polluted the river, and Cr was classified as strong contaminated factors. The Pearson correlation analyses between the heavy metals, TOC, and OM in sediments are shown in Table 3. Correlation among elements reveals close association in some certain heavy metals, including Cu and Cr (r = 0.74), Cu and Cd (r = 0.69), Ni and Cu (r = 0.82), Ni and Fe (r = 0.72). The results suggest similar sources or main distribution pathways for these metals. The positive correlation of Ni with the organic carbon content of the sediment suggests metal ion binding to organic substance which could

control metal mobility. Cu generally shows high affinities to total organic matter (23, 24).

Table 2. Heavy metal concentration (mg/kg) and the total organic carbon (TOC) in the sediment samples of study area

Site	Zn	Cu	Ni	Pb	Cd	Cr	Fe	TOC (%)	OM (%)
1	97	32.1	37	35	0.25	74	29540	1.24	2.13
2	93	34	35	22	0.38	73	29058	1.58	2.72
3	88	33.6	43	25	0.22	78	29300	2.94	5.06
4	95	37	40	31	0.24	82	31468	2.14	3.68
5	85	58	50	29	0.37	114	32700	3.86	6.65
6	104	42	39	29	0.36	80	29020	2.48	4.27
7	108	43	44	24	0.40	76	31890	3.87	6.67
8	95	34.3	41	33	0.28	75	30850	1.71	2.94
9	113	48	52	26	0.43	77	32610	3.95	6.80
10	98	54	48	24	0.41	84	29980	3.95	6.80
Max	113	58	52	35	0.43	114	32700	3.95	6.80
Min	85	32.1	35	22	0.22	73	29020	1.24	2.13
Mean	97.6	41.6	42.9	27.8	0.33	81.3	30641.6	2.77	4.77

Table 3. Pearson correlation coefficients between heavy metal concentrations, total organic carbon and organic matter of sediments from the Darreh-Morad Beyg River

	Zn	Cu	Ni	Pb	Cd	Cr	Fe	TOC	OM
Zn	1								
Cu	0.09	1							
Ni	0.21	0.82**	1						
Pb	-0.15	-0.28	-0.24	1					
Cd	0.53	0.69*	0.50	-0.59	1				
Cr	-0.48	0.74*	0.53	0.06	0.17	1			
Fe	0.22	0.56	0.72*	0.06	0.33	0.49	1		
TOC	0.28	0.83**	0.89**	-0.52	0.63	0.47	0.58	1	
OM	0.28	0.83**	0.89**	-0.52	0.63	0.47	0.58	1.00**	1

**. Correlation is significant at the 0.01 level (2-tailed).

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

3.2. Partitioning of Metal

Sequential chemical partitioning techniques are usually performed to determine the chemical forms of elements which are found in the sediment, and it is assumed that trace metals are derived from geochemical background rather than anthropogenic inputs in these sediments. The concentrations of six heavy metals in surface sediments determined at each sequential extract step reveal four fractions of each metal. The results of average percentage of each fraction ranged from each sequential

extractions in the 10 sampling sites are presented in Table 4. The results of the anthropogenic portion of the existing pollution indicated that most of total Zn was found in the sum of acid soluble, reducible, and oxidizable phase (58.23%), which is indicative of anthropogenic pollution (25). The dominant portion of Cu was concentrated in the residual fraction (69.97%). The next important phases of Cu were the oxidizable (17.04%) and acid soluble (9.02%) phases that were indicative of significant heavy metal input of anthropogenic origin with potential mobility, and were found in the organic phase. Nickel was predominantly associated with residual (71.37%) and reducible (18.86%) fractions. Lead was mostly bound to residual (74.37%) and acid soluble (5.23%) fraction, while Cadmium showed a different partitioning pattern. This metal was mostly concentrated at the residual fraction (69.16%). The next important phase of Cd was the reducible fraction (15.27%). It could be seen that the most percentage of Cr was associated with the residual fraction (93.61%), and only small amounts of Cr were bound to the organic fractions. It meant that Cr was reflecting background geochemical conditions and trace metals in this form with lower mobility were not soluble and held their crystal structure (26).

Table 4. Results of the BCR on the sediment samples in mg/kg (dry weight) and average percentage of each fraction in 10 sampling sites

Metal	Acid Soluble Phase			Reducible Phase			Oxidizable Phase			Residual Phase		
	Range	Mean	%	Range	Mean	%	Range	Mean	%	Range	Mean	%
Zn	1.6-2.1	1.89	1.95	28.8-42	35.28	36.15	18.3-22	19.65	20.13	31.42-52.25	40.77	41.77
Cu	2.9-5.0	3.75	9.02	1.1-2.7	1.65	3.97	6.2-8.8	7.09	17.04	21.4-41.5	29.10	69.97
Ni	1.8-2.5	2.13	4.97	7.2-8.6	8.09	18.86	1.73-2.41	2.06	4.80	24.18-37.07	30.61	71.37
Pb	1.1-1.75	1.52	5.23	3.3-5.25	4.44	15.27	1.25-1.68	1.49	5.13	16.55-28.81	21.64	74.37
Cd	0.0-0.02	0.01	3.00	0.01-0.09	0.05	15.27	0.01-0.07	0.04	12.57	0.14-0.35	0.23	69.16
Cr	0.0-0.38	0.05	0.07	3.3-5.5	3.75	4.60	1.24-2.13	1.40	1.72	68.22-105.99	76.38	93.61

3.3. Assessment of the intensity of metal contamination in sediments

The results of the geo-accumulation index were compared with the values of geo-accumulation index classification presented by Muller (1981) (27) as shown in Table 5. The majority of the metals (Zn, Cu, Ni, Pb and Fe) showed negative I-geo values indicating that sediments were unpolluted (class 0). The sediments quality for Zn at stations 6, 7, 9 and 10, Cu at stations 5, 6, 7, 9 and 10, Ni at stations 5, 9 and 10, Pb at station 1, and Cr at all stations expect station 5, were classified as unpolluted to moderately polluted (Class 1). Also, sediments quality of Cr at station 5 was classified as moderately polluted (class 2).

According to Sakan et al. (2016) classification (28), the mean enrichment factors (EFs) values obtained for Ni, Pb, Cd, and Fe are in the range of 0.05-1.5, which implies that these elements are entirely from crustal abundance or natural processes in the study area. Whereas, the mean EFs values for Zn, Cu and Cr which were greater than 1.5 revealed that the sediments were derived from anthropogenic sources.

The contamination factors (CFs) values indicated that except for Cd and Fe, the other metals are classified as moderate contaminators. The CFs value for Pb in station 2, Cd in all stations and Fe in stations 1, 2, 3, 6, 8 and 10 classified in low contamination. Also, according to the pollution load index (PLI) values, it was found that in the Darreh-Morad Beyg River, the sediments were moderately polluted (Table 6), which could be attributed to municipal and domestic sewage discharge to the river.

Table 5. Geo-accumulation indices and enrichment factors of heavy metals in the Darre-Morad Beyg River sediments

Site	Zn		Cu		Ni		Pb		Cd		Cr		Fe	
	EF	I-geo	EF	I-geo	EF	I-geo	EF	I-geo	EF	I-geo	EF	I-geo	EF	I-geo
1	1.57	-0.01	1.35	-0.22	1.25	-0.33	1.60	0.01	0.24	-2.74	2.51	0.67	1.0	-0.66
2	1.53	-0.07	1.45	-0.14	1.20	-0.41	1.02	-0.65	0.37	-2.12	2.51	0.65	1.0	-0.68
3	1.43	-0.15	1.42	-0.16	1.47	-0.11	1.15	-0.46	0.21	-2.94	2.66	0.75	1.0	-0.67
4	1.44	-0.04	1.46	-0.02	1.27	-0.22	1.33	-0.16	0.21	-2.79	2.61	0.82	1.0	-0.56
5	1.24	-0.20	2.20	0.63	1.53	0.10	1.19	-0.25	0.32	-2.16	3.49	1.29	1.0	-0.51
6	1.71	0.10	1.79	0.16	1.34	-0.25	1.35	-0.25	0.35	-2.18	2.76	0.78	1.0	-0.68
7	1.61	0.15	1.67	0.20	1.38	-0.08	1.01	-0.52	0.35	-2.05	2.38	0.70	1.0	-0.54
8	1.47	-0.04	1.38	-0.13	1.33	-0.18	1.44	-0.06	0.26	-2.56	2.43	0.69	1.0	-0.59
9	1.65	0.21	1.82	0.36	1.59	0.16	1.07	-0.41	0.37	-1.94	2.36	0.73	1.0	-0.51
10	1.56	0.01	2.23	0.53	1.60	0.04	1.08	-0.52	0.38	-2.00	2.80	0.86	1.0	-0.63
Mean	1.52	-0.004	1.68	0.12	1.40	-0.13	1.22	-0.33	0.31	-2.35	2.65	0.80	1.0	-0.60

Table 6. Metal contamination factors (CFs) and pollution load indices (PLIs) for sediments in the Darre-Morad Beyg River sediments

Site	Contamination Factors (CFs)							PLI
	Zn	Cu	Ni	Pb	Cd	Cr	Fe	
1	1.49	1.28	1.19	1.52	0.23	2.39	0.95	1.09
2	1.43	1.36	1.13	0.96	0.34	2.35	0.94	1.07
3	1.35	1.34	1.39	1.09	0.20	2.52	0.94	1.04
4	1.46	1.48	1.29	1.35	0.22	2.64	1.02	1.12
5	1.31	2.32	1.61	1.26	0.34	3.68	1.05	1.35
6	1.60	1.68	1.26	1.26	0.33	2.58	0.94	1.19
7	1.66	1.72	1.42	1.04	0.36	2.45	1.03	1.21
8	1.46	1.37	1.32	1.43	0.25	2.42	0.99	1.12
9	1.74	1.92	1.68	1.13	0.39	2.48	1.05	1.30
10	1.51	2.16	1.55	1.04	0.37	2.71	0.97	1.26
Mean	1.50	1.66	1.38	1.21	0.30	2.62	0.99	1.17

3.4. Cluster analysis

Cluster analysis (CA) was applied to evaluate the similarities of the heavy metal sources. The results of the CA are presented in the form of a dendrogram (Figure 2), which shows all metals were grouped into two clearly distinct clusters. Cluster 1 indicated Zn which is a heavily contaminated metal drived from anthropogenic sources. Cluster 2 incorporated two subgroups where the first subgroup included Cu, Ni, Fe

and Cr deriving from both lithogenic and anthropogenic sources, while the second subgroup consisted of Pb which came from the natural source.

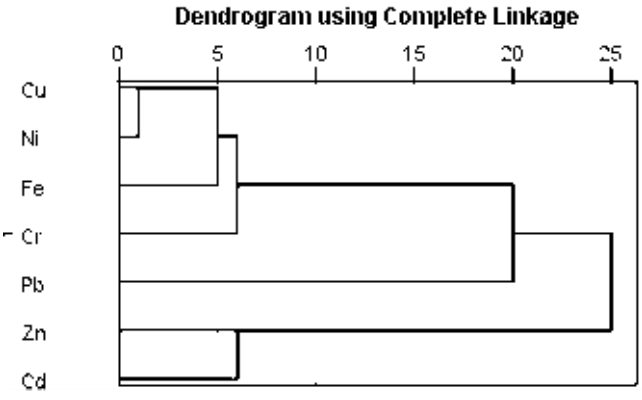

Figure 2. Dendrogram showing clustering of the metals

4. Discussion

The heavy metal levels in sediments were reported to be mainly influenced by particle size and composition of sediments (16, 29). Geochemical approaches have also been successfully used to estimate the impact of human activities on sediments (14, 30, 31). Similarly, the partitioning pattern of metals was important to the potential toxicity and mobility of contaminant metals (32). Therefore, the current study was conducted to investigate the heavy metal (Zn, Cu, Ni, Pb, Cd, Cr, and Fe) pollution and their fractionations in the surface sediment of Darreh-Morad Beyg River. The results showed that the mean concentration (mg/kg) of heavy metal in the sediment samples were 0.33, 81.30, 41.60, 30641.60, 42.90, 27.80, and 97.60 for Cd, Cr, Cu, Fe, Ni, Pb and Zn, respectively. Consistent with this result, the analysis of Mathis and Cummings (1973) regarding the heavy metals in sediment samples of Illinois River reported that the Cd, Cu, Pb and Zn content (mg/kg) in samples were 2.0, 19.0, 28.0, and 81.0, respectively (33). Similarly, the assessment of Gonzalez et al. (2000) about the metal levels in sediment samples of Guadalquivir River revealed that the Cd, Cr, Cu, Fe, Ni, Pb, and Zn content (mg/kg) in specimens were 3.0, 38.0, 25.0, 25000.0, 37.0, 20.0, and 51.0, respectively (34). The comparison of the results of the current study with other studies is shown in Table 7.

Table 7. Comparison of mean heavy metal concentration (mg/kg) in sediment samples from the study area with other rivers

Location	Zn	Cu	Ni	Pb	Cd	Cr	Fe	Reference
Darreh River	97.60	41.60	42.90	27.80	0.33	81.30	30641.60	
Gomti River (India)	41.7	5	15.70	40.33	2.42	8.15	2661	35
Shefa-Rud River (Iran)	59	35.25	50.75	20.25	-	-	2.41	36
Dikrong River (India)	26.40	190	11.20	39	-	50.70	1.75	37
Haraz River (Iran)	73.80	32.10	43.55	26.35	3.45	28	-	5
Nile River (Egypt)	60-262	27-90	54-65	3-685	-	37-46	-	38
Deûle River (French)	5.00	179.00	28.33	2490	-	-	-	39
Tsurumi River (Japan)	381.00	133.00	37.00	41.00	-	103.00	-	40
Changjiang River (China)	129.73	48.61	41.49	50.77	2.82	98.32	-	41
Ponnaiyar River (India)	182.90	81.80	29.50	85.20	-	87.30	-	42
Tigris River (Turkey)	203	344.60	145.60	265.20	1.80	84.70	-	43
Day River (Morocco)	145.50	740.80		135.30		311.70		44
Aras River (Iran)	1.75	9.95	2	1.29	0.96	-	56.42	45
Fez River (Morocco)	67.60	12.50	20.70	12.50		44	22	3
Yellow River (China)	102.87	25.96	38.10	11.36	1.81	110.10	30196.90	7

The concentration of six heavy metals in the surface sediments determined at each sequential extract step revealed four fractions of each metal. The results of average percentage of each fraction in the 10 sampling sites are listed in Table 4. The percentage of four fractions of Zn, Cd and Cr in the sediments follow the same order as residual> reducible> oxidizable> acid soluble, while those of Ni and Pb follow the order as residual> reducible> acid soluble> oxidizable. The percentage of Cu associated with different fractions is in the order of residual> oxidizable> acid soluble> reducible. All metals are found in all of the four fractions. It is notable that the proportions of residual fraction for Cu, Ni, Pb, Cd and especially Cr were relatively high (69.97%, 71.37%, 74.37%, 69.16% and 93.61%, respectively), which imply their lower pollution risks due to low mobility characterization, while Zn mainly associated with the anthropogenic portion of the existing pollution (the sum of acid soluble, reducible, and oxidizable phase) (58.23%), which means an increase in mobility for this element.

The calculated results of I-geo indicated that Cr could be considered as from unpolluted to moderately polluted at all stations. This was on the basis of the mean I-geo values of metals in following order: Cr>Cu>Zn>Ni>Pb>Fe>Cd. The average EF of metals in sediments of Darreh-Morad Beyg River were in the order of Cr>Cu>Zn>Ni>Pb>Fe>Cd. The average EF of Cd showed background levels, whereas the average EF of Fe was 1, which could indicate some crustal origin for this metal. The average EF of Cu, Zn, Ni and Pb was much higher, which belongs to slightly polluted sediments. Also, the average metal contamination coefficients in sediments were in the order of Cr>Cu>Zn>Ni>Pb>Fe>Cd. Cr, which could cause greater pollution. According to the calculated PLI, pollution class of heavy metals in sediments from the Darreh-Morad Beyg River was between 1 and 2, indicating a moderately polluted degree.

Conflict of Interests

The Authors have no conflict of interest.

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References

1. Peng JF, Song YH, Yuan P, Cui XY, Qiu GL. The remediation of heavy metals contaminated sediment. Journal of Hazardous Materials 2009; 161(2–3): 633–40.
2. Amouei AI, Yousefi Z, Mahvi AH, Naddafi K, Tahmasbizadeh M. Heavy metal concentrations in industrial, agricultural, and highway soils in northern Iran, Environmental Justice 2012; 5(3): 153–7.
3. Hayzoun H, Garnier C, Durrieu G, Lenoble V, Bancon-Montigny C, Ouammou A, et al. Impact of rapid urbanisation and industrialisation on river sediment metal contamination. Environmental Monitoring and Assessment 2014; 186: 2851–65
4. Jain CK. Metal fractionation study on bed sediments of river Yamuna, India. Water Research 2004; 38: 569–78.
5. Nasrabadi T, Nabi Bidhendi Gh, Karbassi AR, Mehrdadi N. Evaluating the efficiency of sediment metal pollution indices in interpreting the pollution of Haraz River sediments, southern Caspian Sea basin. Environmental Monitoring and Assessment 2010; 171: 395–410.
6. Mao LJ, Mo DW, Guo YY, Fu Q, Yang JH, Jia YF. Multivariate analysis of heavy metals in surface sediments from lower reaches of the Xiangjiang River, southern China. Environmental Earth Science 2013; 69: 765–71.
7. Shang Z, Ren J, Tao L, Wang X. Assessment of heavy metals in surface sediments from Gansu section of Yellow River, China. Environmental Monitoring and Assessment 2015; 187: 79.
8. Li JL, He M, Han W, Gu YF. Analysis and assessment on heavy metal sources in the coastal soils developed from alluvial deposits using multivariate statistical methods. Journal of Hazardous Materials 2009; 164: 976–81.
9. Luo Ch, Wu Qm, Li S, Yang H, Zhong Ch. Investigation on Metal pollution in the sediment of Chongqing Segment of Yangtse River. Bulletin of Environmental Contamination and Toxicology 2010; 85: 291–94.
10. Varol M, Şen B. Assessment of nutrient and heavy metal contamination in surface water and sediments of the upper Tigris River, Turkey. Catena 2012; 92: 1–10.
11. Azhar M, Muhammad ZC, Nasir A, Tariq J, Abdul G. Metal pollution and ecological risk assessment in marine sediments of Karachi Coast, Pakistan. Environmental Monitoring and Assessment 2013; 185: 1555–65.
12. Zhu XF, Ji HB, Chen Y, Qiao MM, Tang L. Assessment and sources of heavy metals in surface sediments of Miyun Reservoir, Beijing. Environmental Monitoring and Assessment 2013; 185: 6049–62.
13. Habes AG, Yousef A, Marc AR. Application of geoaccumulation index and enrichment factor for assessing metal contamination in the sediments of Kafrain Dam, Jordan. Environmental Monitoring and Assessment 2011; 178: 95–109.
14. Loska K, Wiechula D. Application of principal component analysis for the estimation of source heavy metal contamination in surface sediments from Rybnik Reservoir. Chemosphere 2003; 51: 723–33.
15. Samadi MT, Saghi MH, Rahmani A, Torabzadeh H. Zoning of water quality of Hamedan Darreh-Morad Beyg River according to NSFWQI index using GIS. Journal of Hamadan University of Medical Sciences 2009; 16(3): 38–43. [Persian]
16. Liu C, Xu J, Liu C, Zhang P, Dai M. Heavy metals in the surface sediments in Lanzhou Reach of Yellow River, China. Bulletin of Environmental Contamination and Toxicology 2009; 82(1): 26–30.
17. Rauret G, Lopez-Sanchez JF, Sauquillo A, Rubio R, Davidson C, Ure A, et al. Improvement of the BCR three step sequential extraction procedure prior to the certification of new sediment and soil reference materials. Journal of Environmental Monitoring 1999; 1: 57–61.

18. Kalman J, Riba I, DelValls A, Blasco J. Bioaccumulation and effects of metals bound to sediments collected from Gulf of Ca´diz (SW Spain) using the polychaete Arenicola marina. Archives of Environmental Contamination and Toxicology 2012; 62: 22–8.
19. Baek YW, An YJ. Assessment of toxic heavy metals in urban lake sediments as related to urban stressor and bioavailability. Environmental Monitoring and Assessment 2010; 171: 529–37.
20. Djordjevic L, Zivkovic N, Zivkovi L, Djordjevic A. Assessment of heavy metals pollution in sediments of the Korbevacka River in southeastern Serbia. Soil and Sediment Contamination 2012;21: 889–900.
21. Hakanson L. An ecological risk index for aquatic pollution control a sedimentological approaches. Water Research 1980; 14(8): 975–1001.
22. Wang J, Liu GJ, Fang T. Assessment of pollution characteristics of heavy metals in the sediments of Huaihe River (Anhui section) by pollution load index. Journal of University of Science and Technology China 2013; 43(2): 97–103.
23. Pettine M, Bianchi M, Martinotti W, Muntau H, Renoldi M, Tartari G. Contribution of the Lambro River to the total pollutant transport in the Po watershed (Italy). Science of the Total Environment 1996; 192(3): 275–97.
24. Adamo P, Zampella M, Gianfreda L, Renella G, Rutigliano FA, Terribile F. Impact of river overflowing on trace element contamination of volcanic soils in south Italy: Part I. Trace element speciation in relation to soil properties. Environmental Pollution 2006; 144(1): 308–16.
25. Modak DP, Singh KP, Chandra H, Ray PK. Mobile and bound forms of trace metals in sediments of the lower Ganges. Water Res. 1992; 26(11): 1541–8.
26. Dang Z, Liu C, Haigh MJ. Mobility of heavy metals associated with the natural weathering of coal mine spoils. Environmental Pollution 2002; 118(3): 419–26.
27. Muller G. The heavy metal pollution of the sediments of Neckars and its tributary: a stocktaking. Chemiker-Zeitung 1981; 105: 157–64.
28. Sakan S, Popović A, Anđelković I, Đorđević D. Aquatic sediments pollution estimate using the metal fractionation, secondary phase enrichment factor calculation, and used statistical methods. Environmental Geochemistry and Health 2016; 38(3): 855–67.
29. Jain CK, Singhal DC, Sharma MK. Metal pollution assessment of sediment and water in the river Hindon, India. Environmental Monitoring and Assessment 2005; 105(1-3): 193–207.
30. Çevik F, Göksu MZL, Derici OB, Fındık Ö. An assessment of metal pollution in surface sediments of Seyhan dam by using enrichment factor, geoaccumulation index and statistical analyses. Environmental Monitoring and Assessment 2009; 152: 309–17.
31. Villaescusa-Celaya JA, Gutierrez-Galindo EA, Flores-Munoz G. Heavy metals in the fine fraction of coastal sediments from Baja California (Mexico) and California (USA). Environmental Pollution 2000; 108(3): 453–62.
32. Macklin MG, Dowsett RB. The chemical and physical speciation of trace metals in fine grained overbank flood sediments in the Tyne basin, north-east England. Catena 1989; 16(2): 135–51.
33. Mathis BJ, Cummings TF. Selected metals in sediment, water and biota in the Illinois River. Journal of the Water Pollution Control Federation 1973; 45(7): 1573–83.
34. Gonzalez AE, Rodriguez MT, Sa JCJ, Espinosa AJF, de la Rosa FJB. Assessment of metals in sediments in a tributary of Guadalquivir River (Spain). Heavy metal partitioning and relation between the water and sediment system. Water, Air, & Soil Pollution 2000; 121(1): 11–29.
35. Singh KP, Mohan D, Singh VK, Malik A, Studies on distribution and fractionation of heavy metals in Gomti River sediments—a tributary of the Ganges, India. Journal of Hydrology 312(1-4): 14–27.
36. Karbassi AR, Bayati I, Moattar F. Origin and chemical partitioning of heavy metals in riverbed sediments. International Journal of

Environmental Science and Technology 2006; 3(1):35–42.
37. Chakravarty M, Patgiri AD. Metal pollution assessment in sediments of the Dikrong River, N.E. India. Journal of Human Ecology 2009; 27(1):63–7.
38. Lasheen MR, Ammar NS. Speciation of some heavy metals in River Nile sediments, Cairo, Egypt. Environmentalist 2009; 29: 8–16.
39. Lesven L, Lourino-Cabana B, Billon G, Recourt P, Ouddane B, Mikkelsen O, et al. On metal diagenesis in contaminated sediments of the Deûle river (northern France). Applied Geochemistry 2010; 25(9): 1361–73.
40. Mohiuddin KM, Zakir H, Otomo K, Sharmin S, Shikazono N. Geochemical distribution of trace metal pollutants in water and sediments of downstream of an urban river. International Journal of Environmental Science and Technology 2010; 7(1): 17–28.
41. Song Y, Ji J, Yang Z, Yuan X, Mao C, Frost RL, Ayoko GA, Geochemical behavior assessment and apportionment of heavy metal contaminants in the bottom sediments of lower reach of Changjiang River Catena 2011; 85(1):73–81.
42. Suresh G, Ramasamy V, Meenakshisundaram V, Venkatachalapathy R, Ponnusamy V. Influence of mineralogical and heavy metal composition on natural radionuclide concentrations in the river sediments. Applied Radiation and Isotopes 2011; 69(10): 1466–74.
43. Varol M. Assessment of heavy metal contamination in sediments of the Tigris River (Turkey) using pollution indices and multivariate statistical techniques. Journal of Hazardous Materials 2011; 195: 355–64.
44. Barakat A, Baghdadi ME, Rais J, Nadem S. Assessment of heavy metal in surface sediments of Day river at Beni-Mellal Region, Morocco. Research Journal of Environment and Earth Science 2012; 4(8): 797–806.
45. Nasehi F, Monavari M, Naderi Gh, Vaezi MA, Madani F. Investigation of heavy metals accumulation in the sediment and body of carp fish in Aras River. Iranian Journal of Fisheries Sciences 2013; 12 (2): 398–410.