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
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 (HNO₃/HCl 1 V:3 V, HNO₃ 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 HNO₃ 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′47″ E     | 34°71′82″ N      |
| 2                 | 48°49′30″ E     | 34°72′59″ N      |
| 3                 | 48°51′12″ E     | 34°75′66″ N      |
| 4                 | 48°51′08″ E     | 34°76′09″ N      |
| 5                 | 48°51′06″ E     | 34°77′44″ N      |
| 6                 | 48°51′11″ E     | 34°77′95″ N      |
| 7                 | 48°51′90″ E     | 34°81′58″ N      |
| 8                 | 48°51′87″ E     | 34°82′47″ N      |
| 9                 | 48°52′12″ E     | 34°84′74″ N      |
| 10                | 48°51′63″ E     | 34°85′79″ 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$_2$O$_2$ 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$_2$N$_2$O$_8$S$_2$ 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):

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

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: $I_{geo}$<0 (unpolluted); Class 1: 0 < $I_{geo}$ < 1 (unpolluted to moderately polluted); Class 2: 1 < $I_{geo}$ < 2 (moderately polluted); Class 3: 2 < $I_{geo}$ < 3 (moderately to strongly polluted); Class 4: 3 < $I_{geo}$ < 4 (strongly polluted); Class 5: 4 < $I_{geo}$ < 5 (strongly to extremely polluted); Class 6: 5 < $I_{geo}$ (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:

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

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:

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

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:

$$\text{PLI} = \left(\text{CF}_1 \times \text{CF}_2 \times \text{CF}_3 \times \ldots \times \text{CF}_n\right)^{1/n} \quad (4)$$

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 | 74  | 29540   | 1.24   |
| 2    | 93  | 34  | 35  | 22 | 0.38| 73 | 73  | 29058   | 1.58   |
| 3    | 88  | 33.6| 43  | 25 | 0.22| 78 | 78  | 29300   | 2.94   |
| 4    | 95  | 37  | 40  | 31 | 0.24| 82 | 82  | 31468   | 2.14   |
| 5    | 85  | 58  | 50  | 29 | 0.37| 114| 114 | 32700   | 3.86   |
| 6    | 104 | 42  | 39  | 29 | 0.36| 80 | 80  | 29020   | 4.27   |
| 7    | 108 | 43  | 44  | 24 | 0.40| 76 | 76  | 31890   | 3.87   |
| 8    | 95  | 34.3| 41  | 33 | 0.28| 75 | 75  | 30850   | 2.94   |
| 9    | 113 | 48  | 52  | 26 | 0.43| 77 | 77  | 32610   | 3.95   |
| 10   | 98  | 54  | 48  | 24 | 0.41| 84 | 84  | 29980   | 3.95   |
| Max  | 113 | 58  | 52  | 35 | 0.43| 114| 114 | 32700   | 3.95   |
| Min  | 85  | 32.1| 35  | 22 | 0.22| 73 | 73  | 29020   | 2.13   |
| Mean | 97.6| 41.6| 42.9| 27.8| 0.33| 81.3| 81.3| 30641.6| 2.77   |

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

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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 | 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 | 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 | 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-acumulation index were compared with the values of geo-acumulation 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 |
| 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 | Zn  | Cu  | Ni  | Pb  | Cd  | Cr  | Fe  | PLI |
|------|-----|-----|-----|-----|-----|-----|-----|-----|
|      | EF  | I-geo | EF  | I-geo | EF  | I-geo | EF  | I-geo | EF  | I-geo | EF  | I-geo | EF  | I-geo |
| 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 | 1.85 | 0.14 | 1.07 |
| 3    | 1.35 | 1.34 | 1.39 | 0.78 | 0.42 | 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 driven 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.

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.

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
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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