Journal of Human Environment and Health Promotion

Print ISSN: 2476-5481 Online ISSN: 2476-549X

Grain-Size Analysis and Contamination Assessment of Heavy Metals in Sediments from Ghezel Ozan River in Zanjan Province, Iran (August 2019 to September 2020)

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A R T I C L E I N F O

Article type:
Original article

Article history:
Received: 15 June 2022
Revised: 5 July 2022
Accepted: 11 August 2022

DOI: 10.52547/jhehp.8.3.161

Keywords:

Enrichment Factor
Geo-accumulation Index
Pollution Factor
Pollution Load Index
Geospatial Distribution Patterns

A B S T R A C T

Background: The present study aims to assess the amounts of Zn, Cu, Cd, Pb, Ni, Co, Mn, and Fe by analyzing the particle composition of the surficial sediments in Ghezel Ozan River located in Zanjan, Iran.
Methods: 18 sediment samples were collected from Ghezel Ozan River. After Aqua Regia Digestion, the studied heavy metals in sediment samples were determined by flame atomic absorption spectrophotometry. Several pollution indices, such as Enrichment Factor (EF), Geo-accumulation Index (I_{geo}), Pollution Factor (C_d), and Pollution Load Index (PLI), were calculated.
Results: Observed average values (in unit mg kg^{-1}) were in the range of Zn: 480.0-34294.0, Cu: 7.8-32.00, Cd: not detected -100.0, Pb: 22.0-256.0, Ni: 2.50-60.00, Co: 7.60-34.0, Mn: 144.0-31600.0 and Fe: 9320.0-62300.0. The I_{geo} index confirmed that the average values of Zn, Pb, and Cd are in the heavily contaminated levels. The mean EF index suggested minimal enrichment for Cu, Ni, Mn, and Co, whereas Zn, Cd, and Pb indicated severe enrichment.
Conclusion: The average C_d, RI, and PLI indices for all investigated heavy metals confirmed a considerable contamination level.

1. Introduction

Since riverine water is used for various land uses, its pollution levels are significant. Well documented in the existing literature indicates that rivers are considered as one of the most vital sources for loading the matter in both dissolved and particulate phases [1,2]. The pollution caused by heavy metals is a severe challenge in river environmental assessment and a global environmental problem [2,3]. The most pivotal and crucial characteristics of heavy metals, which distinguish these pollutants from other toxic pollutants, include potential bioavailability and non-degradability in the environment [4,5]. Easy accumulation, indivisibility, and easy bio-methylation of heavy metals in aquatic ecosystems, specifically in aquatics tissues such as fish, increase their ability to penetrate into human food chain, cause diseases, and suppress the immune system, ultimately damaging the central nervous system, and causing health risks [6-9]. Physico-chemical conditions are one of the most influential parameters in sedimentation and sediment composition, especially in river systems, climatological, dynamic, and river currents. The size of the sediment particles makes it possible to create a suitable space for the adsorption of pollution, especially heavy metals

How to cite: Islami M, Abadi M, Zamani AA, Aazami J, Badiee H. Grain-Size Analysis and Contamination Assessment of Heavy Metals in Sediments from Ghezel Ozan River in Zanjan Province, Iran (August 2019 to September 2020). *J Hum Environ Health Promot.* 2022; 8(3): 161-71.

[10]. Generally, grain size measurement makes it possible to predict sediment adsorption capacity and mechanism. Due to having a higher particle surface-to-volume ratio, the content of heavy metals in finer sediments is higher than in larger sediments [11]. This is the case when the pollution source of sediment surface is heavy metal sorption from water; however, it does not apply when the geochemistry of sediments is the main reason. Nonetheless, several investigations concerning the sediments grain size indicated that coarser particles contain similar or even higher heavy metal amounts than finer ones. Coarser particles are possibly responsible for higher metal contribution in the coarser size fractions [12]. Ghezel Ozan River Basin is one of the essential basins in Iran, which supplies different beneficiaries [13]. Moreover, it is one of the most crucial rivers in northwest Iran, with diverse qualities and characteristics in its different spacing. The quality of Ghezel Ozan River, similar to other rivers in Zanjan province, is strongly influenced by the area′s marly-calcareous gypsum geology, diverse water applications in the basin, river basin fluctuation, and urban and industrial wastewater inflow [14]. Activities such as mining, metal industries, and agriculture close to this river have affected the chemical properties of its water. Numerous studies have shown a high level of heavy metals in and around metal mines due to careless and irresponsible disposal of mining waste to the surrounding environment [15]. Therefore, heavy metals in the sediments of rivers have been assessed due to their importance. These rivers transport the materials from upstream and confirm the changes around [16-17]. The main objective of this study is to determine the amounts and spatial distribution of eight selected heavy metals (Zn, Cu, Cd, Pb, Ni, Co, Mn, Fe) in surficial sediments collected from the Ghezel Ozan River in Zanjan province. Briefly, the main objectives of this study include 1) creating an accurate scientific image of the contamination caused by heavy metals, 2) determining input sources for heavy metals, and 3) assessing potential levels of environmental hazards.

2. Materials and Methods

2.1 Study Area

Ghezel Ozan River is one of the largest and longest permanent rivers in Iran, with a length of 800 km [18]. The river basin covers Zanjan, East Azerbaijan, Kurdistan, Ardabil, Hamadan, and some limited parts of Guilan, Qazvin, and the West Azerbaijan provinces (Figure 1) [19]. Ghezel Ozan River Basin is 46 degrees 27 min to 49 degrees 20 min east and latitude 34 degrees 55 min to 37 degrees north 55 min, and its area is approximately 49,800 km² [20]. Its upstream catchment area is approximately 49400 km² [8,21]. From a geomorphological point of view, Ghezel Ozan is an alluvial river with rocky, Clay-silicate, and sandy beds and is affected by specific hydraulic conditions, topography, bedding material, and sidewalks [18]. In addition, the river passes through agricultural, residential, and industrial lands with several different types of ecology. Passing through different lands with diverse applications, the river reaches its final destination, the Caspian Sea [14].

2.2 Sampling Stations

Surface sediment samples (i.e., 0–5 cm) were selected from six stations along the Ghezel Ozan River according to US Environmental Protection Agency [14] criteria, including land use, geology, accessibility, and expert evaluation. In each station, samples were selected with three replications at the upstream, middle sections, and river branches. Then, the location of the selected sampling areas was recorded using GPS. Given that the river is subjected to pollution caused by metal industries in close vicinity to the watershed, population densities, various land uses, geology, and small rivers discharging into the river, sampling stations were selected at an approximate interval of 15 km (Fig.1). Surficial sediment samples were collected from August 2019 to September 2020. Due to the great changes in land uses and sharp slopes, most sampling stations were selected in Mahneshan district.

2.3 Sampling, sample transport, storage, and preparation

Three sediment samples with different grain sizes of about 1 Kg were gathered using a stainless-steel spade from each selected sampling station (Fig. 1). Moreover, three duplicate samples were taken at each station. The samples were collected in polypropylene containers and immediately placed in the iced boxes at 4°C and stored in laboratory freezers for further heavy metal analysis [8]. The sediment samples were grounded and sieved through a 63, 150, and 450 μm mesh before heavy metal determination; then, they were oven-dried at 50°C (48 h) and re-homogenized [8].

2.4 Sample digestion and heavy metal determination

The sediment samples were digested using the conventional aqua-regia procedure. This method has been used in numerous similar studies. Briefly, the mixture of hydrochloric acid, nitric acid, and sediment samples was placed on a hotplate for two h (ISO 11466, 1995). Three duplicate measurements (i.e., one blank and two samples) were used to ensure accurate contamination assessment. In this study, 1 g of powdered sediment samples was mixed in a 100 ml round bottom flask with HCl (Merck, 21 ml, 35%) and HNO_3 (Merck, 7 ml, 65%) after crossing the 50, 100, and 230 ASTM (Grain size 450, 150 and 63 μm) sieve mesh. The water condenser was connected to a flask, and the mixtures refluxed for two h. Subsequently, 25 ml of distilled water was added to the cooled mixture before filtering through a Whatman Filter Paper (No. 42). According to the method reported after the complete reaction, the filtered residue was rinsed twice with 5 ml of deionized water, and the solution was made up to 100 ml in measuring flasks (100 ml).

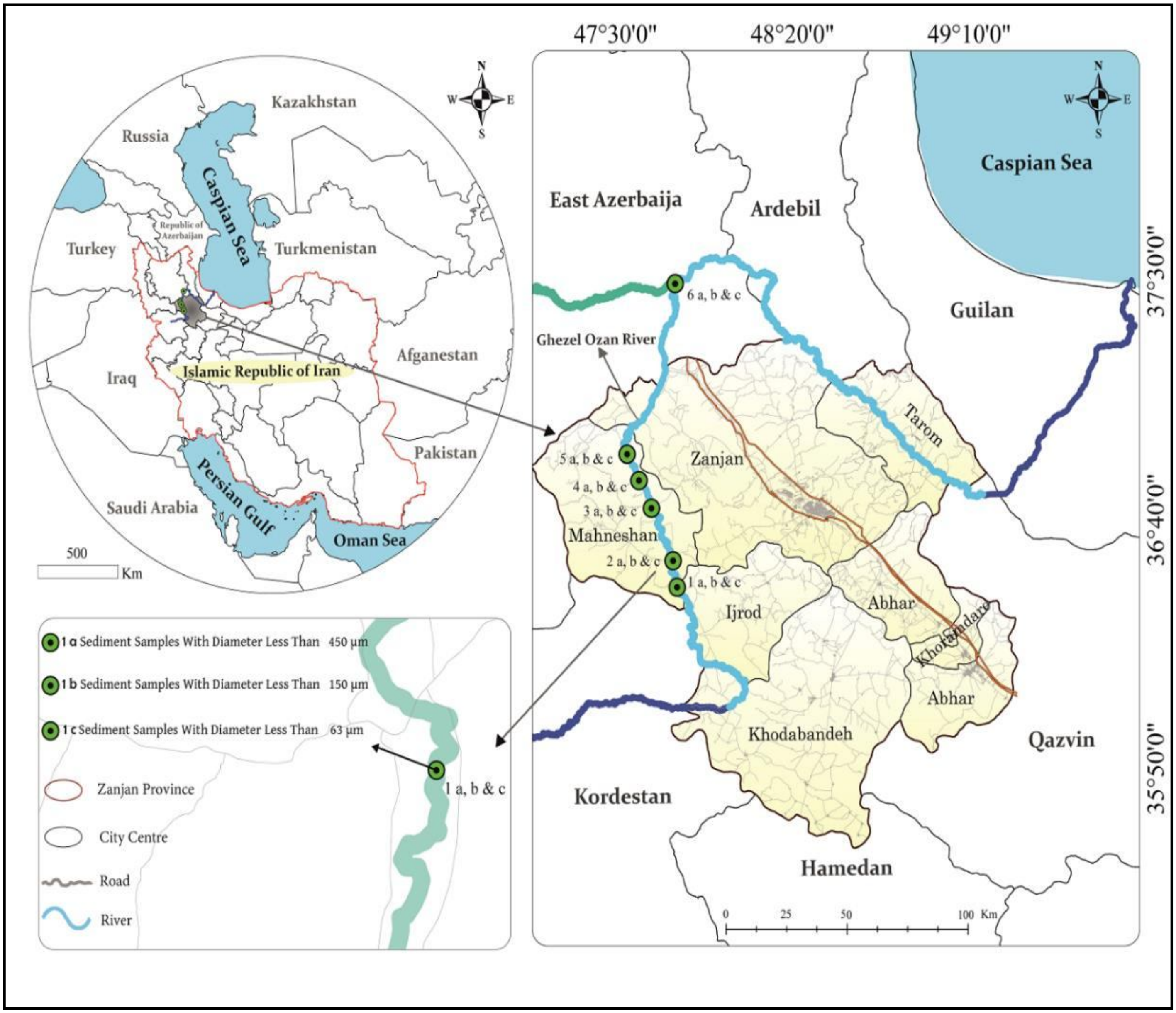

Figure 1: Location of the study area and sampling sites in the Ghezel Ozan River, Zanjan, Iran.

Heavy metals were determined by using a Varian 220AA Flame Atomic Absorption spectrometer (air/acetylene flame). The standard stock solutions were prepared using analytical grade chemicals (Merck and Fluka). Briefly, five mixed samples were used from each station. A sample was sent to the laboratory to measure heavy metals. Three replicate test samples were prepared to measure the amounts of heavy metals. The relative standard deviation of the measurement of these three samples was less than 5% in all stations. In addition, the preparation stages, including design, sampling, sample analysis, and analysis of the results, were done in the Environmental Science Research Laboratory, Department of Environmental Science, Faculty of Science, Zanjan University, Zanjan, Iran. The instrumental operating conditions for heavy metal determination are summarized in Table 1.

2.5 Evaluation Methods

2.5.1 Methods of sediment contamination evaluation

In an attempt to assess sediment pollution with heavy metals in the Ghezel Ozan River and to provide a relative ranking of contamination levels, we used a series of popular indexes and international evaluation techniques such as the Enrichment Factor (EF), Geo-accumulation Index (I_{geo}), Potential Ecological Risk Index (*RI*) and Pollution Load Index (PLI) [22].

Table 1: Instrumental operating conditions for the determination of heavy metals in sediments samples by FAAS

Elements	Wavelength (nm)	Lamp Current (mA)	Slit Width (nm)	Flame Type	LOD	LOQ	RSD
Zn	213.9	10	0.5	Air - acetylene	0.1	0.3	5%
Cu	852.1	16	1.0	Air - acetylene	0.3	1.0	3%
Cd	228.8	8	0.5	Air - acetylene	0.2	0.6	6%
Pb	283.3	10	0.5	Air - acetylene	0.6	2.0	3%
Ni	232.0	12	0.2	Air - acetylene	0.3	1.0	3%
Co	240.7	12	0.2	Air - acetylene	0.5	1.5	3%
Mn	279.5	10	0.2	Air - acetylene	1.0	3.0	3%
Fe	294.4	4	0.2	Air - acetylene	0.5	1.5	3%

nm: Nano Meter, mA: milliampere, LOD: limit of detection, LOQ: limit of quantification, RSD: relative standard deviation

2.5.2 Enrichment factor calculation

Enrichment factor (*EF*) is an analytical tool applied to compare metal contents in sediments with the metal contents of crustal material, as well as to evaluate sediment quality and determine the contamination degree (Eq (1)). Thus, the source of the contamination may be found. In equation 1, C_s/C_{Fe} in the numerator, C_s shows the average studied element level in the sediment sample, and C_{Fe} shows the concentration of Fe in the sediment sample. C_s/C_{Fe} in the denominator was used for background concentrations of the studied element and Fe in the background, respectively. It is noted that Fe or Al elements are applied as a normalization element to decrease the effect of heterogeneous sediments [23].

$$\text{Enrichment factor } (EF) = \left(\frac{C_s}{C_{Fe}}\right)_{\text{sample}} \Big/ \left(\frac{C_s}{C_{Fe}}\right)_{\text{Bacground}} \quad (1)$$

According to the EF values of sediment samples, the studied area was classified into seven levels, including No enrichment: $EF < 1$; minor enrichment: $1 \leq EF < 3$; moderate enrichment: $3 \leq EF < 5$; moderately severe enrichment: $5 \leq EF < 10$; severe enrichment: $10 \leq EF < 25$; very severe enrichment: $25 \leq EF < 50$; and extremely severe enrichment: $EF > 50$ [23,24]. Since no background data regarding studied heavy metals in uncontaminated river sediments in the study area has been reported, the geochemical average shale values were used as 0.3, 90.0, 45.0, 850.0, 68.0, 20.0, 95.0, and 46700.0 (in mg kg^{-1}) for Cd, Co, Cu, Mn, Ni, Pb, Zn, and Fe, respectively [25].

2.5.3 Geo-accumulation Index (I_{geo})

On the way to estimate sediment contamination and gain a better understanding of the extent of contamination in the studied area, another approach index called geo-accumulation index, briefly I_{geo}, was used (Eq (2)) [26].

$$I_{geo} = \log_2(C_n / 1.5B_n) \quad (2)$$

In this equation, C_n and B_n are used to show the concentration of heavy metals in sediment and the geochemical background of the sample. Coefficient 1.5 is the background matrix correction factor due to lithospheric effects [13,8,20]. Seven classes of geoaccumulation have been distinguished with the following I_{geo} values: Class 0 (practically uncontaminated): $I_{geo} \leq 0$; Class 1 (uncontaminated to moderately contaminated): $0 < I_{geo} \leq 1$; Class 2 (moderately contaminated): $1 < I_{geo} \leq 2$; Class 3 (moderately to heavily contaminated): $2 < I_{geo} \leq 3$; Class 4 (heavily contaminated): $3 < I_{geo} \leq 4$; Class 5 (heavily to extremely contaminated): $4 < I_{geo} \leq 5$; and Class 6 (extremely contaminated): $I_{geo} > 5$.

2.5.4 Calculation of Potential Ecological Risk Index

Potential ecological risk index (RI) was also widely used to evaluate the contamination degree and severity as a direct indicator of heavy metals in the river sediments and top soils samples (Eq. 2-5). This index (RI) will be calculated by the following equations (2-5):

$$RI = \sum_{i=1}^{m} E_r^i \quad (5) \qquad E_r^i = T_r^i \times C_f^i \quad (4)$$

$$C_f^i = C_S^i / C_n^i \quad (3) \qquad C_d = \sum_{i=1}^{m} C_f^i \quad (2)$$

Where C_f^i is a contamination factor for i^ts metal; C_s^i is a concentration of studied heavy metal in the sediment sample; C_n^i is a concentration of studied heavy metal in the background for calculation, and C_d is the contamination factor in the form of the monomial and polynomial [27]. Where E_i^i indicates the potential ecological risk factor for heavy metal, either the monomial or polynomial form. Similarly, in this equation, T_r^i shows the toxic response factor of each heavy metal. The amount of T_r^i for studied heavy metals are as follows: Mn = Zn =1, Co = 2, Ni = 6, Pb = Cu = 5 and Cd = 30 [28]. The E_i^i was classified as follows: $E_i^i < 40$, low ecological risk; $40 < E_i^i \leq 80$, moderate ecological risk; $80 < E_i^i \leq 160$, appreciable ecological risk; $160 < E_i^i \leq 320$, high ecological risk; and $E_i^i > 320$, serious ecological risks. RI values were interpreted as $RI < 150$, low ecological risk; $150 \leq RI < 300$, moderate ecological risks; 300 $RI < 600$, considerable ecological risk; $RI > 600$, very high ecological risk for the studied area [29]. The Pollution Load Index (*PLI*) was applied to show the integrated pollution status of all analyzed heavy metals at sampling stations by calculating the nth root of the product of the n CF for the tested metals using the following formula (Eqs (6); [30,14]:

$$\mathrm{PLI} = (CF_1 \times CF_2 \times CF_3 \times ..CF_n)^{\frac{1}{n}}$$

The *PLI* value of > 1 is polluted, whereas <1 indicates no pollution [8,17,22].

2.5.5 Statistical analysis

SPSS (version 20) was applied to analyze obtained data. The nonparametric tests were employed because the homogeneity (Leven test) and normality of the data (Kolmogorov-Smirnov test) was not confirmed. Spearman correlation matrix was applied to confirm a probable common source of the pollutants and evaluate the relationships between different heavy metals [31]. The confidence level used is 95%.

3. Results and Discussion

3.1 The amounts of heavy metals in river sediments

Based on the data obtained, the distribution character was different for studied heavy metals in the examined profile of the sediments from Ghezel Ozan River in terms of their different size and sampling stations. Table 2 indicates the values of measured heavy metals in Ghezel Ozan River sediment samples at different grain sizes. The mean values of heavy metals (mg kg^{-1}) were in the following range: Zn: 480.00-34294, Cu: 7.80-32.00, Cd: ND-100.00, Pb: 22.00-256.00, Ni: 2.50-60.00, Co: 7.60-34.00, Mn: 144.00-31600.00 and Fe: 9320.00-62300.00. Additionally, all heavy metal values in the surface sediments sampled from Ghezel Ozan River were in the order of Fe > Zn > Mn > Pb > Ni > Cu > Co > Cd, respectively. In order to compare the results of the present study to the reported data from other areas in Zanjan province, heavy metal amounts in groundwater, plant and soil were investigated. Mining and metal industries are important sources of heavy metal pollution; however, they are regarded as significant industrial activities in Zanjan province. Numerous studies have emphasized [32] that the ecological vicinity of mines and industries to rivers contributes to the pollution caused by heavy metals scattered from mining operations and anthropogenic sources. For example, in our previous studies, the average concentration of heavy metals in groundwater samples collected around the national Iranian lead and zinc company (NILZ) was as follows Zn > Fe > Cu ≈ Ni> Co > Pb > Cd [33]. The order of heavy metal contents (based on their mean values) in plant leaves in Zanjan varies as Zn >Pb >Fe >Mn >Cu >Cd >Co >Ni > Cr [34]. Moreover, the mean amounts values of the heavy metals in sediments collected from the Ghalechay River (Copper mine area) was Pb >Cu >Zn >Co > Cd [16]. The heavy metal contents order in the topsoil around the NILZ company in Zanjan province-Iran based on their average values varies as Fe > Zn > Pb > Ni > Cu > Cd > Co [32]. Similarly, [35] investigated the heavy metal concentrations of top soils in the vicinity of NILZ company (in Zanjan province) and reported the order of heavy metal concentrations as follows Zn > Pb > Ni > As > Cr > Co > Cd. Likewise, a similar result [36] reported changes in the heavy metal values in the soil with the order: Zn > Pb > Ni > Cu > Cd. These results confirm that anthropogenic sources are the original heavy metal sources in surface sediments collected from the Ghezel Ozan River. Industrial activities, especially mining and lead and zinc industries, are the main pollution sources and affect the surrounding environment. However, the geochemistry of the region is not ineffective in the distribution of heavy metals. All the sediment samples collected along the Ghezel Ozan River bed proved that the heavy metal Cu, Ni, Co, and Fe concentrations were oppositely correlated with the particle size ($p<0.05$). The assessment results of the heavy metal content in sampled sediments from the Ghezel Ozan River demonstrated that fine sediments (<63µm) can amass more than two times the levels of Cu, Co, and Fe and more than three times the levels of Ni in contrast to the sediments samples that are larger than 450µm. Research has confirmed that the finest grain-size fractions of sediments contain more heavy metals [37]. This could be attributed to high Ni, Co, Cu, and Fe values in smaller particle-size sediments since they have a high potential for transporting with river currents. Generally, Zn and Mn distribution in particle size of the surficial sediments from Ghezel Ozan River increased with larger grain size. Zn and Mn amounts were more than four and ten times greater in larger sediments fractions (450 µm) than the sediments finer than 63µm. Furthermore, the concentration of Cd and Pb in grain size (150 µm) showed the highest concentration, and in general, the concentration of Pb and Cd in fine sediments (63 &150 µm) was higher than in large sediments (450 µm). According to the average amounts of heavy metals, the spatial distribution of these elements implied that concentrations of Zn, Cd, Pb, Ni, and Fe reached a peak at Station 3, and maximum levels of Cu and Co were reported in Station 4. In site 3, Fe, Ni, Pb, and Mn concentrations increased in the finer fractions. However, a different behavior (see 450 µm and 150 µm sediment samples for Zn and Cd, respectively) was recorded for Zn and Cd. In site 4, the concentration of Co and Cu increased towards the finer fractions. Levels of studied heavy metals in station 3 indicated that a single anthropogenic source is responsible for their generation; however, this station was affected by Zn mines and the heavy minerals or coarse fractions of mine in its vicinity, and industrial wastes near this site could be the reason for increased Zn concentration in the coarser fractions [38-40].

3.2 Correlation among the heavy metals

Spearman′ s correlation analysis showed the contribution of heavy metals to sediment grain size varies (Table 2). In the sediment grain size of 450 µm, Zn with Fe, and Cu with Cd, have a positive correlation ($p<0.05$ Table 3). In smaller grain sizes (150 and 63 µm), the general relationship between studied heavy metals and grain size increased.

Table 2: Mean grain size and heavy metal concentration (mg/Kg) in the surface sediments of Ghezel Ozan River

Heavy metal (mg/Kg)	Grain size (µm)	Station						Mean	Max	Min
		1	2	3	4	5	6			
Zn	450	8018	34294	7500	1378	1218	480	8814.7	34294	480
	150	1890	1924	3320	2990	2684	3046	2642.3	3320	1890
	63	4818	2138	1197	2256	1730	1540	2279.8	4818	1197
Cu	450	21	17.8	19	17.4	11.6	10	16.1	21	10
	150	22	20	20	26	19.2	7.8	19.2	26	7.8
	63	30	22	26	32	26	22	26.3	32	22
Cd	450	7.8	3.2	17	2.2	1	1.8	5.5	17	1
	150	18	4	100	13	2.6	ND	22.9	100	ND
	63	20	4	4	8	6	4	7.7	20	4
Pb	450	32	32	22	26	54	96	43.7	96	22
	150	106	40	40	256	184	30	109.3	256	30
	63	84	68	138	94	72	54	85.0	138	54
Ni	450	26	2.5	18	2.9	15.4	15.2	13.3	26	2.5
	150	33	34	22	34	26	17	27.7	34	17
	63	60	40	32	58	44	38	45.3	60	32
Co	450	17	15.4	7.8	16.4	12.2	7.6	12.7	17	7.6
	150	22	28	9.6	28	19	14	20.1	28	9.6
	63	32	22	14	30	30	34	27.0	34	14
Mn	450	310	330	195	31600	216	196	5474.5	31600	195
	150	442	460	144	400	270	152	311.3	460	144
	63	708	506	208	538	514	548	503.7	708	208
Fe	450	17970	22950	15200	18600	13730	10575	16504.2	22950	10575
	150	33940	44850	9320	37750	21400	12100	26560.0	44850	9320
	63	49400	49000	16200	43600	44800	62300	44216.7	62300	16200

* The relative standard deviation of the measurement of three replicate test samples in all stations was less than 5%

Table 3: Spearman correlation matrix for the sediment parameters

	Grain Sizes 450 µm							
	Zn	Cu	Cd	Pb	Ni	Co	Mn	Fe
Cu	0.829*	1.000						
Cd	0.714	0.886*	1.000					
Pb	-0.522	-0.667	-0.754	1.000				
Ni	-0.29	0.486	0.371	-0.116	1.000			
Co	0.600	0.600	0.257	-0.319	0.086	1.000		
Mn	0.371	0.086	-0.143	-0.116	-0.543	0.771	1.000	
Fe	0.829*	0.543	0.429	-0.551	-0.429	0.714	0.771	1.000
	Grain Sizes 150 µm							
	Zn	Cu	Cd	Pb	Ni	Co	Mn	Fe
Cu	-0.319	1.000						
Cd	0.029	0.696	1.000					
Pb	-0.319	0.647	0.232	1.000				
Ni	-0.609	0.750	0.232	0.603	1.000			
Co	-0.667	0.603	-0.058	0.515	0.941**	1.000		
Mn	-0.886*	0.464	-0.029	0.290	0.841*	0.899*	1.000	
Fe	-0.714	0.522	-0.086	0.406	0.928**	0.986**	0.943**	1.000
	Grain Sizes 63 µm							
	Zn	Cu	Cd	Pb	Ni	Co	Mn	Fe
Cu	0.559	1.000						
Cd	0.820*	0.844*	1.000					
Pb	0.029	0.736	0.334	1.000				
Ni	0.943**	0.677	0.941**	0.086	1.000			
Co	0.319	0.015	0.370	-0.551	0.406	1.000		
Mn	0.600	0.294	0.638	-0.314	0.657	0.928**	1.000	
Fe	0.257	-0.441	0.030	-0.829*	0.200	0.812*	0.714	1.000

Table 4: Sediment quality geoaccumulation index (I_{geo})

Metals	Grain size (µm)	Station						Statistics		
		1	2	3	4	5	6	Min	Max	Mean
Zn	450	5.81	7.91	5.72	3.27	3.10	1.75	1.75	7.91	4.59
	150	3.73	3.76	4.54	4.39	4.24	4.42	3.73	4.54	4.18
	63	5.08	3.91	3.07	3.98	3.60	3.43	3.07	5.08	3.85
Cu	450	-1.68	-1.92	-1.83	-1.96	-2.54	-2.75	-2.75	-1.68	-2.11
	150	-1.62	-1.75	-1.75	-1.38	-1.81	-3.11	-3.11	-1.38	-1.91
	63	-1.17	-1.62	-1.38	-1.08	-1.38	-1.62	-1.62	-1.08	-1.37
Cd	450	-1.94	-3.23	-0.82	-3.77	-4.91	-4.06	-4.91	-0.82	-3.12
	150	5.32	3.15	7.80	4.85	2.53	0.00	0.00	7.80	3.94
	63	5.47	3.15	3.15	4.15	3.74	3.15	3.15	5.47	3.80
Pb	450	0.09	0.09	-0.45	-0.21	0.85	1.68	-0.45	1.68	0.34
	150	1.82	0.42	0.42	3.09	2.62	–	0.42	3.09	1.39
	63	1.49	1.18	2.20	1.65	1.26	0.85	0.85	2.20	1.44
Ni	450	-1.97	-5.35	-2.50	-5.14	-2.73	-2.75	-5.35	-1.97	-3.41
	150	-1.63	-1.58	-2.21	-1.58	-1.97	-2.58	-2.58	-1.58	-1.93
	63	-0.77	-1.35	-1.67	-0.81	-1.21	-1.42	-1.67	-0.77	-1.21
Co	450	-0.75	-0.89	-1.87	-0.80	-1.22	-1.91	-1.91	-0.75	-1.24
	150	-0.37	-0.03	-1.57	-0.03	-0.58	-1.03	-1.57	-0.03	-0.60
	63	0.17	-0.37	-1.03	0.07	0.07	0.25	-1.03	0.25	-0.14
Mn	450	-2.04	-1.95	-2.71	4.63	-2.56	-2.70	-2.71	4.63	-1.22
	150	-1.53	-1.47	-3.15	-1.67	-2.24	-3.07	-3.15	-1.47	-2.19
	63	-0.85	-1.33	-2.62	-1.24	-1.31	-1.22	-2.62	-0.85	-1.43

Table 5: The enrichment factor (EF) values for heavy metals in the studied sediment

Metals	Grain size (µm)	Station						Statistics		
		1	2	3	4	5	6	Min	Max	Mean
Zn	450	219.34	734.56	242.56	36.42	43.61	22.31	22.31	734.56	216.47
	150	27.37	21.09	175.11	38.94	61.65	123.75	21.09	175.11	74.65
	63	47.94	21.45	36.32	25.44	18.98	12.15	12.15	47.94	27.05
Cu	450	1.21	0.80	1.30	0.97	0.88	0.98	0.80	1.30	1.02
	150	0.67	0.46	2.23	0.71	0.93	0.67	0.46	2.23	0.95
	63	0.63	0.47	1.67	0.76	0.60	0.37	0.37	1.67	0.75
Cd	450	67.57	21.71	174.10	18.41	11.34	26.50	11.34	174.10	53.27
	150	82.56	13.88	1670.24	53.61	18.91	0.00	0.00	1670.24	306.53
	63	63.02	12.71	38.44	28.56	20.85	9.99	9.99	63.02	28.93
Pb	450	4.16	3.26	3.38	3.26	9.18	21.20	3.26	21.20	7.41
	150	7.29	2.08	10.02	15.83	20.08	5.79	2.08	20.08	10.18
	63	3.97	3.24	19.89	5.03	3.75	2.02	2.02	19.89	6.32
Ni	450	0.99	0.07	0.81	0.11	0.77	0.99	0.07	0.99	0.62
	150	0.67	0.52	1.62	0.62	0.83	0.96	0.52	1.62	0.87
	63	0.83	0.56	1.36	0.91	0.67	0.42	0.42	1.36	0.79
Co	450	2.33	1.65	1.26	2.17	2.18	1.77	1.26	2.33	1.89
	150	1.59	1.53	2.53	1.82	2.18	2.84	1.53	2.84	2.08
	63	1.59	1.10	2.12	1.69	1.65	1.34	1.10	2.12	1.58
Mn	450	0.95	0.79	0.70	93.34	0.86	1.02	0.70	93.34	16.28
	150	0.72	0.56	0.85	0.58	0.69	0.69	0.56	0.85	0.68
	63	0.79	0.57	0.71	0.68	0.63	0.48	0.48	0.79	0.64

Table 6: Summary of statistical parameters values, C_d, *RI*, and PLI in surface sediments

Station	*PLI*			*RI*			C_d		
	63	150	450	63	150	450	63	150	450
1	3.25	2.25	1.73	2084.54	1854.59	879.18	126.71	88.57	114.49
2	1.95	1.76	1.39	448.39	438.96	693.20	43.12	39.51	375.38
3	1.45	1.66	1.42	454.53	10050.29	1789.20	35.21	371.92	138.37
4	2.53	2.70	1.52	859.71	1404.78	282.10	59.82	91.44	62.01
5	2.15	1.64	0.87	646.74	341.00	130.51	46.18	48.70	20.53
6	1.99	0.69	0.79	439.73	43.58	212.54	37.06	35.16	17.16
Min	1.45	0.69	0.79	439.73	43.58	130.51	35.21	35.16	17.16
Max	3.25	2.70	1.73	2084.54	10050.29	1789.20	126.71	371.92	375.38
Mean	2.22	1.78	1.29	822.28	2355.53	664.45	58.02	112.55	121.32

Table 7: Comparison of heavy metals levels (mg/Kg) of sediments in Ghezel Ozan River with other rivers of the world

River	Country	Fe (%)	Mn	Zn	Cd	Cu	Pb	Co	Ni		Reference
Ghezel Ozan	Iran	1.6	5474.5	8814.7	5.5	16.1	43.7	12.7	13.3	450 µm	This study
		2.6	311.3	2642.3	22.9	19.2	109.3	20.1	27.7	150 µm	
		4.4	503.7	2279.8	7.7	26.3	85.0	27.0	45.3	63 µm	
Taojiang	China	--	--	156.8	9.1	43.1	48.7	--	--		[41]
Houjing	Taiwan	--	--	341.9	4.4	432.3	57.3	--	71.2		[42]
Red	Vietnam	3.8	806.0	127.0	0.4	83.0	66.0	--	38.0		[43]
Brisbane	Australia	1.6	386.0	106.6	0.3	29.0	25.6	14.9	15.3		[44]
Korotoa	Bangladesh	--	--	--	1.3	76.5	58.5	--	94.5		[45]
Ganga	India	3.1	372.0	67.8	1.7	29.8	26.7	--	26.7		[46]

A positive and significant relationship was observed in grain size of 150µm Zn with Mn, Ni with Co, Mn and Fe, Co with Mn, and Fe, and Mn with Fe ($p< 0.05$, Table 3). Furthermore, in grain size 63µm, between Zn and Cd, and Ni, Cu and Cd, Cd and Ni, Pb and Fe, and Co and Mn and Fe, a positive and significant relationship was evident ($p< 0.05$, Table 3). Correlation analyses also indicated a similar human activity source for some heavy metals. The strongest significant positive correlations were reported for elements Zn, Ni, and Cd in fine sediments [32]. In previous studies, Zn, Ni, and Cd contamination was found to be strongly correlated, confirming that the presence of the common source elements was a significant influence (Zn mines can be one of the sources) [32].

3.3 Values of Geoaccumulation index

The average amounts of I_{geo} indicated that all studied stations are not polluted with Cu, Co, Ni, and Mn (Table 4) (i.e., $I_{geo} \leq 0$). In particular, the degree of Cd, Pb, and Zn contamination has covered a wide range of the study area, especially zinc, which is observed in river sediments contaminated with this metal. The mean values of I_{geo} affirmed that Cd, Pb, and Zn were compatible with class 4 contamination. Generally, heavy contamination was confirmed in all stations. Therefore, zinc, Cd, and Pb were selected as heavy metals with control priority.

3.4 Values of Enrichment factor

Table 5 indicates the values of enrichment factor (EF) in riverine sediment were calculated with the limitation defined by Taylor (1964) [32]. The calculated mean values of EF suggested that levels of minimal enrichment for Ni, Cu, Co, and Mn were moderate enrichment. The mean values of EF for the heavy metals were less than 2; therefore, natural resources were the main reason for their enrichment. The mean values of EF for Zn, Cd, and Ni were higher than 6. The enrichment sources of the mentioned metals are likely to be anthropogenic, affected mainly by human activities. The obtained results suggested that the river sediment in the investigated areas is contaminated with heavy metals (Zn, Cd, and Pb). According to the above analyses, the main source of this contamination is anthropogenic inputs from metal industries and lead and zinc mining since results indicate similar trends to the I_{geo} values.

3.5 Values of Hankinson potential ecological risk index

The higher amounts of C_d and RI were detected in stations 1, 2, and 3. C_d and *RI* levels confirmed the river sediments were very highly contaminated (Table 6). The average PLI value was found in grain size of sediment 450, 150 and 63µm be 1.29, 1.78, and 2.22, respectively. Given that the average pollution load index exceeded 1, the index PLI indicates that metal contamination was detected in the investigated area (Table 6).

3.6 Comparison of heavy metal content in the sediment of Ghezel Ozan River with other rivers

Comparisons of the amounts of the heavy metal in the present study with several studies undertaken in Ghezel Ozan River area and other rivers are presented in Table 7. Comparisons of the heavy metal concentrations in several rivers including Taojiang River [41], Houjing River [42], Red River [43], Brisbane River [44], Korotoa River [45] and the Ganga River [46] proper indicate that Zn and Cd Levels in Ghezel Ozan River are higher compared to those detected in other rivers, while Co, Ni, Fe, and Mn are in a similar range of other rivers. However, Zn, Cd, and Pb values demonstrate higher concentrations at Ghezel Ozan River proper.

4. Conclusion

the content of coarse fractions of the sediments from Ghezel Ozan River consists of heavy metals. In coarse grain size (i.e., 450 µm), Zn and Mn content tends to increase, which can be due to intensive mining and metallurgy activities, especially processing and extraction of zinc near Ghezel Ozan water reservoir in the past and present. Additionally, the highest concentrations of heavy metals Cd and Pb were found in the medium grain size range (i.e., 150 µm). The assessed mean values of I_{geo} index for heavy metals indicated that the average I_{geo} values of the heavy metals Zn, Pb, and Cd are detected in heavily contaminated areas. These metals were recognized as the most serious threat in the present study. The mean values of EF confirm minimal enrichment for Cu, Ni, Mn, and Co, unlike Zn, Cd, and Pb, which indicate severe enrichment. The average values of Cd, RI, and PLI studied for heavy metals demonstrated a considerable contamination level.

Authors' Contributions

Mina Islami: Field investigation; Laboratory investigation; Data analysis; Writing-original draft. Mohammad Abadi: Data analysis; Writing-original draft. Abbasali Zamani: Conceptualization; Study design; Supervision; Writing-original draft; Writing review and Editing. Jaber Aazami: Conceptualization; Study design; Field investigation. Hamid Badiee: Field investigation; Laboratory investigation.

Conflicts of Interest

The Authors declare that there is no conflict of interest.

Acknowledgments

The authors appreciate the University of Zanjan, Zanjan, Iran, for financial and technical support of this study. (Project No. 25019).

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