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Risk Assessment of Heavy Metal Hotspots in Surface Water Bodies: A Case Study of Zanjan Province, Iran

Mohammad Rafiee[a, b], **Mahsa Jahangiri-Rad**[c, d*]

[a] Environmental and Occupational Hazards Control Research Center, Shahid Beheshti University of Medical Sciences, Tehran, Iran
[b] Department of Environmental Health Engineering, School of Public Health, Shahid Beheshti University of Medical Sciences, Tehran, Iran
[c] Water Purification Research Center, Tehran Medical Sciences, Islamic Azad University, Tehran, Iran
[d] Department of Environmental Health Engineering, Faculty of Health, Tehran Medical Sciences, Islamic Azad University, Tehran, Iran

***Correspondence** should be addressed to Ms Mahsa Jahangiri-Rad, **Email:** m.jahangiri@iautmu.ac.ir

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Background & Aims of the Study: Agricultural and industrial activities are primary risk sources of heavy metal (HM) pollution in the water environment. Indices are well-known approaches for assessing HM contamination in the aquatic environment.
Materials and Methods: Water samples were collected in polyethylene bottles and transported to the laboratory for further analysis. Samples were examined during the winter and spring. The inductively coupled plasma was used to determine HMs concentrations collected from 48 stations. The Wilcox signed-rank test was applied to examine the HMs values in two different months. In addition, Spearman's correlation coefficient was used to examine the relationship between HMs.
Results: Based on the findings of the present study, the HM contents in the analyzed samples showed no high values, except for lead and nickel (15% of samples) in spring. The potential ecological risk indices revealed that about 25% and 41% of samples demonstrated high and significantly high pollution levels in spring, respectively, while these values declined to 37% and 8% in winter. Only one sampling point showed risk characterization ratio ≥ 1 for zinc in winter. Moreover, the ecological risk of the surface water potentially decreased in the order of water bodies > dry farming > agricultural lands > barren lands areas.
Conclusion: According to the obtained results, the presence of lead and nickel indicated the main anthropogenic sources of HMs in the studied area, especially in the west and south of Zanjan. Anthropogenic inputs of HMs could be related to mining, agricultural, and industrial activities.

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Background

Although metals and metal compounds constitute the main natural pillar of every ecosystem, excessive amounts of these compounds in soil and water are major threats to the ecosystem and human life (1, 2). Toxic compounds, such as metals in water bodies accumulate through chemical and physical adsorption. Heavy metals (HMs) are important pollutants not only owing to their resistance but also because of their direct effects on organisms. Moreover, aquatic organisms can accumulate

HMs (3, 4). Furthermore, aquatic organisms can transfer, accumulate, and magnify these metals through their biological activities. Consequently, large concentrations of these compounds bring detrimental effects on human health, especially when they are transferred across the food web (5). In spite of differences in the toxicity of metals, environmental factors, exposure time and their concentrations are also determining factors in an ecosystem function (6). The majority of HMs have been subject to extensive investigations due to their environmental and health-related effects. However, in bioavailability and toxicology studies, 10 of them including arsenic (As), cadmium (Cd), lead (Pb), copper (Cu), nickel (Ni), antimony, stannum, zinc (Zn), and chromium (Cr) are of great concern due to their high potential for affecting the environment and human health (7). Rapid industrial growth and agricultural development resulted in increasing HMs contamination posing serious threats to vertebrates, fishes, and humans' lives (8, 9). Methods for assessing the risk of HMs encompasses the potential ecological risk index (RI) (10) and geo-accumulation (11). Moreover, the total contamination index (Zs) is also calculated (12). Among these three indices, the first two are more popular. A sensible and realistic assessment of the ecological effects of HMs is possible by considering the characteristics of each polluted source, which changes the chemical structure of compounds. As compared to the total concentration of dissolved HMs, concentrations of free metal ions indicate more reflective toxicological effects on organisms that are at-risk in aquatic environments (13, 14). On the other hand, considering the reaction of metals with biological ligands (e.g., the fish gill), the toxic effects of HMs can be more precisely explained (15). Related research on this topic led to the development and invention of the biotic ligand models (BLMs) (16). The formation of complex to abiotic ligands (e.g., OH^-, Cl^-, SO_4^{2-}), as well as competition between metals and other cations (e.g., Ca^{2+} and H^-), are important for precise examination of toxicological effects of metals (17). However, there are large barriers regarding the usage of BLM models, the most important of which is the measurement of several physical and chemical water quality parameters. Some of these parameters are not widely available from standard monitoring programs (18). To overcome these problems, the PNEC-Pro model was introduced for the assessment of ecological risks of Zn, Cu, and Ni-based on dissolved organic carbon (DOC) concentration as the most impediment input criteria (19). Predicted no-effect concentration program (PNEC-pro) uses a routine process to choose the highest reliability functions, based on the input parameters entered by users (19). Consequently, the present study analyzed and assessed the risk characterization ratio (RCR) of Cu, Ni, and Zn on ecology using the PNEC-pro and potential ecological RI methods. The aims of the current study were: 1) to determine the contents and spatial distribution of HMs in surface waters of Zanjan province, Iran, 2) to assess the HMs ecological risk in the area of the study by the use of potential ecological RI and RCR, and finally, 3) to identify natural and man-made sources of HMs by applying Zonal statistics using Arc GIS 10.2. The present study was carried out in Zanjan province, Iran, in 2016-2017.

Materials & Methods

Zanjan is situated in the North West of Iran. The aforementioned province has a highland climate portrayed by snowy weather in the mountains and a moderate climate throughout the plains in cold seasons. Agriculture is the main occupation of people, as they grow crops, such as rice, corn (maize), oilseed, fruit, and potato. Poultry, cattle, and sheep are raised as well. Moreover, the province is well-known for its seedless grapes. Zanjan has various industries, including bricks, cement, milled rice, and carpet weaving. The Cr, Pb, and Cu are mined though most of the raw and processed products are imported.

Sample collection

During 2015, water samples were collected in spring and summer using polyethylene bottles placed about 0.5 meters lower than the level of water in rivers. Water samples were collected once in every month (middle of the river stretch) from 48 sites within April-September 2015. The samples were taken using the Nansen type of water sampler. Having been sent to the laboratory, the samples were filtered using 0.45 µ Millipore Nitrocellulose Filters and their pH was reduced to lower than 1 using nitric acid. The HM concentrations were measured by inductively coupled plasma mass spectrometry. Figure 1 depicts the sampling point and map of the studied area.

Dissolved organic carbon analysis

Water samples were preserved with sulfuric acid at pH < 2. The original samples were stored at 4°C, followed by filtration through 0.45 µ membrane filters (Schleicher and Schuell Micro Science). A total organic carbon analyzer (SM5310B Combustion–Infrared) was employed to measure DOC.

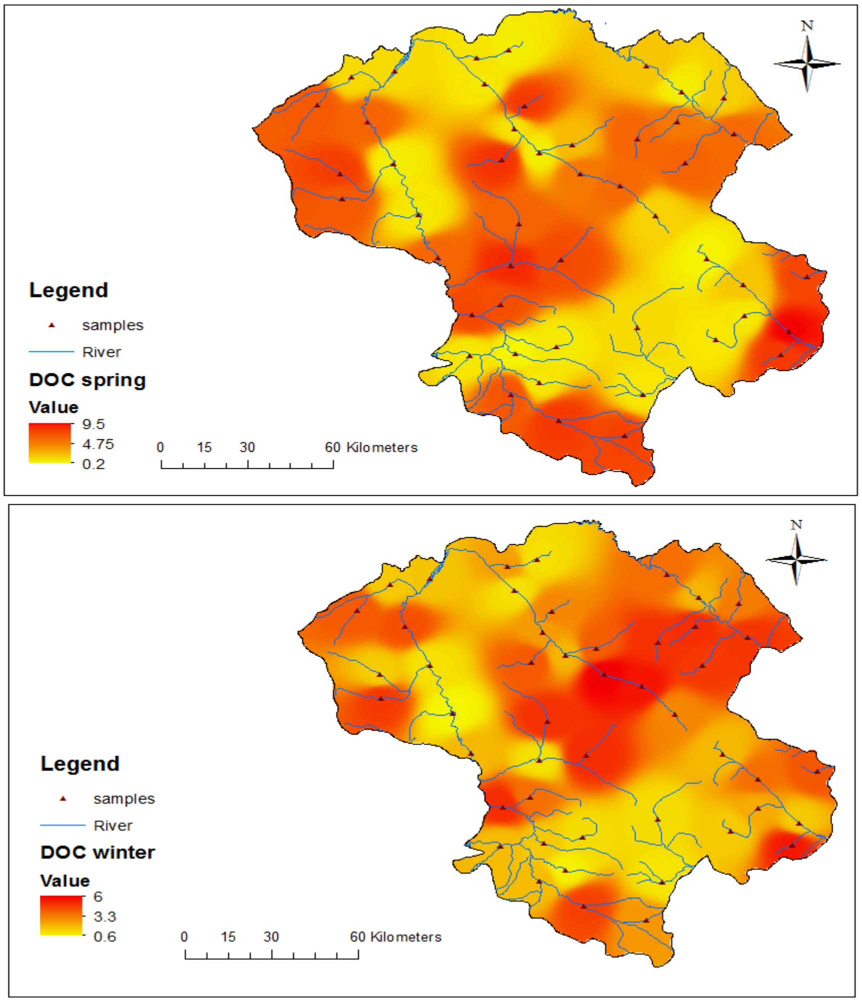


Figure 1) Maps of the studied area, sampling points, and dissolved organic carbon's spatial pattern of Zanjan rivers

Statistical analysis

The collected data were analyzed in SPSS software (version 22). To examine the data the Wilcox signed-rank test was used in two various seasons. A p-value of less than 0.05 was considered statistically significant. Moreover, the Spearman's correlation coefficient was applied to examine the relationship between HMs.

Potential ecological risk analysis

The ecological RI was introduced by Hakanson in 1980 (10), it was used based on the toxicity of HMs and the response of the environment, in this case, surface waters. In this method, the sensitivity of an aquatic environment relies on its productivity according to Equations 1, 2, and 3:

$$RI = \sum E_i \qquad \text{Eq. (1)}$$

$$E_i = T_i f_i \qquad \text{Eq. (2)}$$

$$f_i = \frac{C_i}{B_i} \qquad \text{Eq. (3)}$$

Where the RI denotes the sum of all risk factors related to HMs and T_i is the HM toxicity factor. The toxicity factor which was indicated by Hakanson in 1980 is as follows:

Cd > Pb = Cu = Ni > Zn

The toxicity factor for Pb, Cu, and Ni is 5, while the toxicity factors for Cd and Zn are 30 and 1, respectively (20). The F_i represents the metal contamination factor, C_i denotes the concentration of HM in water, and B_i is the reference HM value. River water reference material for trace elements was used to calculate the reference value (21). The RI denotes the sensitivity of different biological population systems to the total concentration of HMs and indicates the potential ecological risk caused by HMs. Defined five E_i categories and four RI categories are presented in Table 1.

Geostatistical analysis

A geostatistical analyst provides a set of interpolation techniques to predict variable values at unknown locations, based on the sample points values. The main goal of preparing a contamination map of surface waters is to determine the spatial distribution of contamination and contaminated regions (22, 23). The contamination spatial distribution map should be as exact as possible. For this purpose, inverse distance weighting (IDW) is used in most studies for spatial distribution. The IDW puts an assumption that things close to each other are more alike than those that are farther apart into practice (i.e., IDW employs the measured values surrounding the prediction location to predict a value for any unmeasured site). Spatial autocorrelation does not perform in the IDW technique (24). The statistics are calculated through the Zonal Statistics tool for each zone described by a zone dataset, based on values from another dataset (a value raster). A single output value is finally calculated for every zone in the input zone dataset (25). In this regard, the Zonal statistic subset tool was applied in conjunction with land use-land cover map of the studied area for identifying land use- land cover statistics of each area.

Table 1) Risk grade indices and grades of the potential ecological risk of heavy metal pollution

E_i	Risk grade	RI	Risk grade
<40	Low potential ecological risk	≤50	Low potential ecological risk
40-80	Moderate potential ecological risk	50<RI≤100	Moderate potential ecological risk
80-160	Considerable potential ecological risk	100<RI≤200	High potential ecological risk
160-320	High potential ecological risk	RI>200	Significantly high potential ecological risk
>320	Significantly high potential ecological risk		

E_i: Potential ecological risk index of a single element
RI: Risk index

Results

The HMs concentrations measured in surface waters of Zanjan province do not exceed the standards of Iran’s surface waters and that of the World Health Organization (WHO) (Table 2). As depicted, exceeded concentrations of HMs were observed in spring. Metal concentration was lower in winter and their values nearly doubled during spring.

As shown in Figure 2, the mean and median concentrations of each HM did not exceed the WHO guidelines, as well as national water quality standards (Table 1). Similarly, the concentration of DOC is higher in the mentioned sampling areas. Correspondingly, the DOC spatial distribution map showed higher values in spring as compared to the winter (Figure 1).

In order to examine the relationship between the measured elements the Spearman's correlation coefficient was used and its results are displayed in Table 3 (a and b).

Ecological power assessment

Table 4 presents the pollution index (PI) values considering the background concentration of HMs in surface waters.

Hakanson (1980) (10) proposed the RI risk factor, based on eight chemicals (PCB, As, Hg, Cd, Pb, Cr, Cu, and Zn). In the present study, five of these parameters and Ni were applied. Table 5 presents the results of E_i and RI values. The RI values imply the sensitivity of biological communities to toxic substances and reflect the potential ecological risk caused by HMs. The potential ecological RI is illustrated in Figure 3.

Figure 4 shows the RI values calculated for each land uses of Zanjan province. To calculate the spatial distribution of RI for each land use the Zonal statistic tool was applied and levels of land uses were plotted versus RI values. As seen, the RI values with a very high-risk potential during winter were located in dry farming, water bodies, and agricultural lands that cover about 6,000, 5,300, and 4,000 km^2 of these areas, respectively. Forests with an area of approximately 500 km^2 showed the lowest area with high values of RI. Moreover, 85% of the barren lands’ area displayed high extremely large values of RI during winter. A similar trend is observed during spring. As shown 5,700, 5,400, 3,600, and 3,200 km^2 of water bodies, dry farming, built-up, and agricultural

Table 2) Descriptive statistics of the elements in surface water in Zanajn and Iranian Standards for domestic purposes (µg L^{-1})

Season	Variables	Pb	Cu	Ni	Zn	As	Cd
Spring	Mean(mg/L)	3.74	0.62	8.52	4.26	0.13	0.02
	Std deviation	10.84	0.53	8.47	4.23	0.13	0.02
	Kurtosis	28.6	0.75	1.51	1.51	-1.95	-0.53
	Skewness	4.9	1.13	1.48	1.48	0.08	.716
	Range	68.91	2.16	32.64	16.32	0.33	0.08
Winter	Mean	2.31	0.46	4.32	4.13	0.012	0.005
	Std deviation	1.42	0.29	3.03	2.82	0.02	0.012
	Kurtosis	-0.5	5.07	-1.14	-1.12	3.25	4.5
	Skewness	0.23	1.98	-0.024	-0.09	2.01	2.27
	Range	5.78	1.4	9.8	9.36	0.085	0.05
	Max desirable	-	300	50	-	5000	10
	High permissible	50	1000	1500	20	15000	50

Pb: Lead
Cu: Copper
Ni: Nickel
Zn: Zinc
As: Arsenic
Cd: Cadmium

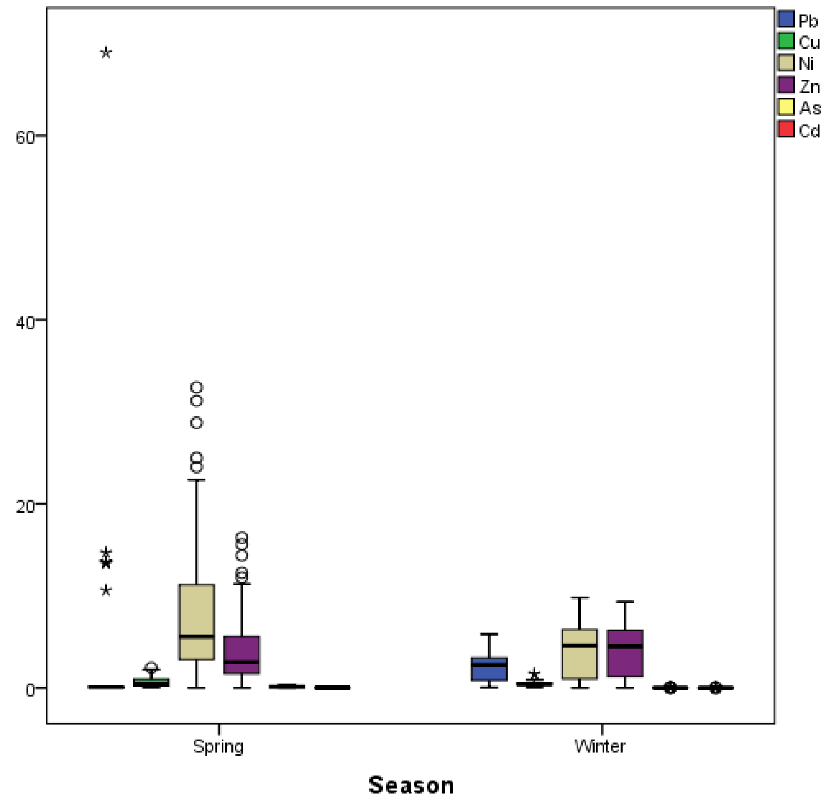


Figure 2) Box plots of the measured heavy metals

Table 3) Spearman's correlation matrix of heavy metals in the surface waters of Zanjan (a: Winter and b: Spring)

(a)	**DOC**	**Pb**	**Cu**	**Ni**	**Zn**	**As**	**Cd**
DOC	1.00						
Pb	0.33*	1.00					
Cu	0.2	0.6**	1.00				
Ni	0.08	0.46**	0.39*	1.00			
Zn	0.14	0.42**	0.44**	0.52**	1.00		
As	0.08	0.35*	0.30	0.18	0.16	1.00	
Cd	0.31	0.45**	0.39*	0.20	0.22	0.21	1.00

(b)	**DOC**	**Pb**	**Cu**	**Ni**	**Zn**	**As**	**Cd**
DOC	1.00						
Pb	0.56**	1.00					
Cu	0.62**	0.52**	1.00				
Ni	0.59**	0.61**	0.67**	1.00			
Zn	0.50**	0.60**	0.65**	0.95**	1.00		
As	0.86**	0.60**	0.64**	0.64**	0.62**	1.00	
Cd	0.79**	0.72**	0.61**	0.65**	0.62**	0.85**	1.00

Doc: dissolved organic carbon
Pb: Lead
Cu: Copper
Ni: Nickel
Zn: Zinc
As: Arsenic
Cd: Cadmium

Table 4) Statistical results of heavy metals pollution index

Element	PI (spring)			PI (winter)		
	Min	Max	Mean	Min	Max	Mean
Pb	3	2300	124.92	1.66	194.4	77.21
Cu	0.001	0.095	0.02	0.004	0.065	0.02
Ni	0	4.94	1.29	0	1.48	0.66
Zn	0	1.48	0.39	0	0.85	0.37
As	0	0.13	0.05	0	0.032	0.004
Cd	0	9.04	0.18	0	0.45	0.05
IPI	0.5	383.4	21.14	0.27	32.88	13.05

PI: Pollution index
IPI: Integrated pollution index
Pb: Lead
Cu: Copper
Ni: Nickel
Zn: Zinc
As: Arsenic
Cd: Cadmium

Table 5) Risk Index and E_i values of heavy metals calculated for Zanjan surface waters

	Spring			Winter		
	E_i (range)	Mean±SD	RI (range)	E_i (range)	Mean±SD	RI (range)
Pb	5.17-3965.5	215.38±623.32	5.19-3995.5 ±138.85	2.87-335.24	133.12 ±82.18	14.98-599.93± 691.91
Cu	0.01-0.58	0.16± 0.143		0.026-0.4	0.12±0.077	
Ni	0-307.92	80.45± 79.96		0-92.45	40.83±28.6	
Zn	0-17.54	4.58± 4.55		0-10.06	4.44±3.03	
As	0-7.68	3.09± 3.09		0-1.93	0.27±0.5	
Cd	0-400	103.64±117.37		0-250	28.64 ±60.36	

E_i: Potential ecological risk index of a single element
RI: Risk index
Pb: Lead
Cu: Copper
Ni: Nickel
Zn: Zinc
As: Arsenic
Cd: Cadmium

land were located in the RI zones with extremely large RI values, respectively (RI>200). However, in this case, barren lands also dedicated the highest percentage of extremely high pollution with 95% of its total area.

Figure 5 demonstrates the mean ecological risk factors of studied HMs. The figure indeed tracks each metal contribution to the total potential ecological risk of the surface waters. Although other metals showed much lower risk levels, Pb with a mean risk factor of 215.38 and 133.12 contributes greatly to the potential ecological risk followed by Cd and Ni in spring and winter, respectively. The mean value of the potential ecological risk indices with regard to surface waters, calculated as the sum of themean risk factors of the HMs, is approximately 208 and 407 during winter and spring, respectively, demonstrating a moderate and high ecological risk posed by HMs at the same seasons.

Risk characterization ratio using PNEC-pro software

The ecological risks of Ni, Zn, and Cu were measured based on the DOC values applied in PNEC-Pro software. Considering the concentration of HMs and DOC, PNEC-pro is able to calculate the PNEC of any concentration of contaminants along with its risk level. Figure 6 shows the results of the software analysis.

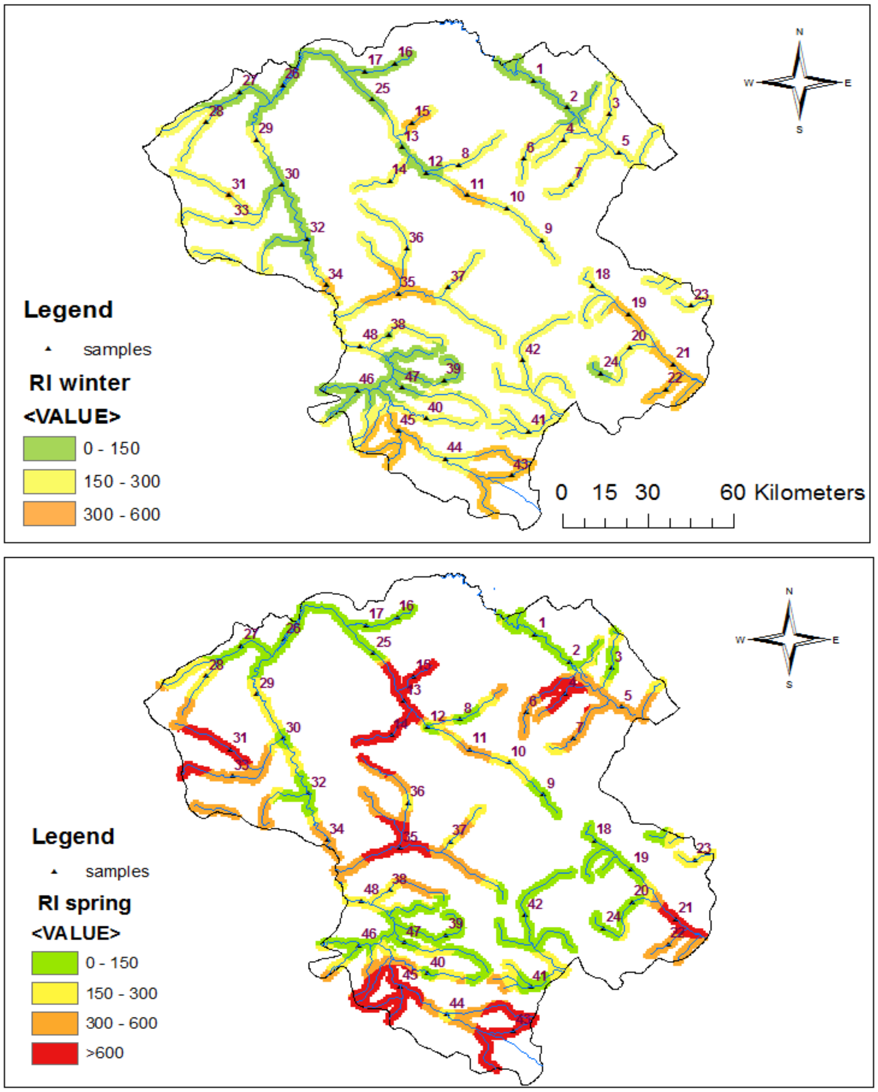


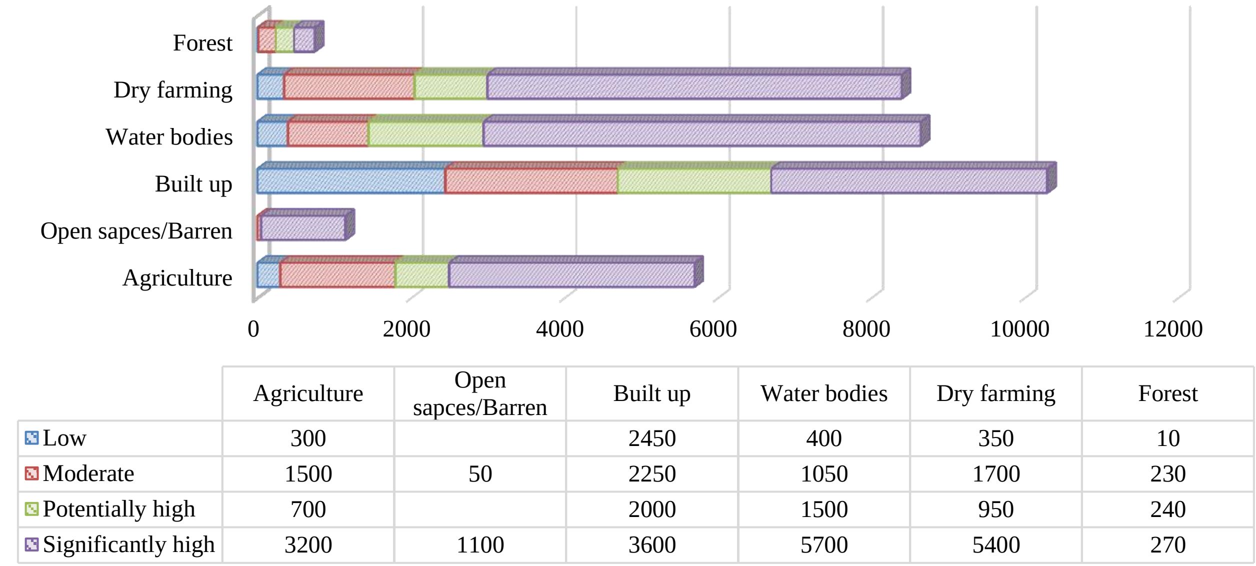
Figure 3) Distribution of grades on the potential ecological risk of the heavy metals in rivers

During spring, sampling areas No. 4, 5, 6, 10, 14, 15, 18, 20, 21, 30, 31, 34, 35, 39, 43, and 45 showed RCR ≥ 1 for Ni; therefore, they are ecologically hazardous (red stars on the map). On the other hand, sampling areas No. 14, 15, 18, 21, 24, 31, 40, and 46 showed RCR ≥ 1 during winter for the same metals; consequently, they are ecologically hazardous. The ecological risk of Zn was observed in sampling No. 18, in winter. In addition, there was no risk regarding the existence of Cu in any of these areas during both winter and spring. Furthermore, the RCR ≥ 1 values were in accordance with higher RI observations.

Discussion

High concentrations of Pb and Ni in spring were detected in sampling areas of No. 14, 15, 20, 21, 30, 43, and 45. These concentrations can be attributed to the discharge of industrial wastewater of units situated around these areas. In addition, most land uses around the sampling regions are agricultural or farming. Probably due to the use of pesticides applied at the

(a)



	Agriculture	Open sapces/Barren	Built up	Water bodies	Dry farming	Forest
▨ Low	300		2450	400	350	10
▨ Moderate	1500	50	2250	1050	1700	230
▨ Potentially high	700		2000	1500	950	240
▨ Significantly high	3200	1100	3600	5700	5400	270

(b)

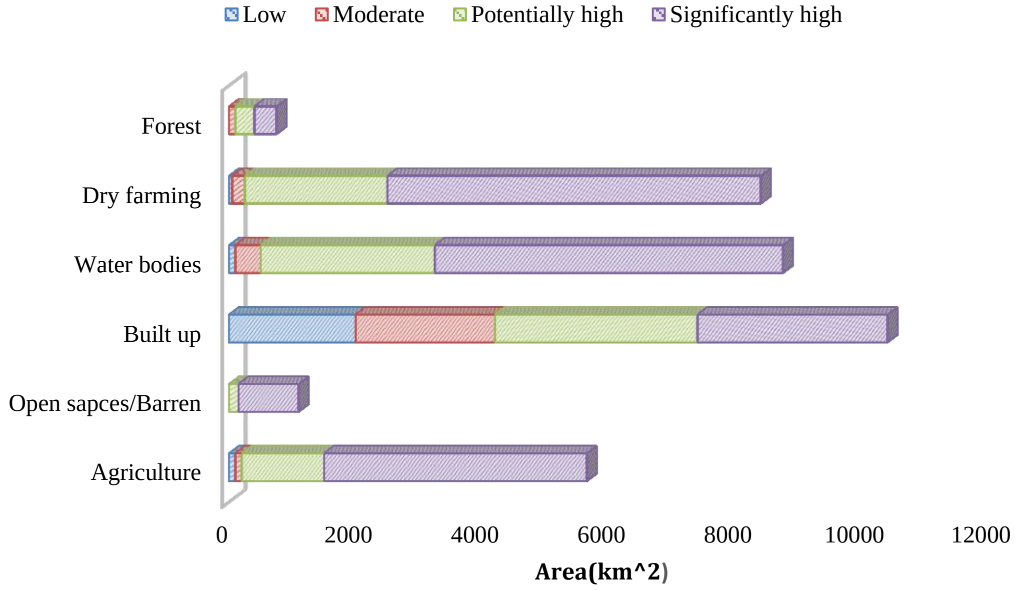


Figure 4) Potential ecological risk levels of heavy metals in the rivers from different land use types in a (spring) and b (winter)

beginning of spring in such areas, a large amount of some HMs enter into water resources and contaminate surface waters. The results of the present study were in accordance with those of other studies and suggest that excessive amounts of Pb and Ni were the major water quality problems in many parts of Zanjan and Iran (26-28). In addition, these results were in agreement with the findings of another study in which the extent and severity of HMs contaminations of top-soils were assessed (27). The study concluded that the main sources for HMs contamination in the studied area were most probably emissions from the Zn industry.

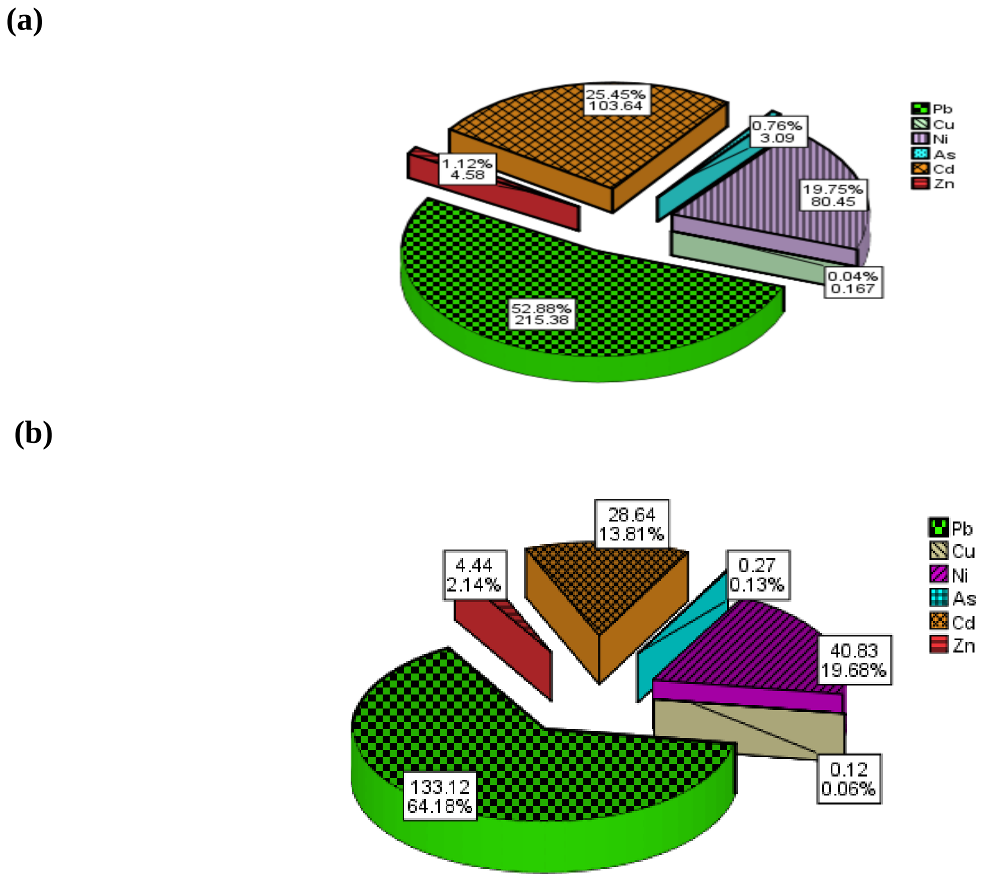


Figure 5) Contributions of individual heavy metals to the mean potential ecological risk of rivers, a (spring) and b (winter)

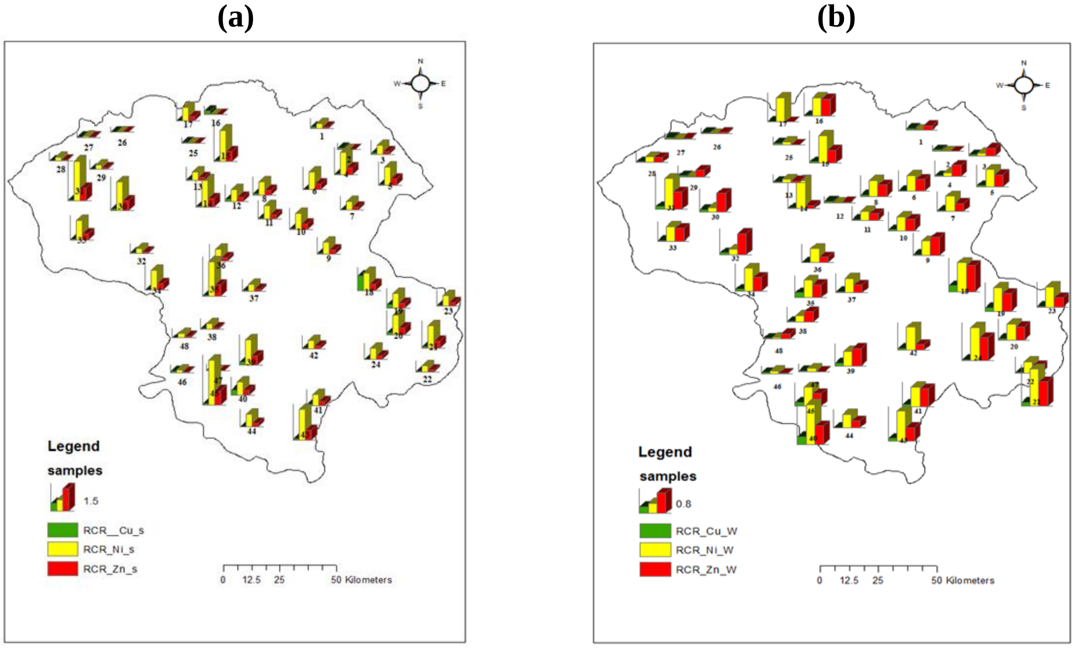


Figure 6) Calculated risk characterization ratio for a (spring) and b (winter)

Such emissions, transported by air, sewage, and industrial effluents (29), held responsible for the increased HM concentrations found in the soils of the central studied area. Along with with our results, Yousefi and Jahangard (2016) monitored the HMs concentration in Qorveh's groundwater and concluded that the concentration of HMs in some cases was very high than the WHO standards (30).

The measured relationship between elements showed that Pb and Cu had a strong relationship with other HMs during winter. However, the relationship between Pb and iron was stronger (r=0.6) suggesting that they originate from one single source. A weaker relationship was observed between As and other HMs, which showed that the source of As in surface waters differed from the source of other elements. During spring, HM elements, especially Zn and Ni (r=0.95) were highly correlated, which indicates anthropogenic sources (e.g., industrial activities) contribute to this contamination. These HMs were most likely formed of pollution produced by industrial units. Weaker relationships between elements resulted from difference in the source metals and their geochemical properties (31). In a study aimed at measuring HMs in wet and dry atmospheric deposition of Zanjan, industrial sources were found to play key roles in the concentration of HMs. The correlation coefficients between the HMs showed that both Pb and Zn resulted from a common source. The authors concluded that the effects of anthropogenic sources in the air quality of Zanjan (32).

The PI values that were lower than one are reflective of low contamination. The As and Cu showed PI values lower than one during spring, whereas Ni, Cu, Zn, As, and Cd exhibited PI values lower than one during winter. However, PI values of Zn (during spring) and Ni (during winter) ranged between 1 and 2, which showed moderate contamination. The Pb is known to have the largest PI value during winter and spring and is considered highly contaminating (PI>3). Higher PI values for Pb were observed in sampling points 21 and 43 which the first is attributed to the Angoran area in Zanjan. This traditional mining region has a large ferrous metal site containing large reserves of Pb. Sampling No. 43 was located in agricultural lands. The Pb showed the highest PI values in both seasons. In sampling point, No. 9 values of Ni were higher during winter, while during spring 1 < PI < 3 observed in 12 sampling points for the same metal. Therefore, these areas were moderately contaminated. In addition, seven sampling points showed PI > 3; therefore, they were highly contaminated with Ni. The highest values of RI (RI>200) were observed during both spring and winter. As seen, except for some sampling points in the north and south parts, most stations showed RI > 300 during spring; as a result, they exhibited high potential ecological risk. However, during winter only 8 stations had RI > 300, which represented high ecological risks. As shown in the RI spatial distribution map, high values of RI in winter and spring showed similar trends. The highest values belonged to industrial and farmlands, whereas the lowest RI values were observed in urban and open spaces areas. The main contributors to the RI were from the most toxic elements Pb, Ni, and Cd. The most important factor influencing RI were extremely high values of Pb and low values of their reference concentrations in surface waters (0.018 ± 0.006). In line with our results Rafiee et al. (2019), reported exceeded levels of Pb and Ni in Zanjan surface waters in spring (33).

Conclusion

The present study aimed to investigate the presence, status, and probable sources of HMs pollution in surface waters of Zanjan province, Iran. The results demonstrated that the mean concentration of the studied HMs in water varied significantly within 0.02-8.52 and within 0.005-4.32 μg/L in spring and winter, respectively. The ecological risk indices for single regulators (E_i) revealed that the severity of pollution of the six HMs declined in the following sequences for the spring and winter, respectively: Pb > Cd > Ni > Zn > As > Cu and Pb > Ni > Cd > Zn > As > Cu. Regarding the ecological risk status of HMs in water, Ni and Zn showed high ecological risks in some sampling points using the PNEC-pro model, while other sampling points were clean or light. Furthermore, the ecological risk status of most of barren, dry farming, and water bodies' areas were potentially high in both seasons. Based on the measured values of water HMs in the studied area, the influences of anthropogenic/geogenic and various land uses should be considered when managing potential pollution sources of waters. Based on E_i values, during spring and winter, Cu, Zn, and As posed very low ecological risks. The potential ecological RIs demonstrated that the pollution severity of the six studied HMs declined in the following sequences for the spring and winter, respectively: Pb > Cd > Ni > Zn > As > Cu and Pb > Ni > Cd > Zn > As > Cu.

Footnotes

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Conflict of Interest

The authors declared that there were no conflicts of interest regarding the publication of the present research.

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