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ORIGINAL PAPER

Evaluation of Water Quality Using Heavy Metal Index and Multivariate Statistical Analysis in Lorestan Province, Iran

Zahra Khoshnam[1], Ramin Sarikhani[1], Artimes Ghassemi Dehnavi[1], Zeinab Ahmadnejad[2]

1. Department of Geology, Faculty of Science, Lorestan University, Khorramabad, Iran
2. Department of Geology, Tabriz University, Tabriz, Iran

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ABSTRACT

In the present study, the water quality of Silakhor River, located in Rahim Abad hydrometric station, was analyzed based on Boron, Iron, Nickel, Fluorine, Manganese, Chromium, Cadmium, Aluminum, Copper, Zinc and Lead pollution. The samples were collected from Silakhor River in Rahim Abad hydrometric station during a one-year period, from December 2012 to November 2013. In addition, metal index (MI) and heavy metal evaluation index (HEI) were applied to evaluate the amount of heavy metal pollution of water resources in the study area. The aforemention indices determined the origin of contamination of water resources, drinking or non-drinking. The findings from the samples showed that the amount of some heavy metals, such as Lead, Chromium, Cadmium and Manganese was higher than permissible limit of WHO standard. However, metal index (MI) and heavy metal evaluation index (HEI) proved that all samples are non-potable. In the present study, statistical studies (correlation coefficient, factor analysis and cluster analysis) were employed to determine the probable origin of the area's elements. The findings indicated a multiple source of pollutants for the region water resources including two major sources; one is associated with the region lithology (the natural factor) while the other is caused by human activity in the region (anthropogenic factors).

Keywords: Silakhor, metal index, heavy metal evaluation index

Introduction

River systems are considered as the main inland water resources for domestic, industrial and irrigation purposes. In addition, they play a major role in transporting industrial and municipal wastewater runoff from agricultural fields, roadways and streets, leading to river pollution.[1] Chemical pollution of surface water may pose a significant threat to aquatic environment causing acute and chronic toxicity to aquatic organisms, accumulation in the ecosystem, losses of habitats and biodiversity, and a potential threat to human health. [2,3] Heavy metals are considered as the most common environmental pollutants whose occurrence in water and biota prove the presence of natural or anthropogenic sources. In fact, the major natural sources of metal in water are chemical weathering of minerals and soil leaching. The anthropogenic sources are mainly associated with industrial and domestic effluents, urban storm, water runoff, landfill leachate, mining of coal and ore, atmospheric sources and inputs rural areas.[4] Moreover, the main anthropogenic sources of heavy metal contamination are mining, disposal of untreated and partial treated effluents containing toxic metals, metal chelates from different industries and indiscriminate use of heavy metals containing fertilizer and pesticides in agricultural fields.[5] A number of researchers have studied various aspects of water quality.[6,16] The present study aims at not only comparing the element concentration of B^-, Fe^{2+}, Ni^{2+}, F^-, Mn^{2+}, Cr^{3+}, Ca^{2+}, Al^{3+}, Cu^{2+}, Zn^{2+} and Pb^{2+} to World Health Organization standards,[17] but also calculating HEI and MI indices using several statistical methods to determine the origin of the elements. Hence,

Ramin Sarikhani
sarikhani.r@gmail.com

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statistical analysis implicated human activities as the main origin of the elements.

Geographical and geological features of the area

The study setting is geologically located between thrust or crushed Zagros and Sanandaj – Sirjan zone, from the north of Boroujerd to the south of Dorud city. Silakhor River is a part of Boroujerd-Lorestan in the northernmost part of Karun River Basin. Flat area of this region covers 162.36 km^2 with the altitude of529.06 km^2. It is always a permanent watercourse of the region due to the arrival of surface flow, sufficient rainfall and snowy mountains. In addition, the area has a cold climate with appropriate precipitation. Considering limestone mountains, adequate precipitation and appropriate alluvial, the region has significant groundwater and permanent rivers like Karun river branches.[18] Figure 1 presents the study area and geological map of Rahim Abad hydrometric station.

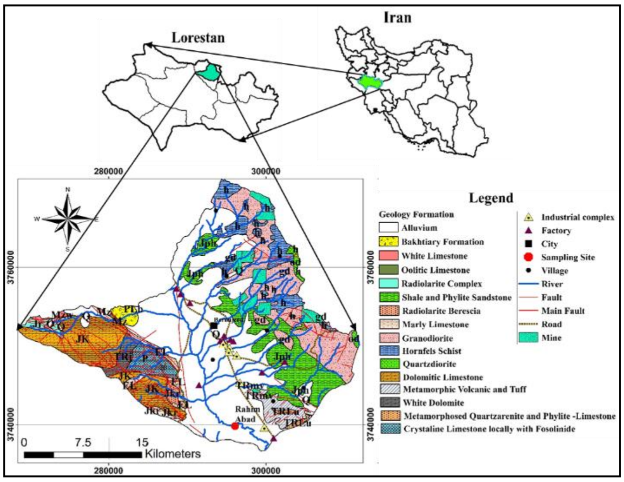

Fig. 1 The geological map of Rahim Abad hydrometric station (After Geological Survey and Mineral Exploration, 2000)

Table 1 Heavy metal concentration of the Silakhor River samples (mg/l)

Sample	B^-	Fe^{2+}	Ni^{2+}	F^-	Mn^{2+}	Cr^{3+}	Cd^{2+}	Al^{3+}	Cu^{2+}	Zn^{2+}	Pb^{2+}
Dec-2012	0.05	0.05	0.02	0.49	0.02	0.03	0.01	0.01	0.01	0.03	0.003
Jan-2013	0.11	0.09	0.05	0.51	0.05	0.05	0.03	0.02	0.03	0.07	0.004
Feb-2013	0.11	0.09	0.045	0.55	0.06	0.055	0.03	0.02	0.045	0.06	0.005
Mar-2013	0.08	0.075	0.03	0.35	0.06	0.055	0.021	0.01	0.05	0.055	0.008
Apr-2013	0.06	0.07	0.03	0.39	0.053	0.04	0.019	0.01	0.052	0.0375	0.01
May-2013	0.05	0.06	0.03	0.42	0.025	0.038	0.02	0.01	0.037	0.025	0.009
Jun-2013	0.05	0.045	0.03	0.37	0.01	0.02	0.01	0.03	0.015	0.035	0.01
Jul-2013	0.05	0.055	0.03	0.42	0.01	0.03	0.01	0.03	0.035	0.035	0.01
Aug-2013	Dry	Dry	Dry	Dry	Dry	Dry	Dry	Dry	Dry	Dry	Dry
Sep-2013	0.04	0.02	0.01	0.45	0.01	0.02	0.005	0.02	0.01	0.02	0.009
Oct-2013	0.05	0.028	0.01	0.51	0.013	0.034	0.007	0.02	0.018	0.024	0.01
Nov-2013	0.04	0.033	0.01	0.46	0.02	0.04	0.006	0.03	0.022	0.033	0.033
WHO 2011	2.4	0.1	0.07	1.5	0.05	0.05	0.003	0.1	2	3	0.01

Outside of the WHO 2011 standard range (shaded)
Inside of the WHO 2011 standard range (unshaded)

Heavy Metal in the Study Area

The water samples were collected from Silakhor River during a one-year period from December 2012 to November 2013. They were analyzed in terms of Boron, Iron, Nickel, Fluorine, Manganese, Chromium, Cadmium, Aluminum, Copper, Zinc and Lead pollution. The findings showed that the values of Cadmium, Lead, Manganese and Chromium were higher than the WHO (2011) standard. Besides, Global Positioning System (GPS) was applied to determine not only the precise location of sampling but also the exact latitude, longitude and altitude. With regard to heavy metals, the WHO (2011) standard was used to determine the water quality of the area.[17] The analysis of samples are presented in Table 1 for Silakhor River. The concentration of most of the heavy metal of the samples were within the range of WHO (2011) standard limit in Silakhor River. As shown in the table below, the amount of Manganese is higher than the standard permissible value in February 2013, March 2013 and April 2013; while Cadmium was high during the whole sampling period. Moreover, Lead was high in November 2013, and chromium in February and March 2013.

Materials and Methods

Quantity Evaluation of Heavy Metal Pollution in Water Resources

In evaluating heavy metal pollution of water resources in the study area, Metal Index (MI) and Heavy Metal Index (HMI) were used to determine the potability of drinking water and the effects of heavy metals on human health, respectively (potable or non-potable for drinking). All samples were collected in 250 ml polyethylene bottles which were acidified with HNO_3 to prevent the precipitation of metal. They were all transferred to the laboratory in iceboxes and refrigerated at 4°C. Inductively coupled plasma mass spectrometry (ICP-MS) was employed to analyze the samples. Moreover, it can recognize both the degree of water contamination and potability of drinking water. The findings revealed that human activities and erosion of lithological formation are the dominant origins of heavy metals.

(HEI) Heavy Metal Evaluation Index

The HEI gives an overall quality of the water regarding heavy metal content. The HEI is computed as follows:

$$HEI = \sum_{i=1}^{N} \frac{Hc}{Hmac}$$

Where, Hc indicates monitored value of the ith parameter and Hmac indicates maximum admissible concentration of the Ith parameter.[19] As shown in Table 2, water quality is classified based on HEI whose values are presented in Figure 2 for Silakhor River. As shown, the HEI value of all samples are high, therefore they are polluted.

Table 2 Classification of Silakhor River water quality based on modified categories for HEI

Index	Class	Description
HEI	<1.24	Low
	1.24-2.48	Medium
	2.48>	High

Metal Index

General metal index (MI) is the other index used for assessing the quality of drinking water [20] which takes into consideration, the possible

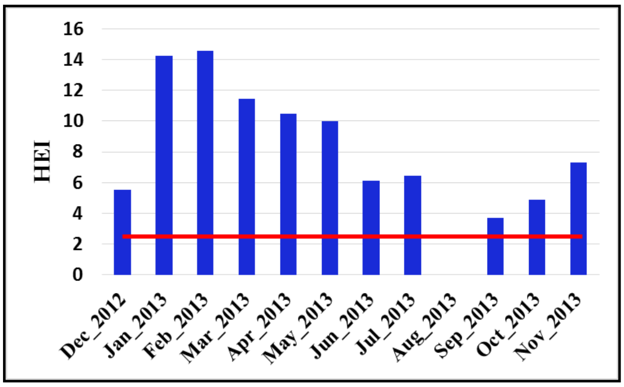

Fig. 2 Heavy metal evaluation index of Silakhor River at various sampling times

additive effects of heavy metals on human health leading to quick evaluation of overall quality of drinking water. Metal pollution index is given by the expression proposed by Caeiro et.al.[21]

$$MI = \sum_{i=1}^{N} \frac{Ci}{(MAC)i}$$

Where MAC indicates maximum allowable concentration and Ci is the mean concentration of each metal. MI value > 1 is a warning threshold.[20] Water quality and its suitability for drinking purpose can be examined by determining its metal pollution index. [22, 23] Given that metalloid and fluorine are not considered as metal, they were ignored in

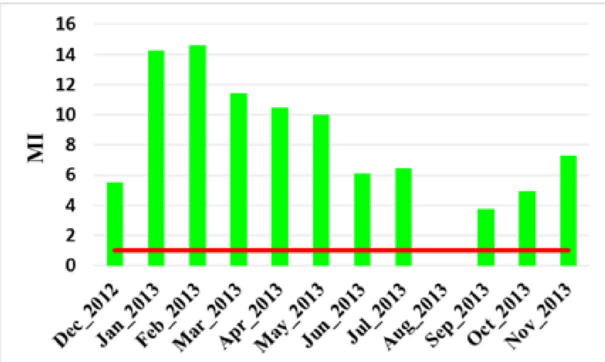

Fig.3 Metal Index (MI) of studied samples of Silakhor River at various sampling times

determining the metal index. Table 3 presents the classification of water quality based on MI.

Table 3 Water quality classification using MI [21]

MI	Characteristics	Class
<0.3	Very pure	I
0.3-1.0	Pure	II
1.0-2.0	Slightly affected	III
2.0-4.0	Moderately affected	IV
4.0-6.0	Strongly affected	V
>6.0	Seriously affected	VI

Besides, index values are presented in Table 4 for Silakhor River. The histogram of Silakhor River is shown in Figure 3, where the red line indicates the standard level of the MI. As shown in Table 4 and Figure 3, the MI value of the samples is often in seriously affected range while some samples are in moderately affected and strongly affected range, thus they are polluted accordingly.

Table 4 Metal Index (MI) of studied samples of Silakhor River at various sampling times

Sample	DeC 2012	Jan 2013	Feb 2013	Mar 2013	Apr 2013	May 2013	Jun 2013	Jul 2013	Aug 2013	Sep 2013	Oct 2013	Nov 2013
MI	5.53	14.25	14.59	11.42	10.46	9.98	6.13	6.44	Dry	3.72	4.91	7.29
Class	V	VI	VI	VI	VI	VI	VI	VI	-	IV	V	VI

Results and Discussion

The correlation coefficient

The correlations among heavy metals demonstrate some facts regarding the origin and migration of these elements. For instance, high correlation between two heavy metals probably indicates that these elements share either similar pollution sources or analogous transformation and migration processes in certain circumstances.[24] In addition, Pearson's correlation coefficient is considered as the most common correlation coefficient. The correlation coefficients can range from -1 to +1 which is independent from units of measurement.[25] The findings from Pearson correlation analysis are presented in Table 5 showing that there is a significant positive relationship among Iron, Manganese, Zinc, Cadmium, Chromium, Copper, Nickel, Boron and Discharge. In addition, they prove the probable pollution of common resources (agricultural waste water, rural sewages or sewages of Boroujerd city).

Table 5 Pearson correlation matrix between the analyzed parameters

	Al^{3+}	Fe^{2+}	Mn^{2+}	Zn^{2+}	Pb^{2+}	Cd^{2+}	Cr^{3+}	Cu^{2+}	Ni^{2+}	B^-	F^-	Temp	Discharge
Al^{3+}	1												
Fe^{2+}	-0.334	1											
Mn^{2+}	-0.502	0.858**	1										
Zn^{2+}	-0.044	0.873**	0.799**	1									
Pb^{2+}	0.496	-00.454	-0.275	-0.282	1								
Cd^{2+}	-0.376	0.956**	0.863**	0.845**	-0.466	1							
Cr^{3+}	-0.347	0.787**	0.891**	0.787**	-0.071	0.803**	1						
Cu^{2+}	-0.368	0.744**	0.796**	0.532	-0.117	0.691*	0.741**	1					
Ni^{2+}	-0.118	0.934**	0.667*	0.836**	-0.519	0.908**	0.576	0.576	1				
B^-	-0.174	0.880**	0.815**	0.940**	-0.461	0.918**	.791**	0.52	0.850**	1			
F^-	0.089	0.088	0.049	00.193	-0.132	0.204	0.219	-0.262	0.094	0.383	1		
Temp	0.25	-0.546	-0.511	-0.612*	0.187	-0.482	-0.601	-0.1	-0.391	-0.592	-0.504	1	
Discharge	-0.21	0.584	0.767**	0.697*	0.145	0.545	0.785**	0.422	0.358	0.620*	0.287	-0.793**	1

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

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

Principal Components Analysis (PCA)

PCA, as a multivariate analytical tool, is used to reduce a set of original variables to extract a small number of latent factors.[26] Principal component analysis (PCA) was used to find potential pollution sources.[27] The analysis of the main element to determine the possible sources of river contamination leads to the extraction of

4 principle elements out of 11, temperature and river discharge. Moreover, the findings prove the correlation among the data. Table 6 shows the percentage of the extracted component total variance. In addition, Table 7 shows the rotational component matrix of water samples. The first component is described in variance of 52.061%, including Iron, Manganese, Zinc, Cadmium, Chromium, Copper, Nickel, Boron and discharge. It is suggested that these elements probably have the same origin, due to agricultural waste water, rural and urban sewages near Rahim Abad hydrometric station. The second component has the total variance of 16.415% containing only Fluorine and discharge. Besides, the temperature of the river has a negative correlation. It is probably located in a separate component due to different geochemical behavior. The third component has a total variance of 12.945% including Aluminum metal. It is probably located in a separate component due to different geochemical behavior or different origin. In fact, there is Aluminum with low concentration in river which is probably attributed to the presence of abundant Granodiorites in the region and rocks analysis.[28] In addition, the source of Aluminum can be related to Granodioritic rock which has high resistance against erosion. Aluminum is often recognized

Table 6 Percentage of the total variance of extracted components

Total Variance Explained					
Component	Extraction Sums of Squared Loadings		Rotation Sums of Squared Loadings		
	% of Variance	Cumulative %	Total	% of Variance	Cumulative %
1	59.344	59.344	6.768	52.061	52.061
2	13.559	72.903	2.134	16.415	68.476
3	11.091	83.993	1.683	12.945	81.421
4	8.931	92.925	1.495	11.504	92.925

Table 7 Rotated component matrix of Silakhor River water samples

Rotated Component Matrix				
	Component			
	1	2	3	4
Al^{3+}	-0.124	-0.002	-0.960	0.214
Fe^{2+}	0.947	0.112	0.192	-0.146
Mn^{2+}	0.851	0.114	0.448	0.144
Zn^{2+}	0.920	0.294	-0.068	0.017
Pb^{2+}	-0.279	-0.108	-0.308	0.878
Cd^{2+}	0.919	0.162	0.205	-0.195
Cr^{3+}	0.805	0.258	0.323	0.309
Cu^{2+}	0.780	-0.363	0.344	0.190
Ni^{2+}	0.907	0.058	-0.084	-0.351
B^-	0.887	0.383	0.028	-0.174
F^-	0.015	0.872	-0.134	-0.132
Temperature	-0.402	-0.784	-0.249	-0.125
Discharge	0.578	0.511	0.268	0.529

Extraction Method: Principal Component Analysis.
Rotation Method: Varimax with Kaiser Normalization.

a. Rotation converged in 8 iterations.

as an insoluble small amount of metal. The fourth component has a total variance of 11.504% containing Lead and Discharge. It is likely to be located in a separate component due to different origin with other elements. The upper values of permissible limit represent the anthropogenic origin of Lead which may be attributed to vehicle emissions. Figure 4 shows the effective characteristics of each factor for better comparison.

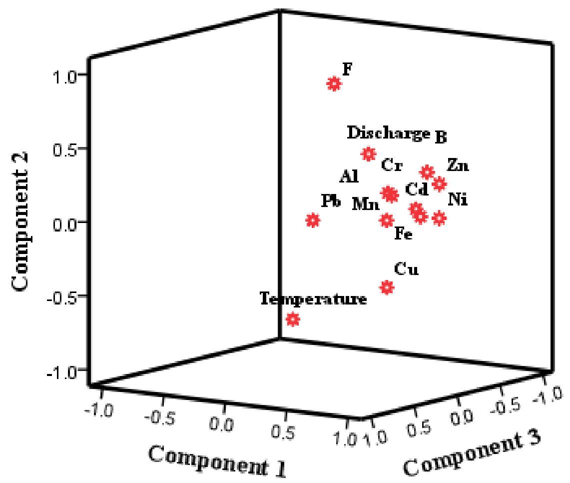

Fig. 4 Factor rotation coefficients diagram

Cluster analysis (CA)

The CA technique is an unsupervised classification procedure that involves measuring either the distance or the similarity among the clustered objects. The resulting clusters of objects should then show high internal (within cluster) homogeneity and high external (between clusters) heterogeneity. Hierarchical agglomerative clustering is the most common approach which provides instinctive similar relationships between each sample and the entire data set, and is typically illustrated by a dendrogram (tree diagram).[29] Cluster analysis of the samples was studied using SPSS 19 software. The cluster diagram of the river water samples is shown in Figure 5 where two categories of A and B are distinct, more samples are in category A. Category A is divided into two groups, I1 and I2. I2 contains only Fluorine, while I1 is divided into two subgroups II1 and II2. II2 contains Copper and is probably related to Copper-Andesite, metamorphic volcanic rocks, and tuff. Besides, II1 is divided into two parts III1 and III2. III1 includes two sub-sections 1 and 2. III2 also includes two sub-sections 1 and 2. The four sub-sections are briefly interpreted as follows: Section III1 (subsection 1) contains heavy metals like Iron, Cadmium and Nickel. High correlation of Iron with Nickel and Cadmium is due to the adsorption of these elements by Iron oxy-hydroxides. Iron is not usually considered as contaminant, but its analysis could be useful because it influences the availability of other metals.[30] Iron usually has a natural origin related to geological characteristics of the area. The residential areas, whose untreated sewage enters the river, are located around the sampling station, thereby increasing various contaminants loaded with heavy metals. Higher concentration of Cadmium than the permisible limit could not be related to the natural origin and area geology. However, it is due to the discharge of rural and urban wastewater without treatment into the river. However, Rahim Abad hydrometric station is located near Boroujerd city, so industrial waste could also have an important role. Section III1 (subsection 2) contains Zinc and Boron elements. Zinc can be related to Granodiorite, although, the anthropogenic origin for Zinc is more probably due to the Granodiorite high resistance against erosion and Zinc location in Section III1. Minor amount of Boron will be probably related to the detergents that entered the river which proves the anthropogenic origin. Section III2 (subsection 1) contains not only Manganese and Chromium, as heavy metal, but also river discharge (subsection 2). According to correlation of Chromium and Manganese with river discharge, it can be concluded that as river discharge increases, river pollution will increase. In fact, it is mostly affected by leaching of contaminated soil with rural sewage and agricultural wastewater, which occurred as a result of rainfall. High correlation of Chromium with Manganese can also indicate the absorption of Chromium by oxy-hydroxides of Manganese. The higher amount of Manganese and Chromium than the standard permissible limit in river could not be considered as the result of basin geology, although inconsiderable natural origin for Manganese and Chromium is possible. The Fluorine is located in the separate component, probably due to the different geochemical behavior or origin. Category B is divided into two groups of 1 and 2. Group 1 consists of Aluminum and Lead metals. Group 2 consists of water temperature of the river. Aluminum and Lead, perhaps originated from different geochemical behavior, are located in separate component. Placement of Lead and Aluminum, as well as the temperature in the category may be attributed to similar behavior of two metals with changes in temperature. Therefore, as the temperature increases and discharge decreases, the metal concentrations increase. These metals are recognized as having standard or high concentration. Aluminum, with natural origin, can be related to Granodioritic rocks in the area. Nevertheless, there is little amount of it in the river which is related to Granodiorite high resistance and insoluble feature of Aluminum.

Lead: The higher or closer values to the permissible level proved the anthropogenic origin of Lead. River placement, Rahim Abad hydrometric station in the road vicinity, vehicle traffic, and vehicle emission are suggested to be considered as a possible origin for the lead.

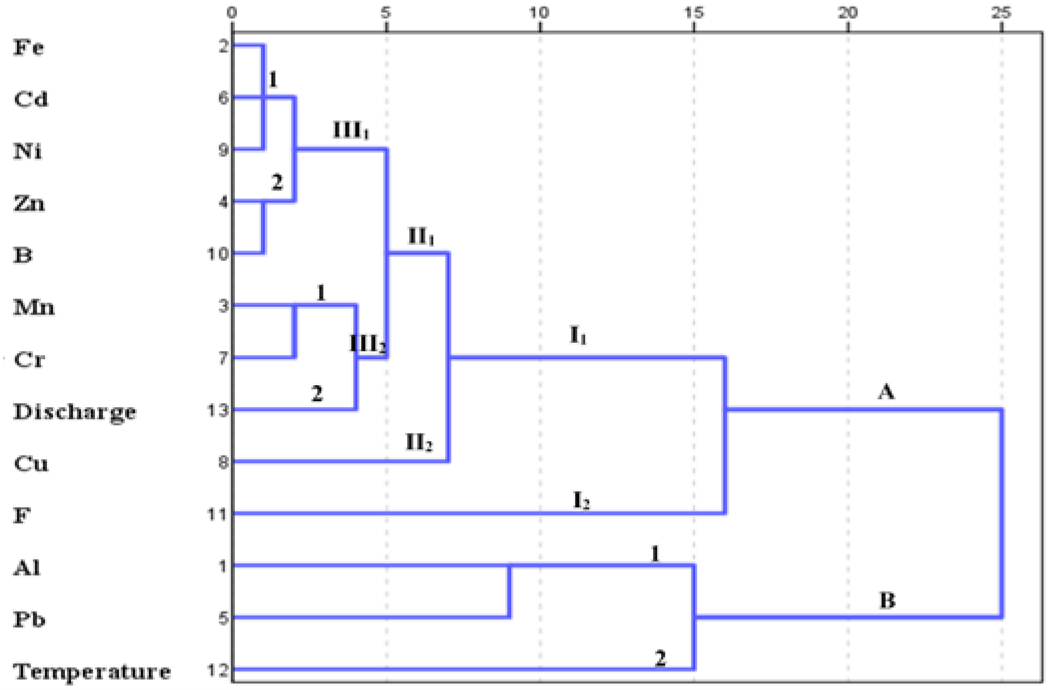

Fig. 5 The cluster diagram of Silakhor River water samples

Conclusion

In the present study, water quality of Silakhor River was analyzed in terms of heavy metal pollution. According to the standard values of WHO, metal index (MI) and heavy metal evaluation index (HEI), it turned out that the amount of some heavy metals were higher than permissible limit in some of the samples. High values might be attributed to agricultural activities, urban and rural sewages, vehicle transit, and Boroujerd industrial wastewater located near Rahim Abad hydrometric station. A calculation of Metal Index (MI) show that most of the samples are in serious affected range while some are in strong and moderate affected range, thus they are polluted and non-potable. In other words, the river water is not appropriate enough for drinking. Moreover, calculating the Evaluation Index of Heavy metals (HEI) shows that all samples are higher than the permissible limit which are not only non-potable but also detrimental to the health of the local people.

Statistical analysis showed that the dominant origin of the elements, particularly Cadmium, Lead, Chromium and Manganese are due to human activities. However, the natural origin and erosion of lithological units can also be considered as the minor-agent for some elements.

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