

## An Index Approach to Metallic Pollution in River Waters

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Received 15 June. 2013;

Revised 25 July 2013;

Accepted 20 Aug. 2014

**ABSTRACT:** Twenty water samples from a river system in southern Caspian Sea basin were collected and analyzed for physicochemical parameters and metals (Cu, Zn, As, Cd, Pb, Ni and Mn). In order to evaluate the risk potential of metal pollution in river water, use of two indices namely heavy metal pollution index (HPI) and contamination index ( $C_d$ ) accompanied by cluster analysis was taken in to consideration. Stations located within the upstream of the river (1 to 13) seemed to encounter low risk potentials while the downstream stations (14 to 20) approved to hold higher risks. The results also showed relatively meaningful correlation among different metals which may be attributed to their same entry source, mainly mining and quarrying activities in the central parts of the basin following by municipal and industrial wastewater discharge to the river in downstream. The convergence of both indices in this study was also of interest. Although the mean values of both indices were below the critical values, severe precautions must be taken into consideration especially in the stations holding high risk potentials. Extreme use of river water for drinking, agriculture and industrial purposes within the water basin, relatively biota-rich characteristic of the river and Caspian Sea as the final sink of the river are among the most significant reasons that make the river monitoring implementation inevitable.

**Key words:** Heavy metal, Index, Risky pollution, River water

### INTRODUCTION

Industrial development accompanied by population and consumption growth has imposed heavy pollution loads to natural resources (Mehrdadi *et al.*, 2006; Mehrdadi *et al.*, 2009; Nabi bidhendi *et al.*, 2007; Nasrabadi *et al.*, 2010a). Pollution by heavy metals is considered to be a serious problem due to their toxicity and their ability to accumulate in the biota (Morillo *et al.*, 2002; Baghvand *et al.*, 2010). One of the most crucial properties of these metals, which differentiate them from other toxic pollutants, is that they are not easily biodegradable in the environment (Rauret *et al.*, 1999; Nasrabadi *et al.*, 2015; Asadpour, 2015; Akbarzadeh *et al.*, 2015). The surface water bodies are among the most sensitive sources that are prone to impacts from human activities which may result in degradation of the resource in the future (Roshan *et al.*, 2013; Afkhami *et al.*, 2013). A cost effective way to protect the quality is to develop a monitoring scheme to assist in the planning, development and guiding human activities including

industrial development to minimize adverse impacts on water quality (Edet & Offiong, 2002).

Lots of studies in the literature have focused on heavy metal pollution of water resources all around the world (Wang *et al.*, 2007; Bird *et al.*, 2005; Zhang *et al.*, 2009; Nasrabadi *et al.*, 2010b; Nabi bidhendi *et al.*, 2007; Nasrabadi *et al.*, 2009; Edet & Offiong, 2002; Prasad & Bose, 2001). The need for monitoring water quality on a regular basis has terminated in lots of studies run to develop, apply and evaluate index methods for water quality assessment regarding metallic pollution (Horton, 1965; Nishidia *et al.*, 1982; Prasad & Jaiprakas, 1999; Prasad & Bose, 2001).

The objective of this study is to evaluate the risk potential in different parts of Haraz River water basin regarding metallic pollution by the use of index approaching and statistical processing. With an average length of 185 kilometers and drainage area of around 5100 km<sup>2</sup>, Haraz River is one of the most strategic rivers meandering northwards from the central Alborz mountains to the Caspian sea. The river's width and slope varies between 5 to 500 m

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and 13 to .1 % respectively from the primary tributaries to the estuary (Nasrabadi *et al.*, 2010b).

Regarding geological characteristics that may contribute in water quality, Paleozoic and Mesozoic dolomite, lime, and shale deposits are the main features within the basin. Due to the existence of Coal-rich layers within the basin, lots of mining and excavation operations have been run during recent decades. A cluster of hydrothermal springs is detected in central parts of the study area that may play the role of metallic pollution source carried to the downstream due to the potential of reactions of sulfide ores with atmospheric oxygen and moisture (Baba & Gungor

2002; Nabi Bidhendi *et al.*, 2007). Furthermore, hydrothermal springs may also facilitate the entrance of toxic metals into the river stream.

On the other hand, the intensive load of urban, agricultural and industrial wastewater to the river that undergoes an increasing trend towards the estuary is also observed within the study area. As a result of all these, the water quality of Haraz River has been seriously influenced. The study area boundaries in south coastline of Caspian Sea accompanied by major mining sites and sampling stations are indicated in Fig. 1.

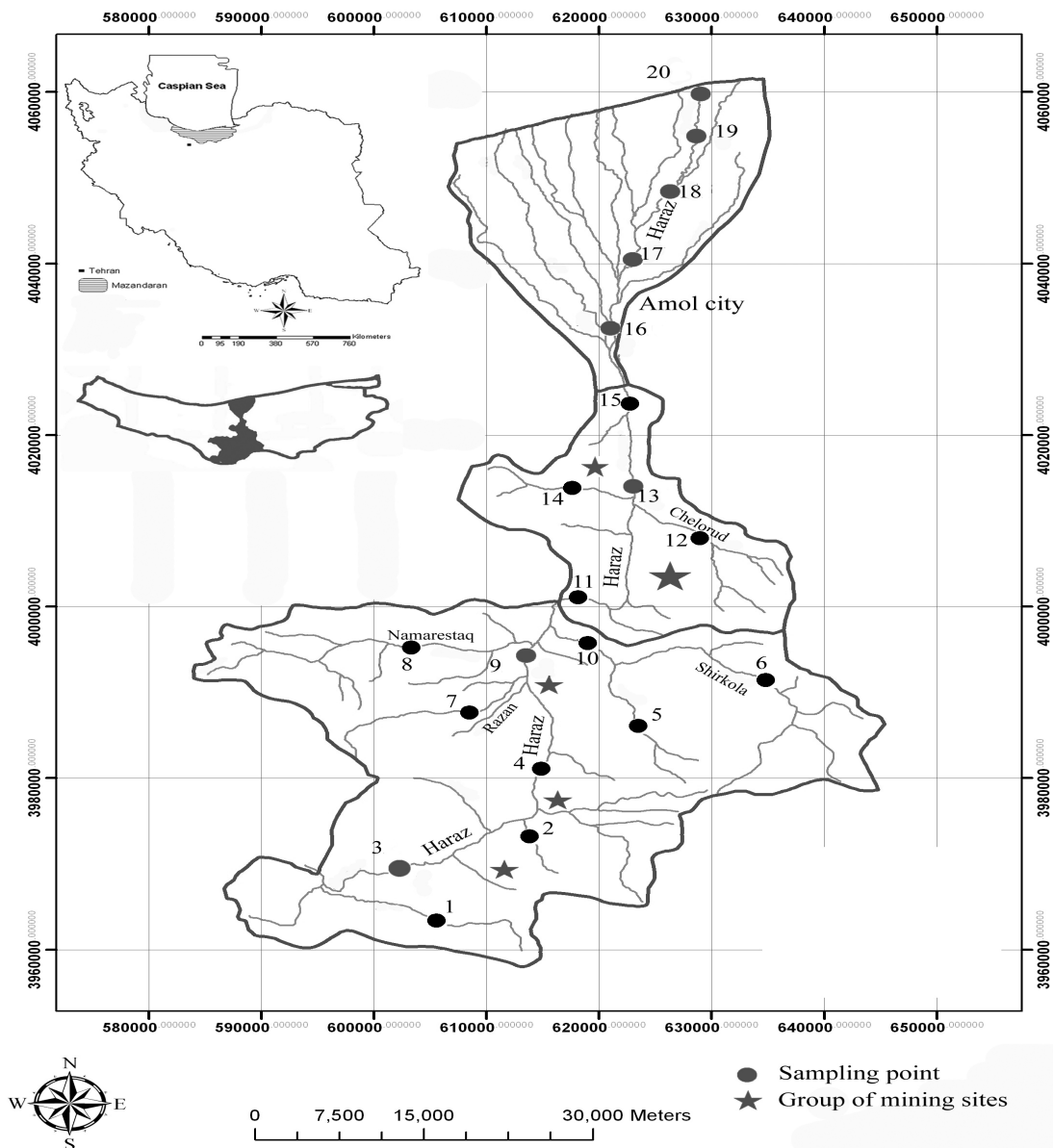


Fig. 1. Location map of Haraz River basin in Iran, the main pollution sources and the sampling sites (Nasrabadi *et al.*, 2010b)

**MATERIALS & METHODS**

This study comprises the main part of Haraz river watershed surrounding the main channel from the origin in Alborz mountains to the Caspian Sea. Site visits and review of the existing data was the first step. Identifying major sources of pollution, water sample collection, data analysis and finally making use of statistical methods like correlation and cluster analysis were also considered. Therefore site visits were made in order to recognize sampling stations. Accordingly, twenty spots were defined as stations all around the study area. The precise location of the sampling points as well as the major mining activity sites within the study area is shown in Fig. 1.

Nature of the examined parameters was selected based on the consequences of mining and quarrying activities and geologic textile of the area. Accordingly parameters like temperature, pH, dissolved oxygen (DO) and the heavy metals like Mn, Cu, Cd, As, Ni, Pb and Zn were taken into consideration. Twenty water samples were collected from sampling stations within the boundaries of study area. Dissolved Oxygen (DO), pH and temperature were measured in situ using Hanna Combo pH/EC/TDS/Temp tester Model HI98129 low range. Samples were collected in polyethylene bottles, which had been carefully washed in the laboratory before the sampling campaign. Water was collected at a certain distance from the riverbed and sufficiently far from the border, natural or artificial obstacles and turbid water zones. Samples were filtered through 0.45 μm filters, acidified to pH 2 with 1% Merck quality nitric acid and transported to the laboratory for analysis. For sample collection, 500 cc polyethylene bottles were rinsed with river water before being filled. The analysis of metals in the solutions was carried out by an inductively coupled plasma atomic emission spectrometer (ICP-AES) according to EPA – 3005 method. Regarding the statistical analysis, the Euclidean distance method and Pearson coefficient were chosen for hierarchical cluster analysis and correlation respectively in the environment of the SPSS 15.0 software.

The referred methods evaluated in this study are the Heavy metal pollution index (HPI) proposed by Prasad and Bose (2001) and the Contamination index (Cd) developed by Backman *et al.* (1998).

Based on weighted arithmetic mean method, HPI indicates the total quality of water with respect to heavy metals (Horton, 1965; Mohan *et al.*, 1996). In order to compute HPI, unit weightage (W<sub>i</sub>) is considered as a value inversely proportional to the recommended standard (S<sub>i</sub>) of the relevant parameter

(Prasad & Bose, 2001 ). HPI (Mohan *et al.*, 1996) is calculated as;

$$HPI = \frac{\sum_{i=1}^n W_i Q_i}{\sum_{i=1}^n W_i}$$

where Q<sub>i</sub> is the sub-index of ith parameter. W<sub>i</sub> is the unit weightage of ith parameter and n is the number of parameters considered. The sub-index (Q<sub>i</sub>) of each parameter is defined by:

$$Q_i = \sum_{i=1}^n \frac{\{M_i(-)I_i\}}{(S_i - I_i)} \times 100,$$

where M<sub>i</sub> is the measured value of ith parameter, while I<sub>i</sub> and S<sub>i</sub> are the ideal and the standard value of ith parameter, respectively. The critical value of HPI for drinking purposes as given by Prasad and Bose (2001) is 100. In computing the HPI for the present study heavy metals As, Cd, Cu, Mn, Ni, Pb and Zn were considered and the weightage (W<sub>i</sub>) was taken as the inverse of standard permissible value.

Contamination index calculates the relative contamination of different metals separately and manifests the sum of generated components as a representative (Backman *et al.*, 1998). Contamination index is calculated via the following equation:

$$C_d = \sum_{i=1}^n C_{fi}$$

Where C<sub>fi</sub> = (C<sub>Ai</sub> / C<sub>Ni</sub>) - 1

C<sub>fi</sub> = contamination factor for i-th component

C<sub>Ai</sub> = analytical value for i-th component

C<sub>Ni</sub> = upper permissible concentration of i-th component

(N denotes the ‘normative value’)

The low, medium and high contamination levels are referred to C<sub>d</sub> values of less than 1, between 1 and 3 and greater than 3, respectively. C<sub>Ni</sub> is considered as the standard permissible value (S<sub>i</sub>) formerly introduced in calculation of HPI.

**RESULTS & DISCUSSION**

The values of temperature, dissolved oxygen and pH as well as metal concentrations followed by descriptive analysis and comparison to standard values are manifested in Tables 1 and 2, respectively. The water temperature ranged from 9 to 18.5 degrees centigrade with the mean and standard deviation (SD)

of 13.65 and 3.38, while the range, mean and SD of DO and pH were evaluated to be 6.9-9.1, 7.99, .78 and 8.10-8.56, 8.33, .14, respectively. Regarding the metal concentrations, mean values of Nickel and Arsenic exceed slightly the standard permissible values, while the concentration of other metals stays relatively far below the critical ones.

The hierarchical cluster analysis using Euclidean distance method was taken into consideration in order to show the similarity of different stations regarding the concentration of heavy metals. Such method is commonly used in data interpretation of river water and sediment studies (Shrestha & Kazama, 2007; Nasrabadi *et al.*, 2010a; Andrade *et al.*, 2008; Kuppusamy & Giridhar, 2006; Singh *et al.*, 2004; Reghunath *et al.*, 2002). As it is seen in the dendrogram indicated in Fig. 2, the whole twenty samples are classified in two distinct clusters; one is attributed to the upstream stations from 1 to 13 (cluster A) with relatively lower metal concentrations, while the other would include downstream stations from 14 to

18 (cluster B) containing more metals in water column. Attendance of stations 19 and 20 in the first cluster is meaningfully justified by the intrusion of salt water from Caspian Sea at the estuary which may cause a sudden drop in the concentration of heavy metals in water column through flocculation, precipitation and complex formation (Turner, 1999; Karbassi *et al.*, 2008; Borja & Dauer, 2008).

The behavior of seven heavy metals Ni, Pb, Cd, Cu, Zn, Mn and As within the river water in different stations shows remarkable correlation coefficients (Table 3). Furthermore, to achieve a kind of analogy among different metals, cluster analysis of stations was also taken in to consideration (Fig. 3).

The overall strong correlation coefficient among heavy metals may indicate their common source of entry. According to the data gathered by the authors in former studies the major metallic pollution sources in water and sediments of the study area are considered to be the mining and quarrying activities in the central

**Table 1. Water physicochemical data and metal concentration of Haraz River**

Stations	T (°C)	DO mg/l	pH	Ni µg/l	Pb µg/l	Cd µg/l	Cu µg/l	Zn µg/l	Mn µg/l	As µg/l
1	12.6	8.3	8.24	16	3	2	13	60	55	39
2	11.2	9.1	8.29	15	4	2	12	45	72	31
3	10.0	8.7	8.11	18	4	2	12	54	60	30
4	9.6	9.1	8.29	18	3	2	12	58	70	29
5	9.1	8.3	8.36	18	3	2	12	52	66	32
6	9.0	8.3	8.11	18	4	2	13	45	64	33
7	11.5	8.6	8.27	19	4	3	11	30	45	28
8	12.3	8.7	8.21	12	3	2	12	30	50	39
9	11.4	8.8	8.33	14	4	2	14	31	81	42
10	11.0	8.6	8.10	21	4	3	12	31	63	48
11	13.7	8.2	8.44	18	4	4	13	42	87	45
12	13.1	7.8	8.42	18	5	2	11	40	82	92
13	14.4	7.1	8.51	27	3	3	12	45	97	55
14	18.0	7.8	8.46	26	4	3	17	77	180	52
15	18.5	7.2	8.56	32	5	3	14	82	210	68
16	17.0	7.1	8.50	39	6	4	17	75	270	67
17	18.0	7.0	8.52	31	5	3	16	71	256	100
18	17.6	7.0	8.31	39	6	3	15	64	263	100
19	17.0	7.1	8.30	22	7	3	11	60	102	90
20	18.0	6.9	8.33	27	7	3	16	63	147	87

**Table 2. Descriptive Statistics of Water physicochemical data and metal concentration of Haraz River**

Parameter	Unit	No.	Minimum	Maximum	Mean	Std. Deviation	Standard permissible value
DO	mg/l	20	6.90	9.10	7.9850	0.77546	---
pH		20	8.10	8.56	8.3330	0.13925	---
T	°C	20	9.00	18.50	13.6500	3.37865	---
Ni	µg/l	20	12.00	39.00	22.4000	7.87000	20
Pb	µg/l	20	3.00	7.00	4.4000	1.27321	50
Cd	µg/l	20	2.00	4.00	2.6500	0.67082	10
Cu	µg/l	20	11.00	17.00	13.2500	1.97017	1000
Zn	µg/l	20	30.00	82.00	52.7500	16.34778	15000
Mn	µg/l	20	45.00	270.00	116.0000	76.40474	300
As	µg/l	20	28.00	100.00	55.3500	25.58428	50

**Table 3. The correlation among the behavior of heavy metals in Haraz River water [Pearson coefficient, No. of data = 20]**

	Ni	Pb	Cd	Cu	Zn	Mn	As
Ni	1						
Pb	.598(**)	1					
Cd	.666(**)	.481(*)	1				
Cu	.675(**)	.399	.468(*)	1			
Zn	.712(**)	.437	.342	.674(**)	1		
Mn	.926(**)	.592(**)	.584(**)	.808(**)	.763(**)	1	
As	.664(**)	.789(**)	.406	.403	.456(*)	.701(**)	1

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

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

**Table 4. Referred values used for computation of indices (Prasad and Bose, 2001)**

Parameter	Standard permissible value (S <sub>i</sub> )	Unit weightage (W <sub>i</sub> )	Highest desirable value (I <sub>i</sub> )
Ni	20	0.050	---
Pb	50	0.020	---
Cd	10	0.100	---
Cu	1000	0.001	50
Zn	15000	6.67E-05	5000
Mn	300	3.33E-03	100
As	50	0.020	10

Dendrogram using Average Linkage (Between Groups)

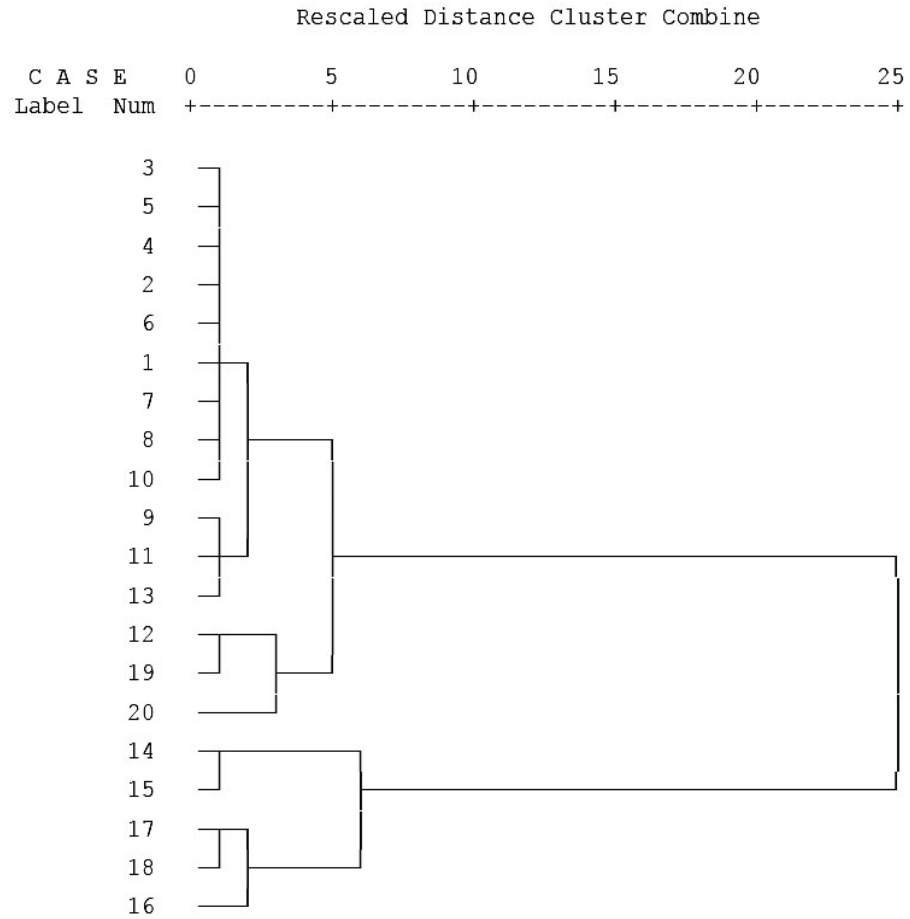


Fig. 2. Dendrogram showing the similarity among the stations regarding water metal pollution

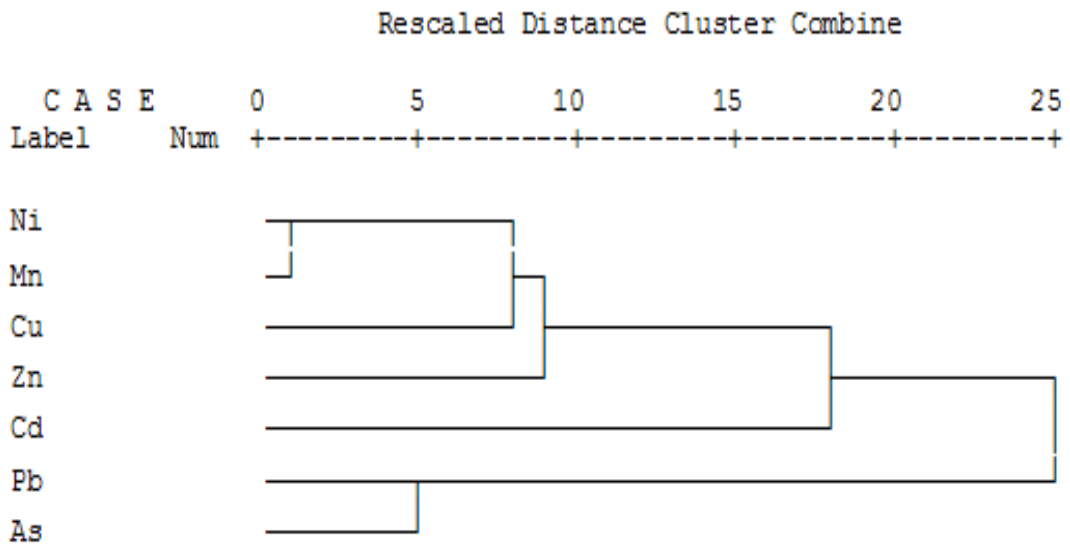
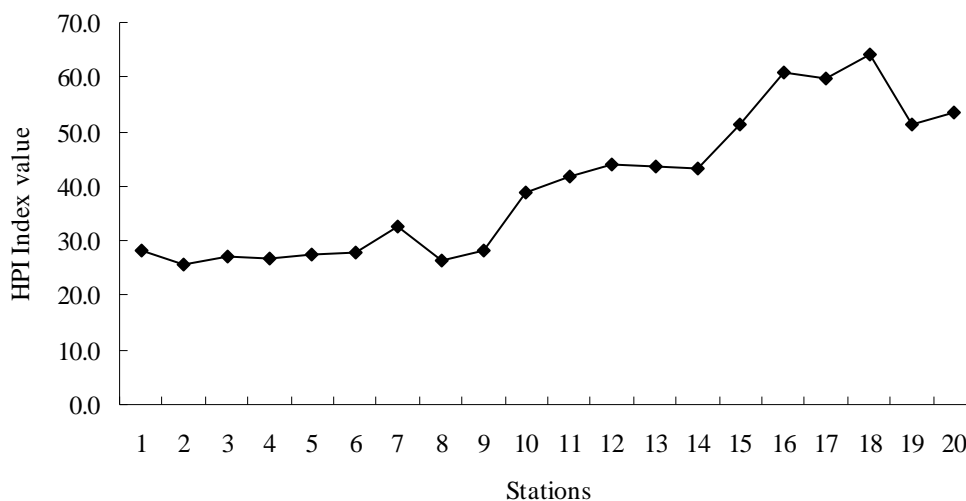


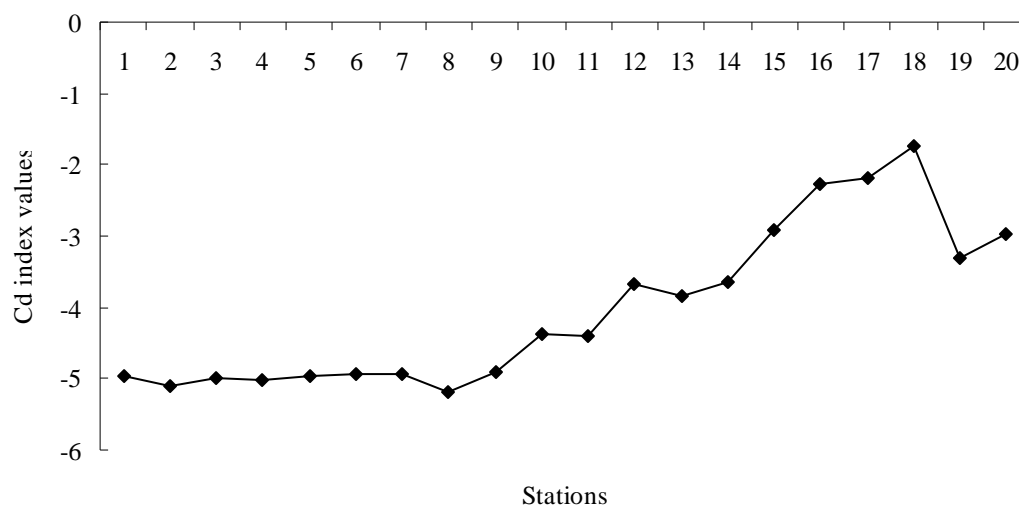
Fig. 3. Dendrogram showing the analogy of metals behavior in river water

**Table 5. Values and deviations of water metallic pollution indices in the stations of Haraz River**

Stations	Value		Mean Deviation		% Deviation	
	HPI	C <sub>d</sub>	HPI	C <sub>d</sub>	HPI	C <sub>d</sub>
1	28.329	-4.960	-15.792	-1.295	-35.793	-35.325
2	25.696	-5.095	-18.425	-1.430	-41.761	-39.018
3	27.152	-5.004	-16.969	-1.339	-38.460	-36.546
4	26.577	-5.011	-17.544	-1.346	-39.764	-36.720
5	27.422	-4.965	-16.699	-1.300	-37.849	-35.458
6	27.924	-4.931	-16.197	-1.266	-36.709	-34.534
7	32.681	-4.947	-11.440	-1.282	-25.928	-34.980
8	26.217	-5.179	-17.904	-1.514	-40.579	-41.319
9	28.041	-4.894	-16.080	-1.229	-36.446	-33.532
10	38.991	-4.386	-5.130	-0.721	-11.627	-19.671
11	41.741	-4.414	-2.380	-0.749	-5.393	-20.442
12	43.891	-3.673	-0.230	-0.008	-0.521	-0.218
13	43.594	-3.852	-0.527	-0.187	-1.195	-5.093
14	43.150	-3.658	-0.971	0.007	-2.200	0.195
15	51.189	-2.921	7.068	0.744	16.019	20.313
16	60.842	-2.268	16.721	1.397	37.898	38.117
17	59.692	-2.176	15.571	1.489	35.291	40.629
18	64.286	-1.734	20.165	1.931	45.704	52.686
19	51.191	-3.305	7.070	0.360	16.023	9.823
20	53.480	-2.960	9.359	0.705	21.212	19.241



**Fig. 4. Values of Heavy metal pollution index (HPI) in different stations of Haraz River**



**Fig. 5. Values of Contamination index ( $C_d$ ) in different stations of Haraz River**

parts and the agricultural, municipal and industrial wastewater discharge in downstream.

In computing the indices HPI and  $C_d$  for present study, standard permissible value [ $S_i$ ] and weightage [ $W_i$ ] as well as the highest desirable value [ $I_i$ ] (Prasad & Bose, 2001) were considered according to the data indicated in Table 4.

Mean and percentile deviation for both indices were computed for each sampling point (Table 5). Analysis showed that 65% of  $C_d$  and 70% of HPI values are lower than the mean value and have the percentile deviation on the negative side which indicates relatively better quality as noted by Prasad and Bose (2001).

The behavior of two indices among different sampling points from the upstream to the estuary is manifested in Figs 4 and 5.

Regarding the risky metallic pollution of river water within the basin, the whole river length may be categorized in two distinct reaches; the reach from station 1 up to station 13 and the other one from station 13 to 20 may respectively be considered to have low and moderate metallic pollution potential risk. Such categorization was also achieved using the hierarchical cluster analysis of the data through Euclidean distance method.

## CONCLUSION

Twenty water samples from Haraz River and its main tributaries were collected and analyzed for physicochemical parameters as well as metals (Cu, Zn, As, Cd, Pb, Ni and Mn) in water column. In order to evaluate the risk potential of metal pollution in river water, making use of two indices namely heavy metal

pollution index (HPI) and contamination index ( $C_d$ ) accompanied by cluster analysis was taken into the consideration.

According to the data gathered the stations located within the upstream of the river (1 to 13) seemed to encounter low risk potentials while the downstream stations (14 to 20) approved to hold higher risk potentials. The results also showed relatively meaningful correlation among the behavior of different metals in water column alongside the river which may be attributed to their same entry source. The main sources are considered to be mining and quarrying activities in the central parts of the basin as well as municipal and industrial wastewater discharge to the river in downstream. Such results are meeting the ones achieved by the author in former studies on the sediment metallic pollution of the same water basin (Nasrabadi *et al.*, 2010a, 2010b). The convergence of both indices in this study was also of interest.

However, the values of these two indices in river water are totally below the critical values but severe precautions must be taken into consideration in central parts and downstream of the river where lots of mining, quarrying and agricultural activities as well as municipal and industrial wastewater discharge to the river are observed. Extreme use of river water for drinking, agriculture and industrial purposes within the basin, relatively biota-rich characteristics of the river and Caspian Sea as the final sink are among the most significant reasons that make the river monitoring implementation inevitable.

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