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Assessment of Heavy Metal Pollution in Tilehbon River Sediments, Iran

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Abstract: In this study, four sediment samples on Tilehbon River were chemically analyzed in order to determine the concentration, origin and pollution intensity of heavy metals (Pb, Cr, Mn, Ni, Cd, Cu, Zn and Fe). The concentration of these elements was determined by using inductively coupled plasma atomic emission spectrometry (ICP-AES). Then a cluster analysis has conducted using MVSP 3.1 software. The obtained results showed that the concentration of heavy elements are transitive as compared with the average concentration of these elements in ground surface and global sediments and they controlled by geological units. Lime units play the most important role to control the concentration of elements. Based on Muller geochemical index, the sediments in Tilehbon River are not polluted.

Key words: Heavy metals, pollution, geochemical index, Tilehbon River, Kiasar Iran

INTRODUCTION

Natural environment which is polluting by heavy elements is considered as a universal problem. The heavy elements released in the environment as the result of human activities, atmospheric depositions and erosions would finally enter in to the aqua systems (Veena *et al.*, 1997). Since, heavy metals are toxic, stable in the environment and potential to combine with the nutritive continuum. Thus, they are considered as one of the most significant pollutant in aqua systems (Desya *et al.*, 2002; Smecka-Cymerman and Kempers, 2001).

Heavy metals are transferred into marine systems via rivers. Intensity and amounts of metal entry into marines depend on their amounts in river's sediments, water and suspense ingredients (Chester, 2003). Because of the importance of sediments to the overall quality of aquatic system, sediment analysis is often included in environmental assessment studies (Adekola and Eletta, 2007). Sediments can also be a potential reservoir of metals, by releasing them to the water column under changing physical and chemical conditions (Karbassi *et al.*, 2007). Geochemical studies on sediment conenters of aqua systems such as rivers, estuary and river beds may be an effective measure to find the origin and scatter pattern of elements and to bio environmentally evaluate the current situation of an area (Paul, 2001).

Methods of multivariate analysis have been widely used to identify pollution sources and to apportion natural and anthropogenic contribution (Mico *et al.*, 2006).

Mining operation is an important industry in Iran. Many of them are near rivers. It is essential to closely investigate the heavy metals concentrations in river sediments in these regions of the country.

In this research, the concentration of heavy metals has investigated via chemical analysis of Tilehbon River bed sediments and determining the origin of heavy metals using cluster analysis. The old mine seeking places in the watershed area of Tilehbon River can be counted as one of the pollutant factors of this river.

MATERIALS AND METHODS

Study area is located at the west part of Baladeh Village in Mazandaran Province and at 100 km distant from south-west of Sari. Baladeh region with an approximate area of 11.8 km² and a rectangular shape, extends from east to west between the altitudes of 53° 37'07" to 53° 40'40" and latitudes of 36° 08'45" to 36° 07'35". Figure 1 shows the location of study area in Iran.

According to geology map of Kiasar with the scale of 1:100000, the region's lithology contains shale, tuff and sandstone, green mica slits, dolomite siltstone associated with coal layers, quaternary sediments and magmatism

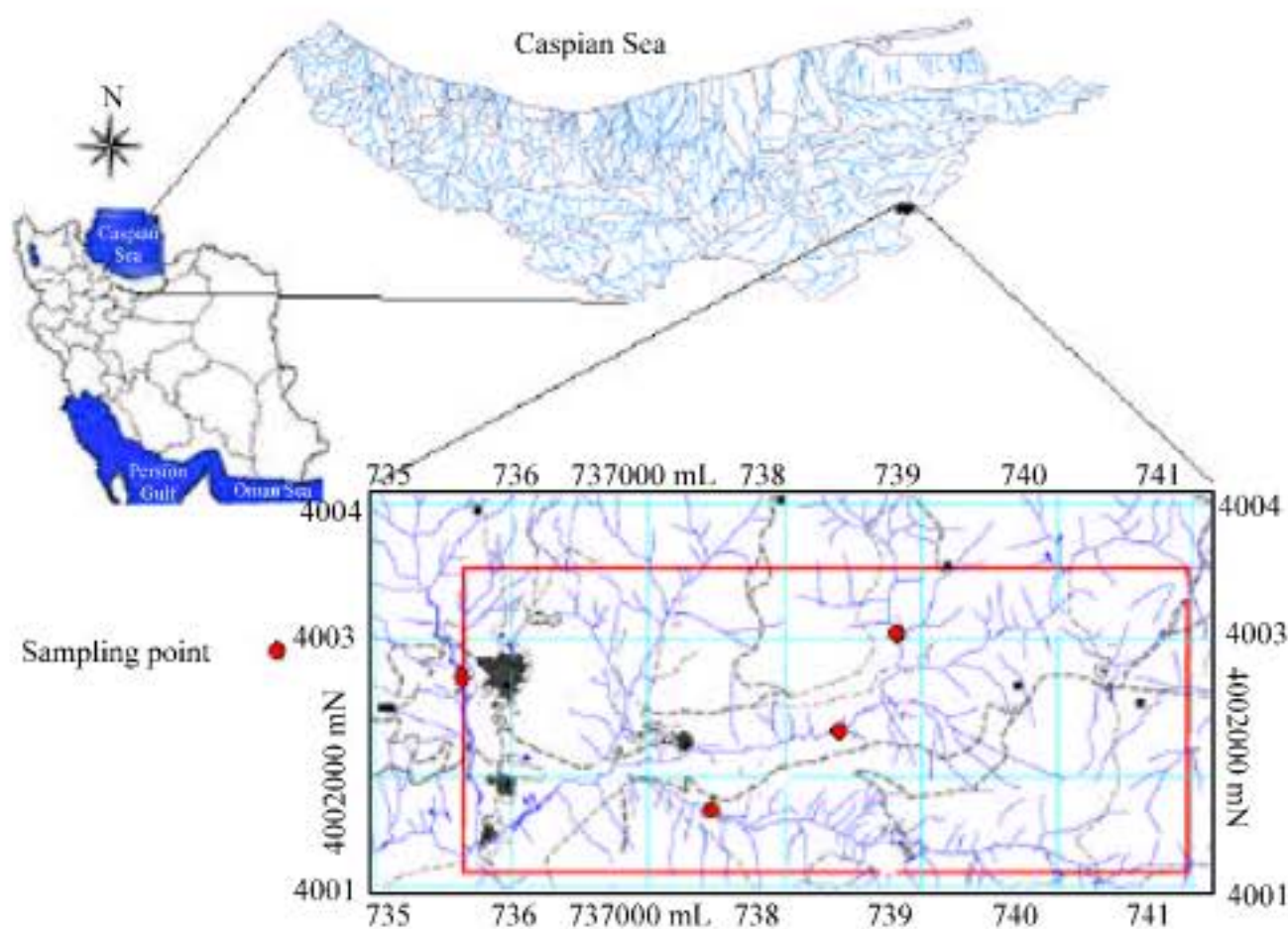


Fig. 1: Location of the study area and sampling points

phase. Tilehbon is the main river in the study area and it flows from east to west. Due to the low depth of Tilehbon River, all sediment samples were directly collected from river bed using plastic dishes. Figure 1 shows the location of the sampling points. Sampling was done in 2007.

Weight of samples measured throughout the study area was 1 kg. All samples were dried under the temperature of 70°C and passed through a 74 µm mesh (equivalent to a No. 200 sieve). About 2 g of powdered sample was placed in a Teflon beaker. The dry samples were then digested with HNO₃/H₂O₂/ HCl and digestate made up to volume with Deionized water (Micó *et al.*, 2006). The concentration of Pb, Cr, Mn, Ni, Cd, Cu, Zn and Fe, were determined by using ICP-AES (Carman *et al.*, 2007).

Cluster analysis is a multivariable statistical method and it was used to find the origin of heavy metals using analytical software of MVSP 3.1. The Weighted Pair Group method (GWP) was used to identify clustering tendencies among the samples (Davis, 1973; Karbassi, 1998; Micó *et al.*, 2006; Thévenot *et al.*, 2007). Cluster tree joins the alternatives of the same weight to create bigger clusters then, their similarities could be evaluated. Muler's geochemical index was used to measure the pollution intensity (Eq. 1).

$$I_{geo} = \text{Log}_2 \left[\frac{C_n}{1.5B_n} \right] \quad (1)$$

where, I_{geo} is geochemical aggregation indicator or pollution intensity indicator, C_n is Sediment metal

concentration, B_n is metal concentration in the shale (Müller, 1979; Gonzalez-Macias *et al.*, 2006). The factor of 1.5 is placed in the equation due to the probability of difference between the primary densities of sediments as the result of earth factors.

RESULTS AND DISCUSSION

Based on the results shown in Table 1, the mean concentration of Pb, Cr, Mn and Ni in Tilehbon River sediments are higher than the mean metal concentrations that are typical of aquatic sediments and crust samples from around the globe (Bowen, 1979). Similar results have been reported from several global locations (Liu *et al.*, 2003). Zn and Cu concentration are located between the global sediment and Earth'crust mean concentration. Cu concentration in river sediments is similarity to other system influenced by mines, such as the Mandovi estuary in India (Alagarsamy, 2006). Concentration of Zn is similar to the river-estuary of system Marabasco (Marmolejo-Rodríguez, 2007). Measurements of Cd are similar to Earth'crust and other world systems near to mine, such as sediments of Tinto and Odiel rivers, Spain (Morillo *et al.*, 2002). Also, River sediments did not show a significant Fe enrichment. Therefore, in Tilehbon may be defined, in general, as a natural system, according to the Cd and Fe background level reported for the Earth' crust (Marmolejo-Rodríguez, 2007). Finally, geological units contain different concentration of heavy metals, Thus comparing them with global sediments and earth crust mean concentration may

Table 1: Concentration of heavy metals in Tilehbon river- surficial sediment

Samples	Pb	Cr	Mn	Ni	Cd	Cu	Zn	Fe (%)
1	58.80	61.0	1650	122.0	1.00	52.60	171.00	4.14
2	13.90	112.0	686	78.0	0.10	25.20	54.50	4.22
3	7.30	373.0	1030	191.0	0.20	44.90	82.20	6.46
4	19.00	64.0	870	43.0	0.00	27.00	61.40	3.76
Max	58.80	373.0	1650	191.0	0.20	52.60	171.00	6.46
Min	7.30	61.0	686	43.0	0.00	25.20	54.50	3.76
Mean (present study)	24.75	152.5	1056	108.5	0.33	37.43	92.28	2.00
Mean Crust*	14.00	-	950	80.0	0.30	50.00	75.00	4.10
Mean (world sediment)*	16.00	71.0	770	52.0	0.20	32.00	127.00	4.10

*Bowen (1979). Concentration of the all elements are in mg kg⁻¹, except Fe

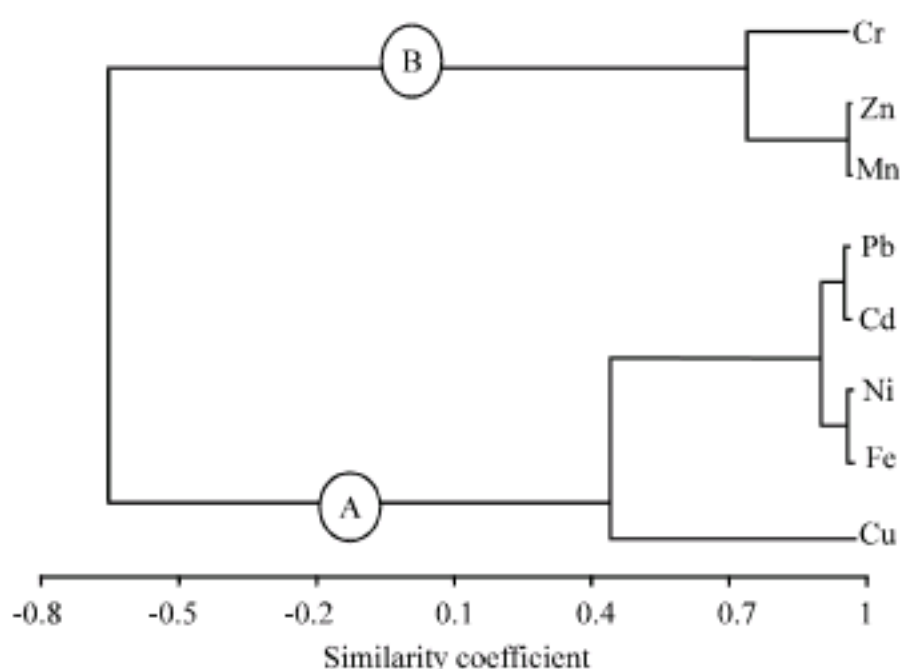


Fig. 2: Dendrogram of metals in Tilehbon river bed sediment using cluster analysis

not be an effective procedure; for instance. Iron concentration is lower than them concentration.

As can be seen in Fig. 2, cluster analysis has used to statistically interpret the heavy metals relationships and to find their origins. Cluster analysis is composed of two branches (A and B). Branch A consists of such elements as Copper, Iron, Nickel, Cadmium and Plumb, therefore, control factors in this branch are similar. While branch B includes Manganese, Zinc and Chromium. The close relations among these three elements indicate their similar behaviors in the nature. There exists a very weak relationship between these two branches which is a meaningful negative relation; thus, it can be concluded that the elements of branches A and B originates from different sources.

As it is shown in cluster analysis, dendrogram of sediments in Tilehbon River was composed of two branches. Copper, Plumb, Iron, Nickel, Cadmium and are presented at branch A (Fig. 2). There is a very significant relationship between the elements in this branch (except for Copper). Since Iron is known as an earth index in cluster analysis, thus it can be concluded that Nickel, Cadmium and Plumb are also originated from the earth. This conclusion is somehow true for Copper. Based on the results of complete segregation of elements (Table 1), there are lower densities of Iron in Tilehbon River

sediments as compared with the averages of global sediments and ground surface, which shows the role of geology to control heavy metal densities. Three elements including Manganese, Chromium and Zinc are presented at branch B. The significantly close relationships among these three elements indicate their similar behavior in the nature. Due to lacking an indicator in this branch, their origin could not be found. However, a very weak and negative relationship exists between branch of A and B. Thus, it could be concluded that Manganese, Chromium and Zinc are not originated from the earth and earth materials make their densities thinner.

Muller's geochemical index was used to measure the pollution intensities in studying area (Muller, 1979). The I_{geo} is associated with a qualitative scale of pollution intensity, samples may be classified as unpolluted ($0 \leq I_{geo} \leq 1$), unpolluted to moderately polluted ($1 \leq I_{geo} \leq 2$), moderately polluted ($2 \leq I_{geo} \leq 3$), moderate to strongly polluted ($3 \leq I_{geo} \leq 4$), strongly to extremely polluted ($4 \leq I_{geo} \leq 5$) and extremely polluted ($I_{geo} \geq 6$) (Muller, 1979; Farkas *et al.*, 2007). Following this classification the sediments collected during sampling can be unpolluted with Pb, Cr, Mn, Ni, Cd, Cu, Zn and Fe. As the results of this study, pollution intensity of heavy metals in Tilehbon River is classified as not polluted area. Pollution intensities are measured as follows:

Cr and Ni $(0) < (0.1)$ Mn and Pb $> (0.2)$ Cd $< (0.4)$ Fe and Zn $< (0.7)$ Cu

CONCLUSION

Based on the results of this study, the measured concentrations are transitive comparing the averages of global sediments and Earth' crust. However, heavy metals' concentrations were significantly different through various geological units and making a comparison between the measured concentration and the averages of ground surface and Earth' crust may not reach the desired results. Finally, the mining operation of Tilehbon basin has not caused negative impact in the surficial sediments of Tilehbon River until now. The measured concentration in this study can be used in future studies.

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