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Study Concentrations Changes of Lead, Chromium, Nickel, Cadmium, Zinc and Copper in Beshar River of Kohgiluyeh and Boyerahmad Province, Iran

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Abstract

Due to the lack of water quality of resources in country, exact review of available water resources quality, especially in terms of heavy elements (heavy metals) has a particular importance. Due to industrial towns 1 and 2 of Yasuj city and also Yasuj wastewater treatment, surveying environmental harmful effects of heavy metals on this river is very important. To investigate the changes of heavy metals (Pb, Cr, Ni, Cd, Zn and Pb) sampling from three stations Qalat, Mokhtar and Pataveh was carried out from September 2012 until May 2013 along the Beshar River. To estimate the severity of the pollution, PI index (Pollutant Index) and cumulative index IPI and mCd were used. Mean values of the elements shows that the maximum and minimum mean value of the elements respectively is related to chromium and cadmium. Calculating of pollution Index (PI) and then cumulative index IPI and mCd based on the EPA,WHO, NAS and FAO standards, shows the low pollution for the whole data in water of Beshar River. The process of elements concentration changes primarily is related to distance between sampling points and sources of pollutants. Being far or near is the important point about this issue. Just when the 1053 standard is used for computing the IPI and mCd indices, these indices are different in contamination degree. In this situation one of the indices is placed in low pollution class and another index will be in very high pollution class.

Keywords: *Beshar River, Heavy Metals, Pollution Index (PI), Cumulative Index IPI and mCd*

1. Introduction

Rivers act as drains for whole water entering watersheds and transferring them outside them. Therefore, they are environmentally significant (Sam, 2011). Water and soil pollution poses a serious threat to the development of an area (Valipour et. al., 2013a; Valipour et. al., 2012; Valipour et. al., 2013b). Regular water quality monitoring of the water resources is absolutely necessary to assess the quality of water for ecosystem health and hygiene, industrial use, agricultural use and domestic use (Poonam et al., 2013).

Among the pollutants available in industrial and mining wastewater was well as urban and agricultural runoff, one can refer to heavy metals. Heavy metals enter surface water, groundwater, and soil in the form of solutions in water and soil and cause the disruption of ecosystems into which they enter. Human beings and animals, by taking vegetables, plants, and food watered by such water or those grown from such polluted soil, and animals and aquatics exposed to such metals, suffer from different kinds of known and unknown diseases. Therefore, it is necessary that some measures be conducted to control and reduce such pollutants in the environment (Manshouri et. al, 2011; Crites et al, 1998). Metal concentration levels as reported by the Department of Environment of Malaysia were used to assess the state of metal contamination of the rivers(Ismail et. al., 2013). Heavy metals naturally enter water environments via the weathering of crust and atmospheric depositions. In addition, more than several decades, the increasing use of metals due to human activities in industrial and agricultural sectors, and also the disposal of sewage and surface runoff in big and small cities, a large part of these elements have entered water ecosystems more than several times the limit of sustainability (Forstner and Wittmann, 1983).

In the study done by Brraich and Jangu (2015) for investigating the intensity of heavy metal pollution discharged from various industries into Harike Wetland, pollution indices of HEI and HPI and statistical methods were used. The analyzed metals were lead, chromium, iron, copper, nickel, zinc and cadmium. The results obtained from the study indicated that a lot of metal ions in the wetland had more concentrations than international standards. In this study, the quality of the water of the wetland was reported to be appropriate for various aquatic animals and for drinking and irrigation (Brraich and Jangu, 2015).

Beshar River considering the existence of different industries on the riverbank and the significance of the river in the lives of the residents of the region, the study of water pollution of the river by heavy metals (particularly lead and cadmium) for preventing pollution and improving the quality of the water of the river seem necessary. In fact, the objective of the present study is to report the basic concentrations for lead and cadmium for investigating the pollution resulting from heavy metals in the Beshar River and obtaining data for controlling environmental changes of the region in the future.

2. Materials and Methods

2.1. The study area

Kohgiluyeh and Boyer Ahmad Province is located from 55 ˚ 19' longitude east to 56 ˚ 59' and from 26 ˚ 58' to 27 ˚ 57' latitude north. The length of the Beshar River is 150 km. in the present study, a range of approximately 98 km of the river running from the border of the province to Pataveh Village, was investigated (RWDR, 2006).

2.2. Methods

Analyzing data was conducted based on SPSS statistical software. The normality of data was measured by Kolmogorov-Smirnov test. After confirming the normality of data, to compare the concentration of these elements in studied stations and also compare their concentrations among upstream, midstream, and downstream of each station, ANOVA was used. To investigate the concentration of heavy elements in the water of the Beshar River and study the amount and way of variations of pollutants, after observing and identifying the region along the river, three stations of 1. Qalat Station, 2. Mokhtar Station, and 3. Pataveh Station was considered. The positions of stations are presented in table 1. Sampling the water of the river was conducted since October 2012 to May 2013 for nine months in the mentioned stations. In each station, using Ruttner bottles, 0.5 liter water samples were collected from upstream, mid-stream, and downstream. Then, the samples were coded and to stabilize the pH of the water and prevent chemical reactions, concentrated nitric acid was added to the samples. Samples were transferred to University of Yazd, digested and the concentrations of heavy elements of lead, cadmium, chromium, nickel, zinc and copper were measured using flame atomic absorption spectrometer, model Analyticjena -350, and the data were classified and analyzed.

Table 1: the positions of sampling stations at Beshar basin

Sampling stations	Longitude	Latitude
Qalat	566014	33808557
Mokhtar	549949	3394661
Pataveh	524148	3424901

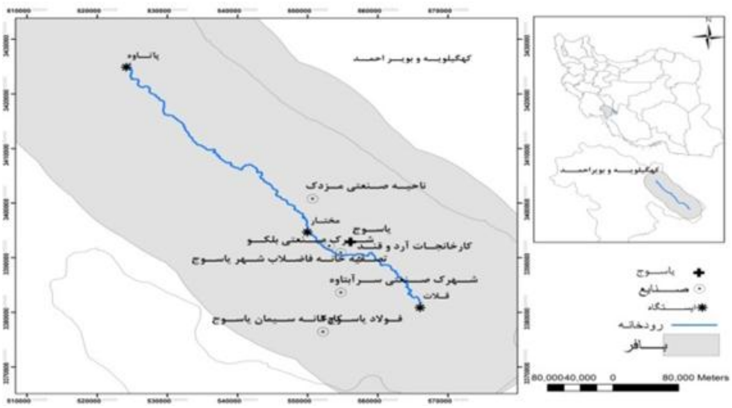

Fig. 1 : Geographical location of Beshar River

2.3. Pollution Index (PI)

The pollution index (PI) is used for estimating the intensity of an environment (Memet and Bulent, 2011). This index is used for water environment in the form of the ratio of the concentration of an element (C_i) in water samples with the ground amount of the same element in the used region (B_i) (equation 1). According to the pollution index, three sets of low (PI≤1), moderate (1<PI≤3), and high pollution (PI>3) have been introduced (Chen et. al., 2001).

$$PI = \frac{C_i}{B_i} \qquad (1)$$

2.4. Accumulated API and mCd

The level of pollution can be obtained using the following method which is the pollution load index and in 1980 was presented by Tamlinson et al(Tamlinson et. Al., 1980). According to the IP, three sets of low (IPI≤1), moderate (1≤IPI<2), and high pollution (IPI>2) have been presented (Hakanson, 1983).

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$$IPI = \sqrt[n]{PI_1 \times PI_2 \times PI_3 \times \ldots \times PI_n} \qquad (2)$$

In this formula, Pi1 and Pin indicate pollution factors calculated for the first sediment sample to n^th sediment sample. Hakanson (1980) presented another pollution index called pollution degree which Abrahim modified it into MC_d in 2005(Hakanson, 1983). To determine pollution variations, these two indices were sued (Hakanson, 1983).

$$C_d = \sum_{i=1}^{n} PI_i \qquad (3)$$

$$mC_d = \sum_{i=1}^{n} \frac{PI_i}{n} \qquad (4)$$

In this formula, Cd is the sum of IPs and MCd is the arithmetic mean of IPs.

Table 3: qualitative classification of indices of the modified pollution degree

Qualitative classification pollution index	Values mCd
very low of pollution degree	$mC_d < 1.5$
Low pollution degree	$1.5 \leq 2mC_d < 2$
Moderate pollution degree	$2 \leq mC_d < 4$
High pollution degree	$4 \leq mC_d < 8$
Very high pollution degree	$8 \leq mCd < 16$
Severe pollution degree	$16 \leq mCd < 32$
Very severe pollution degree	$mCd \geq 32$

3. Results and Discussion

The average concentration of lead, chromium, nickel, cadmium, zinc and copper are respectively 0.185, 0.382, 0.044, 0.004, 0.013, and 0.129 mg/L. lead is the most widespread heavy and toxic elements in the environment so that from polar ice to deep-sea sediments, its effects can be observed (Lee and Touray, 1998). The most amount of lead is related to Pataveh and Mokhtar stations. Chromium is observed in pH from 6 to 8 and usually is with the capacity 6 and in solution (Kabata-Pendias and Mukherjee, 2007). Chromium (Cr) is found in all phases of the environment, including air, water, and soil, and its many chemical forms are pollutants with serious implication to the environment and human health (Shanker, 2014). The highest concentrations of chromium and nickel are related to Pataveh Station. In spite of the very low mobility of nickel in the aqueous phase, its shelf life is very short in this phase and can be easily absorbed by oxides of iron, manganese and clay particles (Vignati, 2004). Cadmium is usually available naturally in groundwater and surface water. Cadmium entering aquatic ecosystems through soil and bedrock erosion, sediment atmospheric pollution caused by industrial plants, waste water and sludge contaminated areas, and the use of fertilizers in agriculture (Nikravesh, 19950). The concentrations obtained from Cadmium indicate that the highest amount of cadmium is in Pataveh Station. Copper is a reddish metal that is extensively used as the metal or alloy in the manufacture of wire, sheet metal, coins, pipe, and other metal products. The European Food Safety Authority has established an acceptable daily intake of 0.15 mg per kg bw per day(Yalcın tepe, 2014). The highest amount of zinc and copper are related to Pataveh and Mokhtar stations respectively which these concentrations can be due to the entrance of wastewater from industrial towns, flour, sugar and cement plants and also the wastewater treatment plant in Yasuj. increasing anthropogenic influence on the environmental, especially pollution loading, have caused negative changes in natural ecosystem and decrease of biodiversity (Matriping et.al., 2014).

3.1 Statistical analysis

The results indicated that differences are not significant. Comparing the mean scores of the mentioned elements in spring, autumn, and winter using ANOVA indicated significant differences among these seasons. In the next stage, to separate different groups, the Duncan multiple range test was used. According to charts 2 to 4, the results of the Duncan test indicate that for lead, the difference of spring with autumn and spring is significant, but the difference of autumn with winter is not significant. For lead, the highest mean scores is related to winter and equals 0.2464 mg/L. for chromium, the difference of autumn with spring and winter is significant, but there is no significant difference between winter and spring. In addition, the highest mean scores is related to autumn and is equal to 0.4508 mg/L. for nickel, each three seasons of spring, winter, and autumn has significant differences with each other and the highest mean scores is related to spring which is equal to 0.0561 mg/L. for cadmium, there is significant difference between spring and seasons of autumn and winter, but autumn has no significant difference with winter. And the highest mean scores is related to winter equal as 0.0054 mg/L. the results of the Duncan test on zinc indicated that there is no significant differences between winter and autumn, but there is a significant difference of seasons of winter and autumn with spring. The highest mean scores is related to spring equal as 0.0209 mg/L. at last, the results of the Duncan test indicated that for copper, there is significant differences among each three seasons of winter, autumn, and spring and the highest mean scores is equal to 0.138 mg/L.

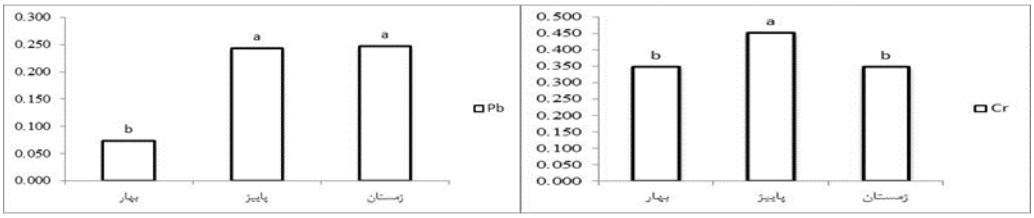

Fig. 2: Mean scores of water-soluble chromium and lead in autumn, winter, and spring (different alphabets indicate the existence of significant differences then same alphabets indicate the lack of significant differences

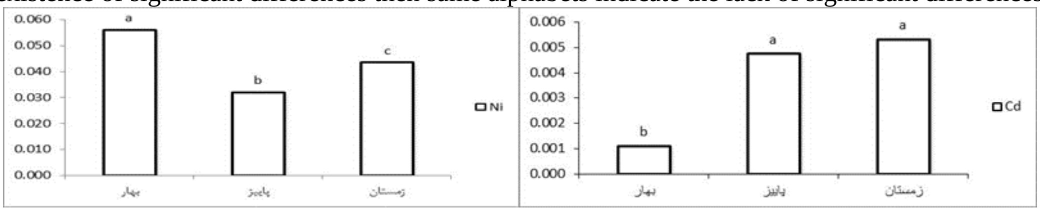

Fig. 3: Mean scores of water-soluble cadmium and nickel in autumn, winter, and spring (different alphabets indicate the existence of significant differences then same alphabets indicate the lack of significant differences

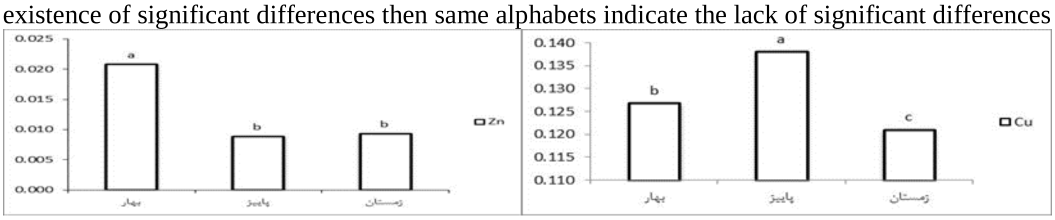

Fig. 4: Mean scores of water-soluble copper and zinc in autumn, winter, and spring (different alphabets indicate the existence of significant differences then same alphabets indicate the lack of significant differences

3.2 Correlation coefficient of elements in the aquatic environment of the Beshar River

The correlation of cadmium with elements of lead, chrome, and copper at the probability level 1% is positive and significant and is equal to 20.518, 0.00, and 0.095. The correlation of lead with chromium at the probability level of 5% is positive and significant and is equal 0.230. The correlation of lead with copper at the probability level 1% is positive and significant equal as 0.036. The correlation of chrome with copper at the probability level 1% is positive and significant equal as 0.568. In addition, the correlation of nickel with zinc at the probability level 1% is positive and significant equal as 0.117.

3.3 Findings of the PI in water instances of the Beshar River

To calculate the PI instead of the ground value of each element, Standard 1053 of the Ministry of Power and qualitative standards wastewater treatment used in irrigation of IRNDOE, standards of WHO, EPA, FAO, and the standard of NAS were used. The mean scores of the PI in case which Standard 1053 was used for this index, indicated that the water of the Beshar River is highly polluted by lead and chromium, is moderately polluted by nickel, and is lowly polluted by zinc and copper.

Table 2: standard values used for calculating the PI

Studied standards	Pb	Cr	Ni	Cd	Zn	Cu
1053	0.01	0.05	0.07	0.003	15	2
EPA	5	0.1	0.2	0.01	1	0.2
WHO- FAO- NAS	5	0.1	0.2	0.01	2	0.2
IRNDEO	1	1	2	0.05	2	0.2

In cases where instead of standard values, values of standards of EPA, WHO, NAS, and FAO are used, the values of pollution index for lead, nickel, copper, and zinc of all data are classified in the category of low pollution. For chromium, all data are classified in the category of high pollution. For the element cadmium, 94.87% of the data are classified in the category of low pollution, and 5.13% of the data are classified in the category of moderate pollution. In case where instead of standard values, the values of the standard of IRNDOE are used, all data for elements of lead, chromium, nickel, cadmium, copper, and zinc are classified in the category of low pollution. By using Standard 1053 of the Ministry of Power and also standards of EPA, WHO, NAS, and FAO for the IP, the results indicate that, for Chromium, 100% of the data are classified in the category of low pollution based on these standards.

3.4 Results of accumulative IPO and mC_d

In case that Standard 1053 of the Ministry of Power, EPA, WHO, NAS, and FAO are used for calculating the PI and consequently the calculation of the Accumulative IPI, the values of the Accumulative IPI indicate that all data are classified in the category of low pollution. As for calculating the Accumulative IPI, the standard of IRNDOE was used. All data are categorized at low pollution. As these calculations indicate, Standard 1053 of the Ministry of Power, EPA, WHO, NAS, and FAO have the same results regarding the accumulative pollution of the water of the Beshar River.

In conditions which to calculate the accumulative index of mC_d, standards of EPA, WHO, NAS, FAO, and IRNDOE are used, 100% of data are classified in the category of low pollution. The values of accumulative index of mC_d in case which Standard 1053 of the Ministry of Power is used, indicate that 15.38% of the data are classified in the category of low pollution, 25.64% of them are classified in the category of moderate pollution, 51.28% of the them are classified in the category of high pollution, and 7.7% of the data are classified in the category of very high pollution. Regarding the fact that the two indices of IPI and mC_d are different in terms of formula, (IPI is the geometric mean scores of the PI and mC_d is the arithmetic mean scores of the PI); therefore, the results obtained from these two pollution indices are different from each other. In case that Standard 1053 are used for calculating pollution indices, in terms of the IPI, the highest amount of pollution is related to the upstream of Qalat station in October, and this sample is classified in the category of low pollution, and in terms of the index mC_d, the highest amount of pollution is related to the downstream of Pataveh station in December and is classified in the category of very high pollution. In condition which the standards WHO NAS, and FAO are used, the highest amount of pollution is related to the sample of upstream of Qalat Station in October which is classified in the category of low pollution. But the index of mC_d, the highest amount of pollution is related to the downstream of

Pataveh sation in October which is classified in the category of very low pollution. When the IRNDOE Standard is used for calculating IPI and mC_d indices, in terms of both indices, the highest amount of pollution belongs to the upstream of Qalat Station which in terms of the IPI is in the category of low pollution and in terms of the mC_d, it is in the category of very low pollution. But in terms of the mC_d, the highest value is related to the downstream of Pataveh sation in October which is in the category of very low pollution. This is while in the present study, high levels of pollution were not observed in the Beshar River. In addition, the results of research done by Khorasani et al (2005) investigated the concentration of heavy metals (zinc, copper, iron, chromium, and lead) resulting from industrial and economic activities on the marine environment of coastal regions and indicated the pollution of the region by copper, zinc, and chromes. These researchers indicated that industrial and commercial activities in the region has resulted in the pollution by these elements (Khorasani et. al., 2005).

The results obtained from the evaluation of elements of lead, iron, copper, and cadmium in the sediments of Anzali Wetalnd in autumns and winters indicated that in terms of seasonal changes, the values of the concentration of lead, cadmium, and iron increase from autumns to winters and in this regard, no change was observed in the concentration of the element of copper in autumns and winters (Babaee, 2007).In the present study, the mean concentration of copper, cadmium, and lead are 0.129, 0.994, and 0.185 mg/L and in terms of seasonal changes, the values of concentration of studied elements, the results indicate that for elements lead and cadmium, gradually from springs to autumn, due to the flood conditions of the Beshar River as well as the melting of snows on Dena Mountain around this river, the concentration of pollution reduces. In case of element chromium, this process is observed except for this difference that the values of pollutions in spring have no much downturn compared to cadmium and lead. In case of nickel, such a pattern can be observed in April and May except for the sample obtained in May in the downstream of Pataveh Station in which the concentration of nickel increased. This data can be due to sampling errors. In case of two elements of zinc and copper, such a pattern cannot be observed. The results of research done by Zarei et al(2013) indicated mean concentration of metals in water found to be in the following order: Pb> Fe>Zn>Cu>Cr. while in the present study,mean concentration of metals in water found to be in the following order: Cr> Pb>Cu>Ni>Zn>Cd(Zarei et. al., 2013).The results obtained from measuring the value of heavy meals in water, the sediment and wild bird coots in the southeastern edge of the Caspian Sea indicated that the highest concentration of heavy metals in the water samples belonged lead and sediment samples belonged zing (HasanPour, 2011). Wile in the present study, the highest concentration is related to chromium.

4. Conclusions

The changes of concentration of elements in the first place are influenced by the farness and closeness to the points of sampling from pollutant resources (the entrance of municipal and industrial wastewater and industrial towns). In general, regarding the fact that sampling stations of Mokhtar and Pataveh are located in the downstream of industrial regions, and also regarding the accumulative effects of these pollutions in mentioned stations, approximately the concentration of all elements studied in this research are in Mokhtar and Pataveh Stations is higher than that of Qlat Station. The mean values of elements indicate that the highest mean values are related to chromium and the lowest mean values are related to cadmium. The correlation coefficients obtained among elements of the study in the water of the Beshar River indicate that lead and cadmium, chromium and lead, and copper and chromium have positive and high correlations with each other and may be due to having the same origin along the river. As investigations indicate, the IPI and mC_d in conditions which use standards of EPA, WHO, NAS, and IRNDOE and also the minimum values for each element for calculating these indices, same results are obtained in terms of pollution degree. Only in conditions which Standard 1053 is used, the IPI and mCd are different from each other in terms of pollution degree, and one is in the category of low pollution and the other is in the category of very high pollution.

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