



## Evaluation of heavy metal contamination and associated health risk assessment in water body of the Jajrood River, Iran

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**ABSTRACT:** The purpose of the present study is to assess the water quality of Jajrood River as one of the key drinking water resources of Tehran, Iran. Heavy metal contamination of the river is one of the major environmental concerns because of toxic effects, long-term persistence, and accumulation capacity of heavy metals in aquatic environment. The concentrations of Cr, Co, Cd, Pb, Cu, Zn, Al, Mg, Sn, Se, and Ba as well as related temporal variations were determined by collecting 784 samples from eight hydrometric stations between spring 2016 and winter 2017. Observations indicated that the Al had the highest mean concentration (0.49353 ppm), which is more than allowable limit, while the concentration of other heavy metals was within the acceptable range. The highest Average Daily Dose (ADD) value (41.361  $\mu\text{g}/\text{kg}$  day) was obtained for summer while the lowest value (0.003  $\mu\text{g}/\text{kg}$  day) for spring. It was found that Heavy Metal Pollution Index (HPI) values at all stations for four seasons ranged from 10.31 to 21.55 ppm. Moreover, obtained results showed that Hazard Quotient (HQ) values of studied heavy metals were below allowable limit ( $<1$ ). The results also indicated that further attention should be paid to adjust the high concentration of Al since its presence in drinking water supplies can lead to several health problems for residents of Tehran.

### Review History:

Received: 2019-04-09

Revised: 2019-05-26

Accepted: 2019-05-28

Available Online: 2019-05-28

### Keywords:

Water Quality

Heavy Metal Pollution Index

Jajrood River

Tehran

## 1. INTRODUCTION

Fresh water is a vital resource for any land-based life, and thereby any changes in the fresh water quantity and quality will have devastating impacts on human lives and ecosystem. The fresh water is a unique compound that can absorb, adsorb, dissolve, and suspend pollutant compounds, and so it can be contaminated easily [1]. The fresh water pollution can be caused by a variety of sources, including both anthropogenic and natural processes. River is one of the water bodies that can be utilized for agricultural, industrial, and urban purposes. It should be noted that any change in water quality and contamination of rivers could persist for years, thus imposing long-term negative effects.

The term heavy metal refers to a group of high-density metals and metalloids with potential toxicity in environmental contexts. The river contamination by heavy metals is one of the major environmental concerns because of toxic effects, long-term persistence, and the accumulation capacity of heavy metals in aquatic environment [2]. Some heavy metals (such as Cu, Fe, Zn, and Mn) are trace elements in aquatic systems and essential micronutrients, but they are highly toxic agents at high concentrations. Moreover, other heavy metals, including Mercury (Hg), Lead (Pb), Cadmium (Cd), Chromium (Cr), Arsenic (As), have carcinogenic nature and can seriously threaten the human health even at low concentrations [3].

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The heavy metals can also be released into the rivers through natural and anthropogenic processes. The natural processes are mainly mineral weathering and erosion, decomposition of polluted compounds, atmospheric deposition and heavy metal transportation [4]. The anthropogenic processes are mainly associated with discharge of untreated or partially treated domestic and industrial effluents, runoff polluted by pesticides and fertilizers in agricultural areas and also runoff polluted by municipal solid waste in urban areas into the rivers [5].

The heavy metals can also be suspended in the water, which depends on a variation of abiotic and biotic factors. These compounds can form inorganic complexes capable of binding to organic matter and penetrating to the food chains. The heavy metals are non-biodegradable and can be accumulated easily in the organs and consequently can cause many severe disorders [3].

Several studies demonstrated that the contamination of rivers by heavy metals has been a common and growing environmental problem over the last decades [6].

Yang et al. [7] monitored the heavy metal concentrations (Hg, Cd, Cr, Pb, and As) at 26 monitoring stations in Wei River in Shaanxi Region of China. The concentrations of Cd and Pb were below 0.1 and 3  $\mu\text{g}/\text{L}$  and detection rates of the remaining studied heavy metals were in the order of  $\text{Hg} > \text{Cr} > \text{As}$ . Giri and Singh [8] studied the concentrations



of Al, As, Ba, Cr, Co, Cu, Fe, Mn, Ni, Se, V and Zn from 21 sampling stations throughout the Subarnarekha River in India. Their results demonstrated that the concentrations of studied heavy metals had significant seasonality. Protano et al. [9] monitored the concentration of As, Pb, Hg, and Cd in water body of four rivers (Crati, Mesima, Angitola, and Esaro) all located in the Calabria region in southern Italy. The heavy metal concentrations were in the order of  $As > Pb > Hg > Cd$ . They reported that As and Cd concentrations tended to increase seasonally. In addition, the highest Pb concentrations were found in the Mesima, Crati, and Esaro rivers in fall (2.69, 2.18, and 1.22  $\mu\text{g/L}$ , respectively). Niu et al [10] studied the heavy metal pollution in 11 inflow rivers to Lake Taihu in China. The highest mean concentration was found for Zn, followed by Cu, Cr, Pb, and Ni. It was mentioned that high pollution of heavy metals in the studied area was mainly because of discharging large amounts of wastewater from various local industrial into the rivers. Evaluating and monitoring the water pollution in the rivers are necessary due to the direct effects of water pollution on the human beings and ecosystem. The assessment of heavy metal concentration in the rivers can also be truly useful for policy-makers to develop sustainable water resources management plans over the years.

Different water quality indices have been introduced to evaluate the pollution level in aquatic systems. Several studies used these indices for assessing water quality [11]. Heavy metal Pollution Index (HPI) is one of the indices frequently used for the evaluation of heavy metal contamination in surface water [12]. The HPI can be considered as a rating method reflecting the combined effects of each heavy metal on the water quality.

Yang et al. [7] found that the reduction in HPI had no seasonal trend and most likely resulted from the continued improvement in heavy metal pollution control strategies, which is combined with an improvement in wastewater treatment capacities. Moreover, the health risk for the five studied heavy metals in this region were within the acceptable levels for drinking water sources (HQ was less than 1 and CR ranged from  $10^{-4}$  to  $10^{-6}$ ). In a study by Giri and Singh [8], the HPI values showed great variations (between 3.55 and 388.9) and all stations fall under low (HPI less than 15) to medium classes (HPI between 15 and 30) of HPI, except few stations where were under the influence of industries, mining or near the estuary. Milivojević et al. [13] assessed the water pollution of Uglješnica River, Serbia, in terms of heavy metals through the HPI. The water samples were collected from four different stations to measure the concentrations of Pb, Cd, Fe, Zn, Mn, Cu, As and Hg. The mean HPI value was 67.487 and 80.676 for spring and fall, respectively. The highest HPI value (112.722) was found during the fall at sampling stations under the landfill and close to the highway, which was over the critical index limit. In addition, it was reported that increasing rainfall in spring leads to a rise in river water level and the subsequent dilution effect of rainfall results in a decrease of the heavy metal concentrations.

Average Daily Dose (ADD), Hazard Quotient (HQ) and Carcinogenic Risk (CR) are other indices for health risk

assessment, which can be employed for the estimation of probability and nature of negative health impacts of heavy metals on the humans.

Rivers can be considered as one the key sources of drinking water in different cities in Iran. The drinking water for Tehran in Iran is mainly supplied from Jajrood River. Therefore, any water pollution in Jajrood River can pose a serious threat to the water supply in Tehran. This river originates from the Alborz Mountains in northern Iran and flows to the southeast into the Latyan dam. Jajrood River also serves as a major irrigation source in addition to the drinking water sources.

Most of the previous studies on the contamination of Jajrood River has been related to organic pollution (such as ammonia nitrogen) [14], and only limited studies evaluated comprehensively the heavy metal pollution in this region to provide environmental management guidance. The main objective of the current study is to determine the levels of heavy metals (including Cr, Cd, Pb, Cu, Zn, Mg, Cobalt (Co), Aluminium (Al), Tin (Sn), Selenium (Se), and Barium (Ba)) in Jajrood River by collecting samples from 8 stations during the period of Spring 2016 to Winter 2017 to provide baseline data on heavy metal pollution, which will be helpful for the rational water management of Jajrood River. Furthermore, the temporal changes in the water quality were evaluated and the derived results were compared with the water quality standards of freshwater.

## 2. MATERIALS AND METHODS

### 2-1- Study area

Jajrood River originates from the Alborz Mountains in northern Iran and flows through Alborz and Tehran provinces. The length of Jajrood River is about 40 km and extended from  $51^{\circ} 22'$  to  $51^{\circ} 50'$  in north and  $35^{\circ} 45'$  E to  $36^{\circ} 5'$  in east (Fig. 1).

The catchment of this river covers an approximate area of  $790 \text{ km}^2$  [15] and is limited to Karaj basin from north and west, Lar basin from north and east, Eyvanakey basin from South and Sooleghan basin from southwest. The study area has cold and semi-arid climate with annual average air temperature of  $26^{\circ}\text{C}$  (a maximum of  $32^{\circ}\text{C}$  and a minimum of  $-8^{\circ}\text{C}$ ) [15]. The precipitation pattern is mostly similar to Mediterranean climate precipitation and the annual precipitation is 500 to 1100 mm [15]. Moreover, the annual mean flow of Jajrood River is  $295 \times 10^6 \text{ m}^3$  near Latyandam, which strongly is influenced by precipitation pattern (especially snow melt) [16].

The study area is considered as an important agricultural and industrial zone and several industrial units are located along Jajrood River. This river can also be regarded as one the key sources of drinking water for Tehran metropolitan area through Latian dam. Considerable amounts of industrial effluents as well as runoff contaminated by pesticides and fertilizers in agricultural areas are directly discharged into Jajrood River. This river is close to the several residential areas (including villages and small towns), especially in Alborz province. It is estimated that 20 mcm/y of untreated domestic wastewater is discharged into this river [17]. It should be

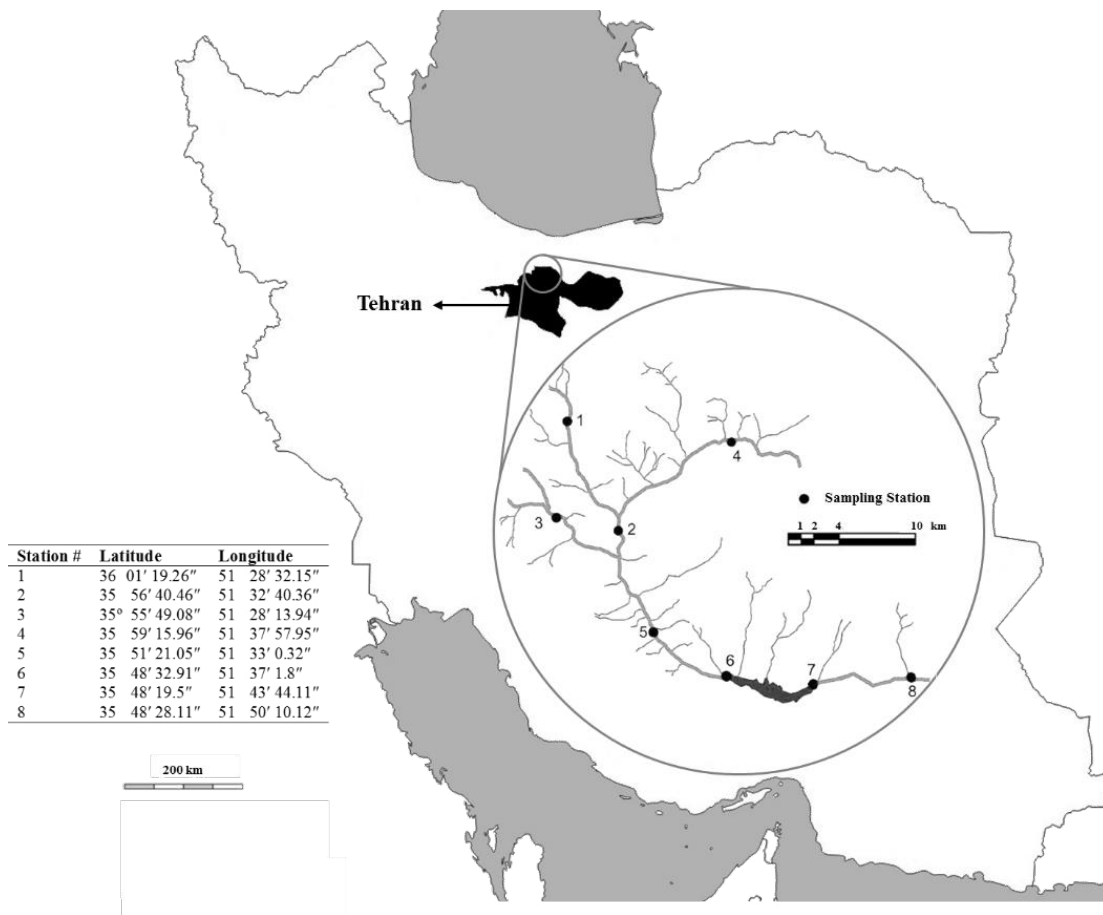


Fig. 1. Sampling stations along Jajrood River in details

mentioned that there is no active wastewater treatment plant in the study area [17].

### 2-2- Sampling process and analysis

In the current study, 748 samples of water were collected from eight sampling stations (including six stations in the main stream and two stations in the main tributaries) along the Jajrood River (as shown in Fig.1). The sampling station was sampled monthly based on a prepared schedule during March 2016 to Winter 2017. Most of selected sampling stations were near major agricultural, industrial and residential areas where receive relatively considerable amounts of wastewater. Details of sampling stations and their latitude and longitude are shown in Fig.1.

The water samples were collected from the depth of 20 to 30 cm using grab method and were transferred into high-density polyethylene (HDPE) containers previously washed by HNO<sub>3</sub>. Triplicates were collected in each sampling station and mixed as in-situ. The containers stored in coolers with a temperature of 4°C and then transported to the laboratory for further analysis.

Preservation of samples and analysis conducted based on established rules for surface waters, reported in the previous studies [18]. The samples were filtered by Whatman No. 42 filter paper (with pore size of 0.45 μm) using a vacuum suction

technique and then acidified by concentrated HNO<sub>3</sub> to adjust the pH values to less than 2. The filtered water samples were stored in pre-washed HDPE containers and refrigerated at a temperature of 4°C.

The analyses of selected heavy metals were conducted by an atomic absorption spectrometry (AAS) (Perkin-Elmer, 3300/96, MHS-10) equipped with special lamp for each particular metal. The analytical grade reagents were utilized for all measurements (without additional purification) and all used glassware was properly washed.

The data quality was ensured by calibration (blank and independent) and duplicate samples. Triplicates were analysed for each sample and the mean value was reported for each measurement.

### 2-3- Heavy metal pollution index

The HPI was applied determine the magnitude of the selected heavy metals in Jajrood River. It is a rating approach indicating the overall quality of water with respect to co-effect of each specific heavy metal [19]. The HPI can be calculated based on the Eq. (1).

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

Where,  $W_i$  is defined as the unit weight of the  $i^{\text{th}}$  parameter that is inversely proportional to the highest permissible value of the  $i^{\text{th}}$  parameter in drinking water ( $S_i$ ). The  $S_i$  refers to a maximum allowable concentration of the  $i^{\text{th}}$  parameter in drinking water when other parameters are absent. In addition,  $n$  shows total number of parameters and finally  $Q_i$  is the sub-index of the  $i^{\text{th}}$  parameter calculated as Eq. (2):

$$Q_i = \sum_{i=1}^n \frac{\{M_i(-)I_i\}}{(S_i - I_i)} \quad (2)$$

Where,  $M_i$  is monitored value of heavy metal (of  $i^{\text{th}}$  parameter) and  $I_i$  is defined as the maximum desirable value for drinking water of the  $i^{\text{th}}$  parameter (ideal value). It should be noted that sign (-) refers to numerical difference of  $M_i$  and  $I_i$  regardless of related algebraic sign. All  $S_i$  and  $I_i$  values in the current study were taken from Iranian drinking water standards [20], which do not provide a standard for  $S_i$  and  $I_i$  values, and standards of [21] and [22] were used for the calculations.

Moreover, the value of critical pollution index is considered 100 according to the particular category in Iranian drinking water standards [23]. When the HPI value is more than the mentioned critical value (100), the quality water will not be considered suitable for usage.

#### 2-4- Health risk assessment

The health risk assessment is defined as a process for estimating the health effects as a result of human exposure to the both carcinogenic and non-carcinogenic compounds through possible exposure pathways (including ingestion, dermal contact, and inhalation) [21]. The health risk assessment mainly consists of hazard identification, exposure assessment, toxicity assessment, and risk characterization [21]. The approach adopted in the current study for the health risk assessment was according to the method established by USEPA [21].

The purpose of hazard identification is to detect the presence of any potentially toxic compounds and their location, concentration and spatial distribution.

The exposure assessment aims at measuring the occurrence, intensity as well as period of human exposures to the specific environmental contaminant. The exposure assessment of each identified heavy metal compound was performed through determination of ADD based on the Eq. (3).

$$ADD = \frac{C \times IR \times ED}{BW \times AT} \quad (3)$$

Where,  $C$  represents the contaminant concentration (mg/l),  $IR$  is the Ingestion Rate per unit time (L/day) with reference value of 2.881 L/day,  $ED$  is defined as Exposure Duration (years) with reference value of 70 years,  $BW$  is Body Weight ( $\mu\text{g/L}$ ) with reference value of 65  $\mu\text{g/L}$ , and  $AT$  is Average Time (years) with reference value of 75 years [24].

The toxicity assessment estimates the toxicity due to exposure levels of chemicals, calculating of the Reference

**Table 1. RfD and SF values for different heavy metals.**

Heavy Metal	RfD ( $\mu\text{g kg}^{-1} \text{day}^{-1}$ )	SF ( $\mu\text{g kg}^{-1} \text{day}^{-1}$ ) <sup>-1</sup>
Cr	3	5.00E-04
Co	0.3	-
Cd	0.5	-
Pb	3.6	-
Cu	40	-
Zn	300	-
Al	1000	-
Mn	140	-
Sn	600	-
Se	5	-
Ba	200	-

Dose (RfD) of each specific heavy metal compounds. The RfD is defined as the highest acceptable dose such that more than that humans are susceptible to toxic substances.

The risk characterization predicts the potential health risk in the study area through integrating exposure assessment and toxicity assessment. The HQ, HI, and CR can be used for estimation of human health risk caused by heavy metals.

The HQ is a unitless parameter defined as the ratio of ADD of each specific heavy metal compound to the corresponding toxicity threshold value (RfD) and can be determined by the Eq (4). The reference values of RfD are given in Table 1.

$$HQ = \frac{ADD}{RfD} \quad (4)$$

The  $HQ < 1$  indicates no adverse health effects, while the  $HQ > 1$  implies the potential adverse effects on human health [25].

The HI is the composed toxic effects of the heavy metal combination, which can be calculated based on the Eq. (5).

$$HI = \sum HQ_i = \sum \frac{ADD_i}{RfD_i} \quad (5)$$

The  $HI < 1$  implies heavy metals with toxic influence on human health, while the  $HI > 1$  means a risk of negative health impacts, which increases by increasing the HI values [26].

The CR is defined as probability of a specific cancer development during a lifetime because of exposure to the carcinogen [24]. The CR can be calculated as Eq. (6)

$$CR = ADD \times SF \quad (6)$$

Where, the SF is defined as slope factor and the ADD defined as probability of developing cancer per unit exposure level of mg/kg/day; the SF values are given in Table 1. It should be noted that the acceptable CR value is in the range of  $10^{-4}$  to  $10^{-6}$  and the  $CR < 10^{-6}$  implies negligible risk of cancer, while the  $CR < 10^{-4}$  means high risk of cancer [27].

### 3. RESULTS AND DISCUSSION

#### 3-1- Distribution of metals in water

The mean and standard deviation of concentration for

eleven individual heavy metals in Jajrood River for four seasons are represented in Table 2. The mean concentration of Cr, Co, Cd, Pb, Cu, Zn, Al, Mn, Sn, Se and Ba during the total

period of monitoring was found to be 4.34, 1.20, 0.265, 9.06, 2.33, 12.34, 493.53, 56.73, 0.40, 0.17, 65.66 µg/L, respectively. The concentrations of studied heavy metals, except for

**Table 2. Heavy metal concentrations (ug/L) at sampling stations along Jajrood River from March 2016 to February 2017.**

Heavy Metals	Spring (March to May) 2016									
	Station #									
	1	2	3	4	5	6	7	8	Total Mean	SD
Cr	3.48	2.39	1.79	3.48	5.08	2.08	1.57	3.12	2.87	1.16
Co	1	0.67	0.93	0.86	0.67	1.61	1.5	1.77	1.12	0.44
Cd	0.07	0.07	0.06	0.06	0.07	0.06	0.06	0.07	0.07	0.01
Pb	11.21	7.34	8.33	11.86	9.61	10.61	7.93	3.11	8.75	2.79
Cu	2.29	3.44	2.67	0.86	3.44	2.67	1.92	3.33	2.58	0.89
Zn	11.71	13.44	10.5	7	12	12.76	20.17	11.33	12.36	3.7
Al	275	1394	185	335	1863.33	768	1176	80	759.54	654.79
Mn	66	258.67	28.83	56.86	365.56	159.55	98.08	56.33	136.23	118.76
Sn	0.26	0.21	0.21	0.26	0.35	0.25	0.27	0.44	0.28	0.08
Se	0.2	0.25	0.1	0.2	0.24	0.04	0.07	0.4	0.19	0.12
Ba	75	66	40	55	73.33	66	72	40	60.92	14.33
Heavy Metals	Summer (Jun to August) 2016									
	Station #									
	1	2	3	4	5	6	7	8	Total Mean	SD
Cr	3.57	6.96	9.25	6.24	12.03	13.82	5.24	10.23	8.42	3.52
Co	1.82	0.67	2.88	0.37	0.86	1.1	0.45	2.31	1.31	0.92
Cd	0.57	0.33	0.75	0.57	0.71	0.26	0.27	0.35	0.48	0.2
Pb	11.58	11.39	9.63	6.58	8.03	9.65	10.12	7.83	9.35	1.76
Cu	2.86	3.44	2.88	1.43	2.14	1.81	0.82	1.13	2.06	0.93
Zn	11	12.44	9.25	8.29	10.57	7.67	10.73	6.75	9.59	1.93
Al	190	6473.33	30	105	725	372.86	57.5	45	999.84	2224.05
Mn	35.43	215.78	9.25	10.86	30.71	20.76	29.45	16.5	46.09	69.22
Sn	0.6	0.28	0.32	0.3	0.73	0.31	0.19	0.3	0.38	0.18
Se	0.1	0.06	0.13	0.08	0.13	0.18	0.32	0.23	0.15	0.09
Ba	75	136.67	40	60	50	51.43	45	45	62.89	31.76
Heavy Metals	Autumn (September to November) 2016									
	Station #									
	1	2	3	4	5	6	7	8	Total Mean	SD
Cr	1.78	1.66	2.77	3.93	7.88	4.29	6.7	2.25	3.91	2.31
Co	0.17	1.39	0.06	0.67	0.9	1	0.24	1.28	0.71	0.51
Cd	0.21	0.26	0.24	0.22	0.18	0.24	0.26	0.23	0.23	0.03
Pb	10.69	8.83	9.42	9.69	12.31	7.63	7.52	5.05	8.89	2.21
Cu	1.56	1.55	3	1	2.3	2.45	2.62	4.5	2.37	1.08
Zn	12	11.09	8.22	12.67	15.4	12.72	20.85	27.25	15.03	6.16
Al	186.67	144	63.33	33.33	116.67	142.45	106.5	87.5	110.06	48.85
Mn	17.44	8.91	6.11	4.11	17.7	16.76	22.69	30.25	15.5	8.79
Sn	0.06	0.13	0.05	0.05	0.13	0.31	0.24	0.27	0.15	0.1
Se	0.25	0.15	0.27	0.2	0.25	0.24	0.13	0.27	0.22	0.05
Ba	70	82	43.33	40	126.67	98.18	80	110	81.27	30.34
Heavy Metals	Winter (December 2016 to February 2017)									
	Station #									
	1	2	3	4	5	6	7	8	Total Mean	SD
Cr	1.42	3.23	2.04	3.2	1.61	2.33	2.31	1.01	2.14	0.8
Co	2.14	1.09	1.63	1.86	2.4	1.76	0.85	1.42	1.64	0.52
Cd	0.29	0.31	0.25	0.31	0.4	0.28	0.16	0.22	0.28	0.07
Pb	8.35	7.02	6.71	10.66	8.96	8.48	11.19	12.6	9.25	2.07
Cu	1.71	1.64	3.13	0.86	3.4	2.97	1.62	3	2.29	0.94
Zn	8.71	10.27	9.88	11.71	19.4	9	22.54	7.5	12.38	5.51
Al	116.67	42.5	25	26.67	86.67	278	122	140	104.69	83.12
Mn	47.71	13.82	5.38	4	25.3	40.38	54.08	42	29.08	19.66
Sn	0.27	1.24	1.76	0.25	0.7	0.62	0.34	0.95	0.77	0.53
Se	0.1	0.06	0.14	0.17	0.08	0.07	0.35	0.05	0.13	0.1
Ba	53.33	65	35	36.67	63.33	75	72	60	57.54	14.98

Al, are lower than levels determined by the drinking water guidelines (including [22] and [27] standards for water quality). Furthermore, the concentrations of Cr and Cu (which are considered as priority toxic pollutants for aquatic

life protection [27]) are less than the Criterion Continuous Concentration (CCC) and the Criterion Maximum Concentration (CMC) values [27].

Additionally, Fig.2 depicts spatial and temporal variations

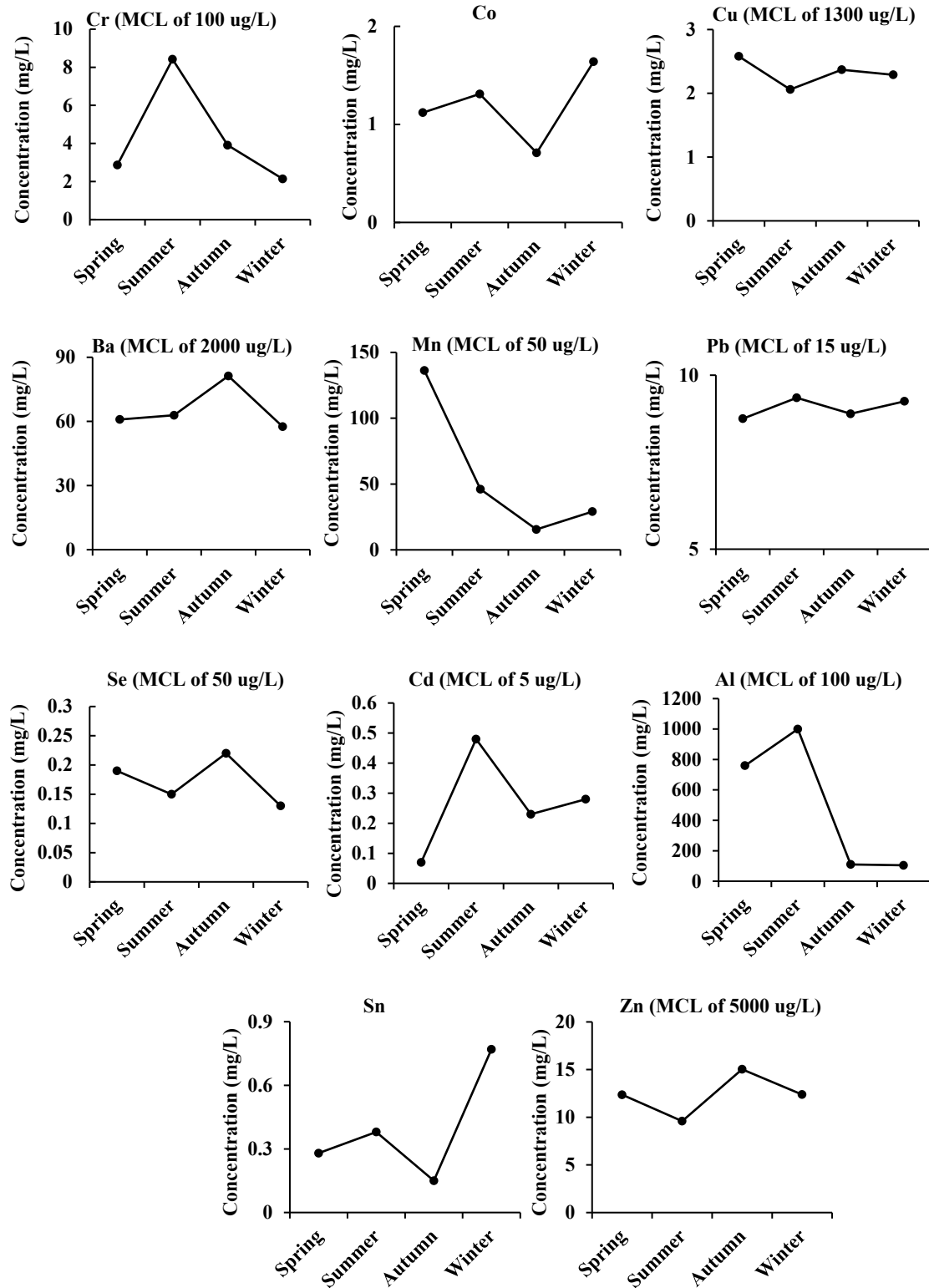


Fig. 2. Temporal variations of heavy metal concentration based on mean values in all sampling stations

**Table 3. Comparison of results from similar studies**

Heavy Metal	Current study (mean value) (ug/L)	Ağca et al. 2014 (ug/L)	Bilgin and Konanç 2016 (ug/L)	Tiwari et al. 2015 (ug/L)	Giri and Singh 2014 (ug/L)
Cr	4.34	28.88	0.78	1.25	0.73
Co	1.20	12.62	3.04	-	0.36
Cd	0.265	10.87	0.827	-	-
Pb	9.06	-	8.9	-	-
Cu	2.33	17.95	117.97	2.25	8.26
Zn	12.34	16.17	92.4	7.6	6.56
Al	493.53	-	-	59.9	49.3
Mn	6.73	91.68	90.8	14.8	6.83
Sn	0.40	-	-	-	-
Se	0.17	-	-	0.44	2.53
Ba	65.66	-	-	63.35	42.9
Total	596.025	178.17	314.717	149.59	117.47

of heavy metal concentration along Jajrood River during the period of spring 2016 to winter 2017. It should be noted that in some samples, observed data are much less than allowable limits so the allowable limit graph is not being seen in those diagrams. Among the studied heavy metals, the Al has the highest mean concentration (0.49353 ppm). The allowable and desirable concentrations of Al, according to the Iranian standard for water quality [20], are 100 and 200 mcg/L, respectively. It can be seen that the concentration of Al in 6 (during spring) and 3 (during summer) of studied stations are 7.5954 and 9.9984 times more than allowable concentration, while concentration of Al in all studied stations was less than allowable concentration in fall. Generally, there was no significant changes in the overall seasonal concentrations of studied heavy metals (excluding Al), implying that the variation in concentrations was mostly caused by anthropogenic activities instead of natural processes [28, 8]. In addition, previous studies [28] reported the similar trend for seasonal changes in concentrations of heavy metals in Upper Han (China) Rivers [28].

The concentrations of studied heavy metals (excluding Al) were lower in the wet seasons in comparison to the dry seasons. The higher concentrations in the dry seasons can be related to severe anthropogenic activities [29] and higher temperature in the dry seasons, thereby leading to evaporation and consequently increasing the concentration of studied ions in sample solutions [30]. Furthermore, higher precipitation in the wet seasons can cause dispersion and dilution of studied heavy metals [31]. It should be noted that more than 80% of annual precipitation fall in the wet seasons in studied area, which subsequently causes dilution the river pollutants [8].

Among the studied heavy metals, the Sn had the highest seasonal fluctuation (with a maximum of 413.3% seasonal changes in concentration), while the Cu has the lowest seasonal fluctuation (with a maximum of 3.37% seasonal changes in concentration). The seasonal fluctuation of all the others (except Al) was in the range of 4% to 193.4%.

Moreover, the variation in concentrations of heavy metals over time was different such that the mean concentrations of

Co, Zn, Sn and Cd increase over time. In contrast, the mean concentrations of Cr, Cu, Se, Ba, Mg and Al generally increase with time.

The maximum concentration of total studied heavy metals was observed at the second station where two branches of the river joined (as shown in Fig.1). This can be attributed to the fact that the place has three recreational centres (winter sports complexes) due to appropriate climatic conditions and a special topography, which has led to the construction of many resorts and restaurants. As a result, this area became an attraction area for tourists. The unprocessed release of wastewater of these centres and the wastes of tourists into the rivers has increased the concentration of pollutants at this station.

Furthermore, the obtained results are compared to those in other rivers as presented in Table 3. In previous study by [32], all samples had higher Cd concentration than those recommended by [33] for drinking water. Almost 90% of samples had Co concentration higher than the allowable limit of Co content (10 ug/L) recommended by [34] and the mean Cr concentration is over than 20 ug/L (permissible limit of Cr set by [34]). All other heavy metals are under the permissible values. In the research by [35], all the heavy metal contaminations are in appropriate limit. In addition, Tiwari et al. [12] reported that the concentrations of Zn, Mn, Se, Al, Ba, Cu, and Cr are less than the desirable limits recommended for drinking water in either season. It should be noted that in the pre-monsoon season, the concentrations of heavy metal were higher, which can be related to the relatively higher evaporation in this season and also anthropogenic activities in summer.

### 3-2- Heavy metal pollution index

In order to evaluate the generic or comprehensive pollution status of the studied heavy metals, the HPI values were calculated; the derived results in all stations are shown Fig.3. It should be noted that detection limits would be used for the calculation of HPI values if the concentrations of heavy metals could not be detected. The highest heavy metal

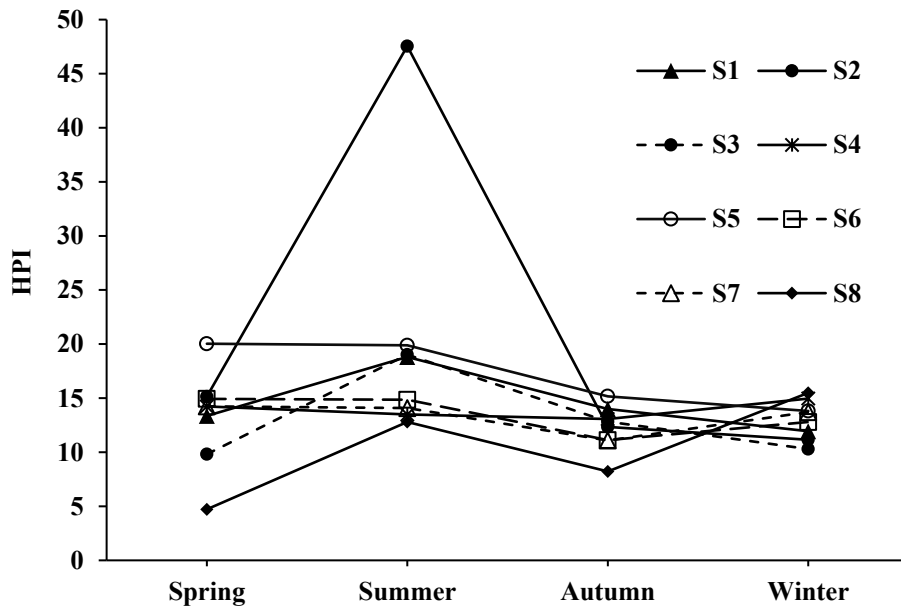


Fig. 3. Temporal variations of HPI value.

concentrations were observed in summer in comparison to the other seasons and, thereby the maximum HPI values (with a mean of 20.6) were obtained for this season. On the other hand, the minimum HPI values (with a mean of 12.23) were calculated for fall. The results reveal that the HPI values for studied heavy metals were mainly fluctuated from spring to fall and then these values were relatively constant in the mentioned period. Moreover, no significant seasonal variation in the HPI values was observed, which re-implies that the changes in HPI was mainly influenced by human activities [28].

The seasonal HPI values were less than critical value of 100 for all studied seasons, which implies that the pollution status of studied heavy metals was within the acceptable levels according to the Iranian drinking water standards [20]. The calculated HPI varied between 10.31 and 21.55. The minimum HPI value was obtained for last station that is the source of Jajrood River and the maximum value was calculated for second station that is under the influence of anthropogenic activities. Considering the classes of HPI defined by [36], excluding the stations 2 and 5 fallen into the medium class (HPI 15–30), the HPI values of all stations fall into the low class (HPI < 15). Calculated HPI value in the station 5 where is affected by industrial activities and urban or agricultural wastes, based on spring, summer and fall data drops into the medium class (HPI 15–30) and in winter falls into the low class (HPI < 15).

Taking into account that Jajrood River is considered as one of the main sources of drinking water for residents of Tehran, the concentrations of heavy metals in water is vital from the aspect of health risks. This matter is very important since most of drinking water treatment plants of Tehran use conventional methods for removal of heavy metals.

Along Jajrood River, agricultural activities are mainly the

irrigation of recreational gardening and crops. In addition, there are several villages and small towns with population of 200,000, and these towns and resorts near to the river discharge their wastewater into the river directly (it is estimated that rate of discharge is about 20 mcm/y); while there are not active wastewater treatment plants in mentioned area. It should be noted that the mentioned industrial discharges into Jajrood River can also observed along river [37]. Moreover, other factors such as population growth rate (6%), which is mainly as a result of booming residential development, large flux of residents of Tehran for six months in a year, and hydrologic regime of the related basin have influenced the quality of water in Jajrood River.

### 3-3- Human health risk assessment

The field survey in studied area indicated that the residents were mainly using stream water of Jajrood River for drinking and domestic purposes. Thereby, human health risk assessment was performed for estimating the health effects because of heavy metal exposure in stream water of Jajrood River.

### 3-4- Exposure assessment

The ADD values are presented in Fig.4. The trend for the mean ADD values was in the order of Al > Ba > Mn > Zn > Pb > Cr > Cu > Co > Sn > Cd > Se. The highest mean ADD values (41.361  $\mu\text{g}/\text{kg}\cdot\text{day}$ ) were obtained in summer while the lowest values (0.003  $\mu\text{g}/\text{kg}\cdot\text{day}$ ) in spring.

The ADD values are also compared to findings of Boateng et al. [38], who carried out a research on risk assessment of heavy metals (including Mn, Pb, Fe, Cd, Cu and Zn) in Ejisu-Juaben Municipality, Ghana. According to their results, the ADD values varied from  $2.45 \times 10^{-5}$  to  $8.04 \times 10^{-2}$  mg/kg/day for Fe,  $6.12 \times 10^{-5}$  to  $2.00 \times 10^{-4}$  mg/kg/day for Mn,  $3.67 \times$



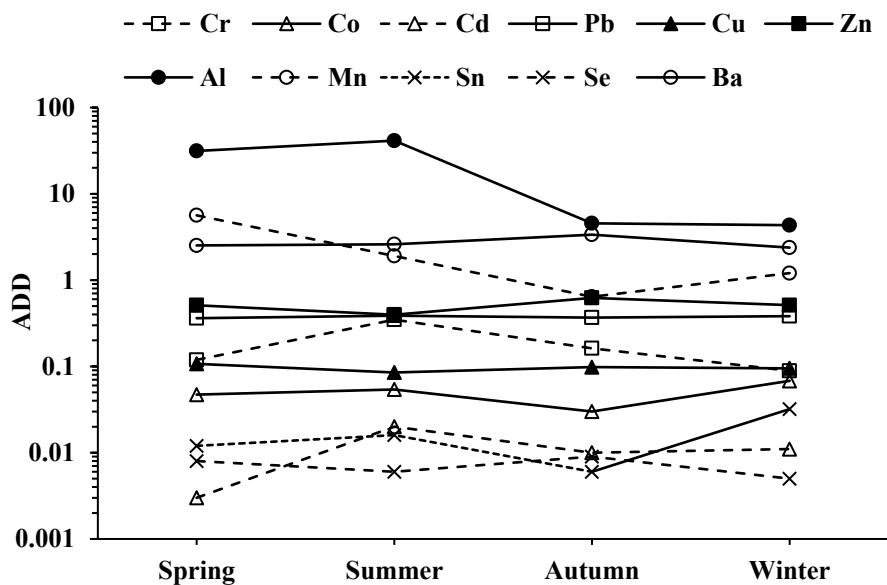


Fig. 4. Temporal variations of Average daily dose (ADD).

$10^{-5}$  to  $2.00 \times 10^{-4}$  mg/kg/day for Cu,  $2.45 \times 10^{-5}$  to  $6.00 \times 10^{-4}$  mg/kg/day for Zn,  $1.22 \times 10^{-5}$  to  $5.00 \times 10^{-4}$  mg/kg/day for Pb, and  $1.22 \times 10^{-5}$  to  $2.45 \times 10^{-5}$  mg/kg/day for Cd [38] which are lower than those found in the current research.

### 3-5- Carcinogenic risk

In the current research, only the carcinogenic risk of Cr was estimated because the SF values are unavailable for the other studied heavy metals. The CR was  $5.3 \times 10^{-5}$ ,  $7.36 \times 10^{-5}$ ,  $8.2 \times 10^{-5}$ ,  $8.71 \times 10^{-5}$ ,  $1.38 \times 10^{-4}$ ,  $1.16 \times 10^{-4}$ ,  $8.18 \times 10^{-5}$ ,  $8.58 \times 10^{-5}$  for stations 1 to 8, respectively. Moreover, the CR of Cr was  $5.94 \times 10^{-5}$ ,  $1.74 \times 10^{-4}$ ,  $8.08 \times 10^{-5}$  and  $4.43 \times 10^{-5}$ , in spring, summer, fall, and winter, respectively, which are in the acceptable risk limit (a range of  $10^{-6}$  to  $10^{-4}$ ).

The highest CR value was obtained for the station 5, which can be attributed to industrial activities. The industries can produce toxic compounds legally or illegally (which can be the main product or by-product during production process or waste that should be dump) that finally can transfer to land or bodies of water. The toxicity of these compounds depends on different parameters, such as route of exposure, dose, and chemical formulation, as well as gender, age, genetics, and nutritional condition of exposed individuals. In addition, Cd, Cr and Pb have high degree of toxicity and because of their damage to multiple organs, even at lower degree of exposure, they are also categorized as human carcinogens according to the International Agency for Research on Cancer [39].

Wu et al. [40] carried out a risk assessment for 19 elements of water samples from the Yangtze River in China. With regard to the calculated risk of Cd that ranged from  $7.13 \times 10^{-6}$  to  $1.01 \times 10^{-5}$  and three order higher risk of As, their results indicated that the As and Cd in Yangtze River pose potential health risk to the residents [40].

Liand Zhang [28] performed a risk assessment study in the upper Han River, China for 11 heavy metals in a period of 2005 to 2006. According to their study, in the rainy season carcinogenic risk of As exceeded the target risk of  $1 \times 10^{-4}$ , implying that the water consumption can result in increasing the risk of cancer over a long life time [28].

### 3-6- Hazard Quotient (HQ) indices

The HQ indices of studied heavy metals are shown in Fig.5. It should be noted that the concentration of all studied heavy metals, excluding Al, was less than the allowable concentration determined by the Iranian standard for water quality [20], while the HQ values of all studied heavy metals, including Al, was acceptable (less than 1). The highest HQ value (with a mean of 0.04373) was obtained for the station 5, which is attributed to industrial activities.

The impacts of industrial pollution are far reaching and can influence the ecosystem for a long period. Moreover, related cleanup procedure to industrial pollution is a complicated process and sometimes the complete cleanup is impossible. In the studied area, most industries require large amounts of water for their production process. When involved in a series of processes, the water is exposed to heavy metals, harmful chemicals, radioactive waste and even organic sludge. Sometimes, the water stores the toxic substance in unsafe locations instead. Whatever the reason, in the absence of appropriate water treatment plants, eventually the substance makes its way into either surface or groundwater. Therefore, Jajrood River is contaminated by heavy metals, which extremely influences on the health of ecosystem. The water of Jajrood River can be also used for irrigation purpose that finally affects the quality of food.

Moreover, the highest HQ value (0.046821) was obtained

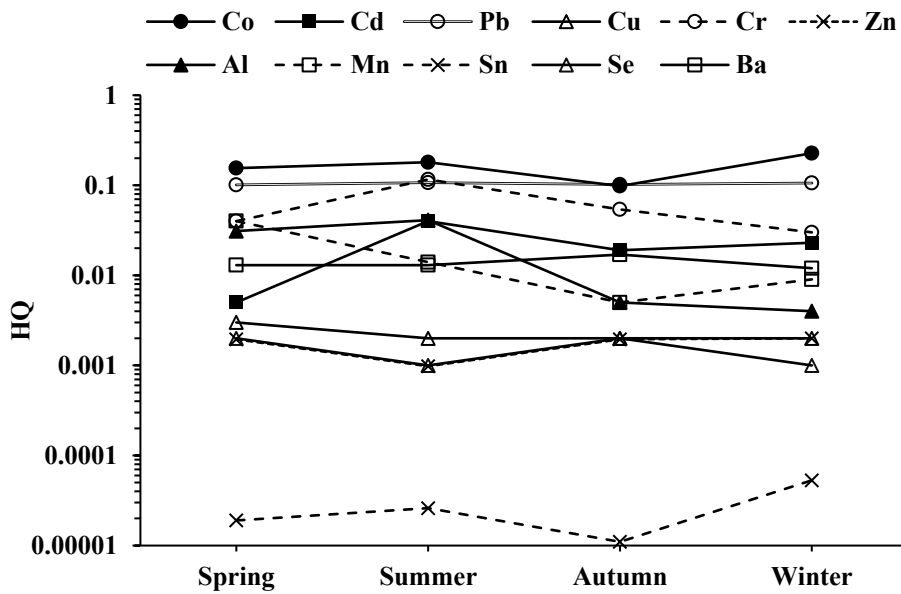


Fig. 5. Temporal variations of Hazard quotient (HQ)

in summer, while the lowest value (0.027819) was found in fall. Similarly, Li et al. [28] reported a difference in the HQ values in different seasons. Furthermore, in a research by Wu et al. [40], their results indicated that  $HQ_{\text{ingestion}}$  (HQ related to the ingestion) of all studied elements were smaller than 1, which is similar to the findings of the current research.

The results indicated that the calculated HI was less than 1 for studied heavy metals in all stations (0.395, 0.443, 0.389, 0.348, 0.432, 0.441, 0.331, 0.426 for stations 1 to 8, respectively). The seasonal HI was in the order of summer (0.516) > winter (0.415) > spring (0.391) > fall (0.306), which implies relatively low human health risk.

#### 4. CONCLUSION

The current research assessed the heavy metal concentrations in Jajrood River, as one of the main sources of drinking water of Tehran in Iran. The water samples were collected from eight stations located along the Jajrood River and then the concentrations of 11 different heavy metals (Cr, Co, Cd, Pb, Cu, Zn, Al, Mn, Sn, Se and Ba) were analysed. The Al had the highest mean concentration (0.49353 ppm), which is more than allowable limit determined by Iranian standard. Moreover, the data analysis results showed that the Al concentrations in spring and summer were 7 to 9 times more than allowable limits in some stations; however, the Al concentrations in fall were observed to be less than allowable limit. Moreover, the HPI values were determined to evaluate the generic status pollution caused by heavy metal in Jajrood River. The derived results for four seasons in all stations revealed that the HPI values range between 10.31 and 21.55. The lowest HPI value was obtained for the last station as the origin of Jajrood River and the maximum value was associated with the second station, which is impacted by anthropogenic activities. Based on the HPI values, the stations 2 and 5 fall into the medium class (HPI 15–30) and all other stations into

the low class (HPI < 15). Additionally, the ADD values of heavy metals were determined to exposure assessment of each identified heavy metal. The trends of the mean ADD values for the heavy metals were in the order of Al > Ba > Mn > Zn > Pb > Cr > Cu > Co > Sn > Cd > Se. The highest mean ADD value (41.361  $\mu\text{g}/\text{kg}\text{-day}$ ) was obtained for summer, while the lowest value (0.003  $\mu\text{g}/\text{kg}\text{-day}$ ) for spring. The data analysis results demonstrated that the HQ values of all studied heavy metals, including Al, were below allowable limit (less than 1). The stations in proximity of industrial station were observed to have higher HQ value. As an example, Station 5 where is affected by industrial activities had the highest HQ value (0.04373 on average). Overall, based on data analysis results, it can be concluded that the concentration of Al is higher than allowable limits in some seasons and some stations. Hence, further attention should be paid to identify the source of Al pollution in Jajrood River. Other heavy metals mainly had lower concentrations than allowable limit of USEPA and Iranian standard. However, in order to prevent water pollution caused by these heavy metals in the future, it is recommended that the water quality indexes of Jajrood River should be monitored by collecting samples regularly.

#### NOMENCLATURE

$W_i$	Unit weight of the $i^{\text{th}}$ parameter
$Q_i$	Sub-index of the $i^{\text{th}}$ parameter
$S_i$	Maximum allowable concentration of the $i^{\text{th}}$ parameter in drinking water when other parameters are absent
HQ	Hazard Quotient
HPI	Rating approach that shows the overall quality of water with respect to combined influence of each specific heavy metal
$M_i$	Monitored value of heavy metal (of $i^{\text{th}}$ parameter)

$I_i$	Maximum desirable value for drinking water of the $i^{\text{th}}$ parameter (ideal value)
C	Concentration of the contaminant (mg/l)
IR	Ingestion Rate per unit time (L/day) with reference value of 2.881 L/day
ED	Exposure Duration (years) with reference value of 70 years
BW	Body Weight ( $\mu\text{g/L}$ ) with reference value of 65 $\mu\text{g/L}$
AT	Average Time (years) with reference value of 75 years
ADD	Exposure assessment of identified heavy metal compound
RfD	Reference Dose (RfD) of specific heavy metal compound
CR	Probability of a specific developing cancer during a lifetime because of exposure to the carcinogen
SF	probability of developing cancer per unit exposure level of mg/kg/day

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**HOW TO CITE THIS ARTICLE**

A. Khoshand, S. Kanani, N. Emaminejad, Gh. Rostami, K. Rahimi, *Evaluation of heavy metal contamination and associated health risk assessment in water body of the Jajrood River, Iran, AUT J. Civil Eng., 4(2) (2020) 209-220.*

DOI: [10.22060/ajce.2019.16099.5566](https://doi.org/10.22060/ajce.2019.16099.5566)

