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Study of Seasonal Qualitative Changes in Tehran Surface Waters and Pollution of Heavy Metals (Pb, Cd and Ni) in Use for Irrigation (Case Study: The Main Watercourses in Tehran)

[1]Keyvan Jabbarzadeh, [2]Akbar Baghvand and [3]Ali Vosoogh
[1]Department of Civil Engineering, Environmental Engineering,
[2]Department of Environment, Faculty of Environment, University of Tehran, Tehran, Iran
[3]Department of Hydraulics and Environment, Faculty of Civil Engineering,
Iran University of Science and Technology, Tehran, Iran

Abstract: Reuse of water in arid and semi-arid areas is unavoidable. Considerable amounts of wastewater, lack of good quality water for irrigation and require more agricultural products demands are the main causes of using unusual water. In some parts of South Tehran in the area of several acres of irrigated agricultural region of South Tehran on water from wastewater treatment plants is used for irrigation. The anomalous application and mismanagement of the water resources can cause environmental problems and affect soil and water resources. Heavy metals in the water can be a factor limiting the use of these waters. In this paper study 16 water samples were taken from Kan and Sorkhehesar Water courses and the result showed that the amount of lead in old road stations in 23 July to 22 August and 23 October to 21 November was 0.3 mg L^{-1} higher than Canada, China, Taiwan and Saudi Arabia standards. Also, in Saveh highway this value was 0.5 mg L^{-1} in 23 July to 22 August and 0.4 in 23 October to 21 November was higher than Canada, China, Taiwan and Saudi Arabia standards. Cadmium was 0.02 mg L^{-1} higher than Canada, the US, Iran, Tunisia and Australia and FAO standards. It is recommended that in order to educate the citizens the responsibilities of state and municipal institutions be separated in the field of implemented management strategies. Also, agencies carry out their duties regarding the creation of appropriate structures, preparation and execution of the program and the separation of pollutants from the source more carefully and with caring.

Key words: Heavy metals, surface runoff, sewage, irrigation standards, agricultural

INTRODUCTION

The use of wastewater for agricultural production is widespread in many parts of the world. This irrigation source although, increases agricultural production also have health and environmental hazards. Therefore, most countries have limited use of sewage and municipal wastewater in agricultural products. Sewage is a rich source of macronutrients and micronutrients required by the plant. The amount of organic matter, nitrogen and phosphorus in sewage sludge is five, three and three times of that of the manure. Additionally, the wastewater contains heavy metals enter into agricultural land and will remain there in the soil for many years.

The metallic elements with high atomic weights, some are necessary for living organisms in a small amount but their increase leads to toxicity in plants, animals and humans. The ability to absorb, transfer and accumulation of heavy metals in the upper parts of plants according to the genetic characteristics, the amount of element in the soil and etc., varies and is expressed as transmission coefficient. Runoffs have been identified as the number one into surface water contamination.

MATERIALS AND METHODS

Scope of the study: Tehran is located at the Southern slopes of the Alborz mountains in the central part of Iran between 35° 34, 35°-50 the Northern latitude and 37 51°, 08-51° Eastern longitude. Its North, Center and South elevations are 1700, 1200 and 1,100 m, respectively. Tehran's climate is generally warm and dry. Average air temperature is 18°C with a maximum of 38.7°C and a minimum of 7.4°C and annual precipitation is 245-316 mm. The city covers an area of about 664 km^2 with twenty-two urban areas. According to the last census in 2006, Tehran population is about 12.3 million people where an average of 12,350 people lives per square kilometer (ANZECC, 1992) (Fig. 1-2 and Table 1).

Sampling and testing: In this study, preliminary investigations carried out in Tehran watercourses and

Corresponding Author: Keyvan Jabbarzadeh, Department of Civil Engineering, Environmental Engineering, Faculty of Environment, University of Tehran, Tehran, Iran

Fig. 1: Tehran location, Iran

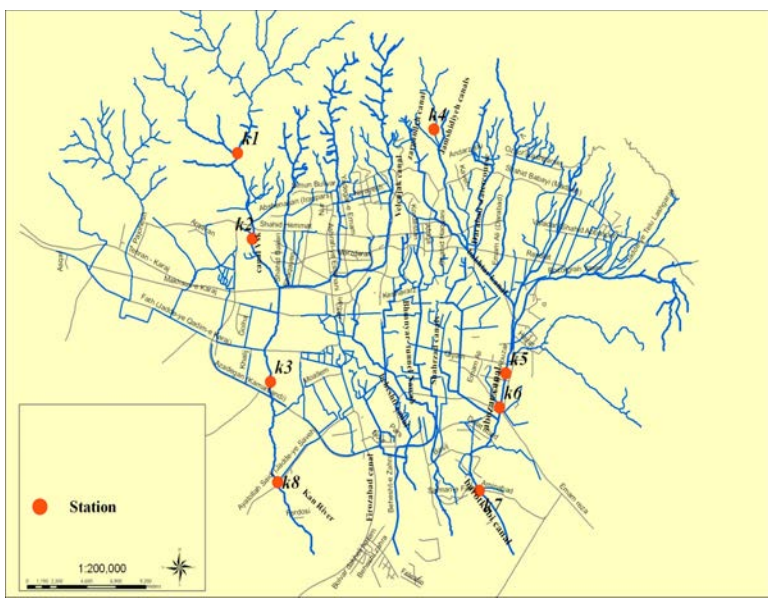


Fig. 2: The location of water samples collection from the study area

Table 1: Geographical coordinates of the sampling stations

Station No.	Geographic coordinate X	Geographic coordinate Y	Station No.	Geographic coordinate X	Geographic coordinate Y
1	51.236	35.875	5	51.482	35.645
2	51.270	35.825	6	51.490	35.633
3	51.278	35.825	7	51.470	35.617
4	51.430	35.808	8	51.280	35.830

samples were collected and analyzed from different parts of it during 23 July to 22 August and 23 October to 21 November, 2013. The 16 samples were collected in 150 mL polyethylene containers water samples containers which were made of polyethylene were washed using powder detergent and were kept in 5% Nitric acid pickling for a specific time period to probable contaminants be washed away. Then, rinsed with 3 times distilled water and then dried and the lids were closed.

The US Environmental Protection Agency guidelines was used for suitable storage and transport of water samples. According to the guidelines and based on objective parameters one storing procedure should have been selected. Given that the purpose was to evaluate and measure heavy metalls of Pb, Ni and Cd in surface water, the sample pH, value should be <2 using concentrated Nitric acid. The samples will then be stored up to 28 days and at the end the digestion is done as follows:

- First we transfer 100 mL as the representative agent (control) liquid to beaker and well mix it and add 3 mL of Nitric acid to and then we cover it with a watch glass or similar object. We place beaker on the heater or the like until sample volume is reached to 5 mL and reflux action is done
- Usually when the sample becomes bright and beaker is cool the digestion is complete; HCL ratio of 1:1 was added to the sample and was again placed on the heater for 15 min
- Beaker and its inside walls were washed with distilled water; the samples were filtered through Whatman to eliminate silicates and other metals that block device pipes. Filter and beaker were washed to eliminate all metals. Samples were prepared for analysis

Atomic absorption device model GBC 903 was used to measure the concentrations of lead, cadmium, nickel.

The global standard for agricultural irrigation: Table 2 shows Different Countries Standards For Agricultural Irrigation (First Consulting Engineers, 2007).

Statistical analysis

ANOVA: ANOVA Analysis of Variance test is a parametric test in which the variance of more than two populations is discussed. ANOVA is used when we are dealing with a case with various states to test hypotheses.

Table 2: Different countries standards for agricultural irrigation (First Consulting Engineers, 2007)

Parameters	Tunisia	Saudi Arabia	Hungary	Taiwan
Cadmium	0.01	0.005	0.02	0.01
Lead	1.00	0.100	1.00	0.10
Nickel	0.20	-	1.00	0.50

RESULTS AND DISCUSSION

The results of the measurement of the concentration of heavy metals such as lead, nickel and cadmium in sample water is shown in table. The table also shows the average concentration of heavy metals.

As observed, the amount of nickel is from 0.01-0.02 with a mean of 0.0125 in 23 July to 22 August and 0.0125 in 23 October to 21 November and accordingly, the amount of cadmium is 0.02 and 0.04 mg L^{-1}. Table 2 shows that the amount of lead is 0.01-0.5 ppm with a mean of 0.1375 in 23 July to 22 August and 0.1063 in 23 October to 21 November. Table 3 shows the results of the concentration of heavy metals:

- K1: Sangan waterfall
- K2: Kan River
- K3: old road
- K4: Tajrish Bridge
- K5: Abozar Canal
- K6: Afsariye three ways
- K7: Barot Kubi Canal
- K8: Saveh highway

According to the Tunisia standard that is 0.01 mg L^{-1} (First Consulting Engineers, 2007), the pollution in this element is seen in two watercourses. Given the above considerations and the concentration of this element in the table it is observed that the concentration of this element in most stations is 0.02 mg L^{-1}.

The maximum allowable concentration of lead in the water for agricultural irrigation is 0.1 mg L^{-1} according to Taiwan and Saudi Arabia standard and 1 mg L^{-1} according to Tunisia and Hungary 1 (First Consulting Engineers, 2007), respectively.

Based on this research, lead concentration at stations 3 and 8 in Kan watercourse is higher than Taiwan and Saudi Arabia standards and also table shows that the amount of lead element in Sorkhehesar River watercourse from upstream to downstream is increasing. The region has a higher lead dispersion, since a large amount of lead pollution occurs through the air.

Table 3: The results of the concentration of heavy metals

Station	23 October to 21 November			23 July to 22 August		
(mg/L)	Cadmium	Nickel	Lead	Cadmium	Nickel	Lead
1	0.02	-	0.01	0.02	-	0.01
2	0.02	-	0.01	0.02	-	0.01
3	0.04	0.02	0.03	0.30	0.02	0.03
4	0.02	0.01	0.02	0.02	0.01	0.02
5	0.02	0.01	0.04	0.02	0.01	0.03
6	0.03	0.02	0.05	0.03	0.02	0.03
7	0.02	0.02	0.07	0.02	0.01	0.05
8	0.04	0.02	0.50	0.03	0.02	0.04

Nickel standard is 0.2 in Tunisia, 0.5 in Taiwan and 1 mg L^{-1} in Hungary (First Consulting Engineers, 2007), respectively. Based on the study results, the concentration of nickel was between 0.01-0.02 mg L^{-1}. According to the table, the highest concentrations go for lead while the lowest is in nickel. Also, we see that the mean concentration is higher in 23 July to 22 August compared to that of 23 October to 21 November.

Elements concentrations and their comparison with the standards

The concentration of cadmium: Table 2 presents the amount of cadmium in surface water samples from the Kan River and Sorkhehesar in 23 July to 22 August and 23 October to 21 November. Accordingly, the amount of cadmium is 0.02-0.04 mg L^{-1}.

It should be noted that the allowable level of this element in the water is 0.01 mg L^{-1} based on Taiwan and Tunisia standards and 0.02 and 0.005 mg L^{-1} (Table 3) based on Hungary and Saudi Arabia standards (First Consulting Engineers, 2007). The amount of cadmium in all sampling stations was measured more than the standard rate. Accordingly, we can say water samples are on undesirable situation from the perspective of cadmium contamination (Fig. 3-5).

The concentration of nickel: Table 2 presents the amount of nickel is 0.01-0.02 with the mean amount of 0.0125 in 23 July to 22 August and 0.01125 in 23 October to 21 November. Figure 5 shows the samples and standards in different countries. The allowable amount of this element in irrigation water is 0.2 ppm according to Tunisia standard and 0.5 ppm according to Taiwan standard (First Consulting Engineers, 2007). Given the results of water samples study, nickel is in good condition in terms of nickel contamination (Fig. 6-10).

The concentration of lead: Table 2 presents the amount of lead is 0.01-0.5 ppm with the mean amount of 0.1375 in 23

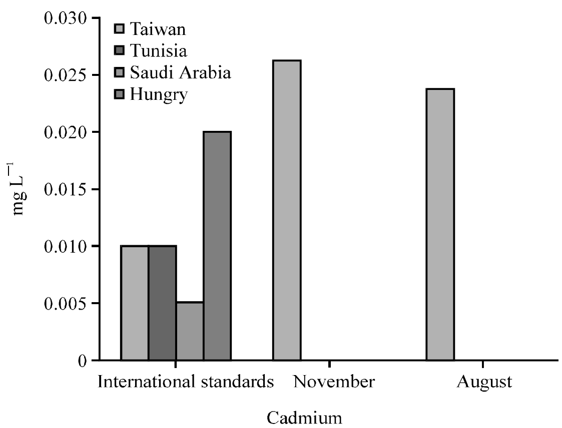


Fig. 3: Comparison of cadmium with international standards for irrigation

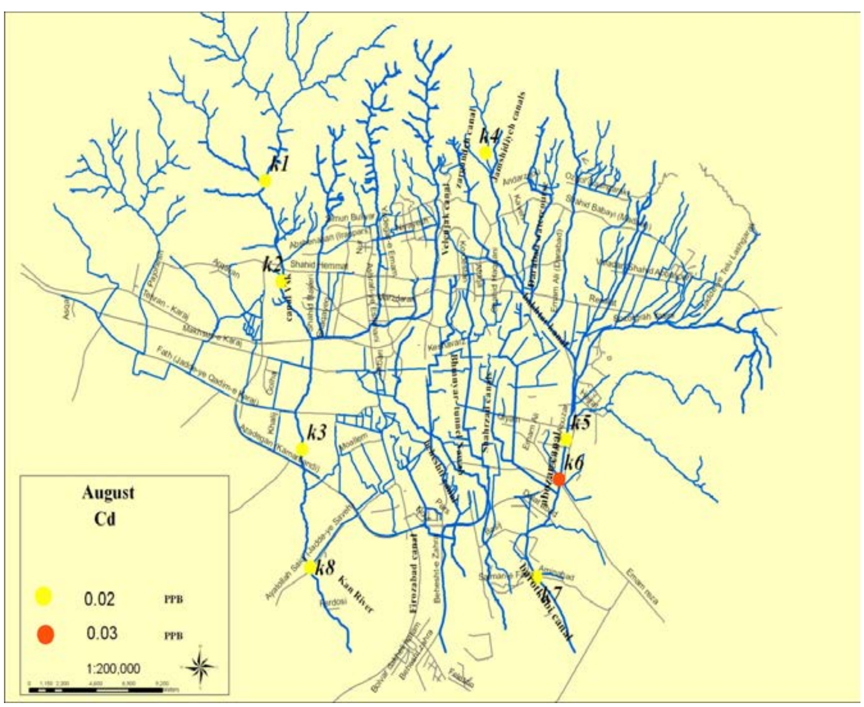


Fig. 4: Comparative map of the concentration of cadmium in the studied watercourse

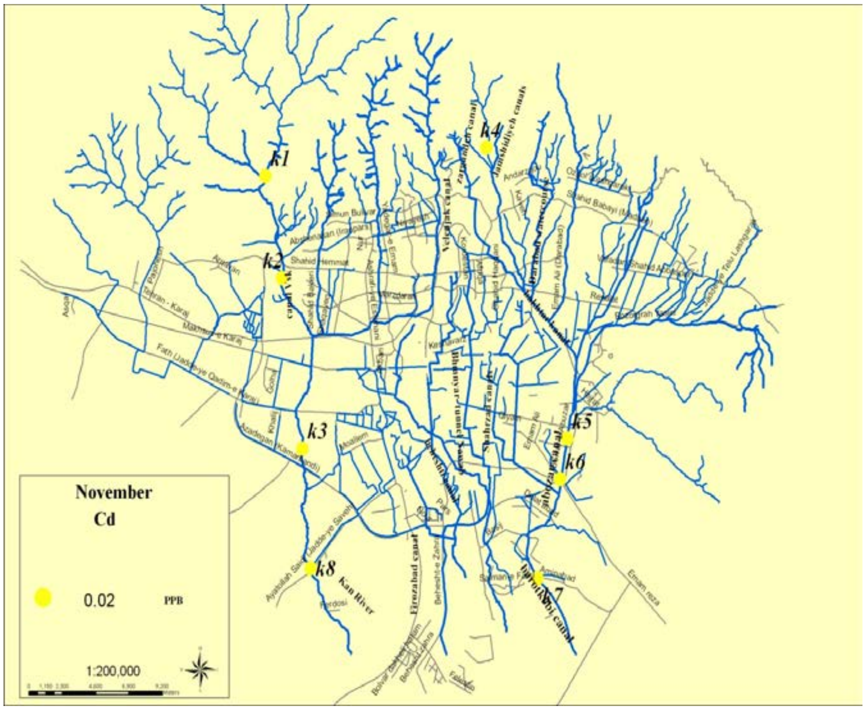


Fig. 5: Comparative map of the concentration of cadmium in the studied watercourse

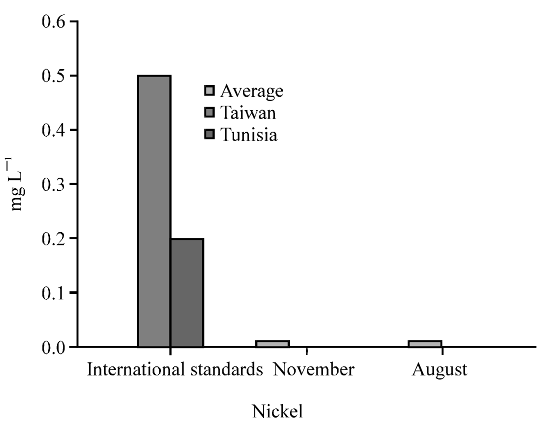


Fig. 6: Comparison of nickel with global standards for agricultural irrigation

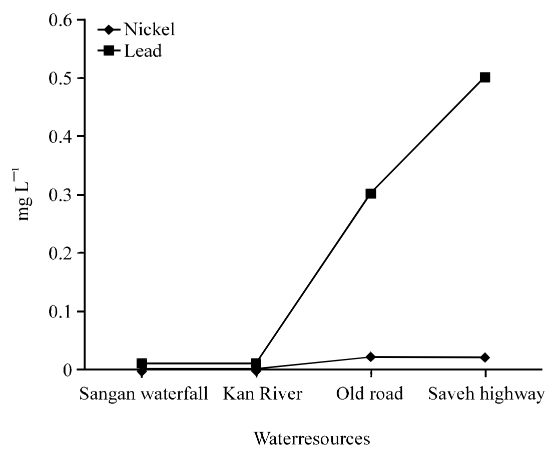


Fig. 7: Changes in Western watercourse in 23 July-22 August

July to 22 August and 0.1063 in 23 October to 21 November. The allowable amount of this element in irrigation water is 0.1 ppm according to Taiwan and Saudi Arabia standards and 1 mg L^{-1} according to Hungary and Tunisia standards (AWQG and ANZECC, 1992). Given the figure, the amount of lead is higher than Taiwan and Saudi Arabia standards. The maximum concentration of lead is observed in stations No. 3 and No. 8 and in my opinion the most likely is the cause of vehicles pollution in the region (Fig. 11-13).

ANOVA test: The study of significance relationship between elements in different stations in 23 July to 22 August and 23 October to 21 November using ANOVA (one-way) (Table 4).

According to the analysis of variance and Table 4 we can see that there is no significant difference between the mean of the elements in the various stations in 23 July to 22 August and 23 October to 21 November, $p<0.05$ (Table 5).

In Table 5 each of the elements in the 2 months of 23 July to 22 August and 23 October to 21 November are compared. According to the Table 5, the mean of all elements had dropped in all stations in 23 October to 21 November (the mean change in the amount of elements regardless of water station, just at two different times).

According to Table 6, the mean difference in the 2 months of 23 July-22 August and 23 October to 21 November are as follows:

- Cadmium: 0.0025
- Lead: 0.0312
- Nickel: 0.00125

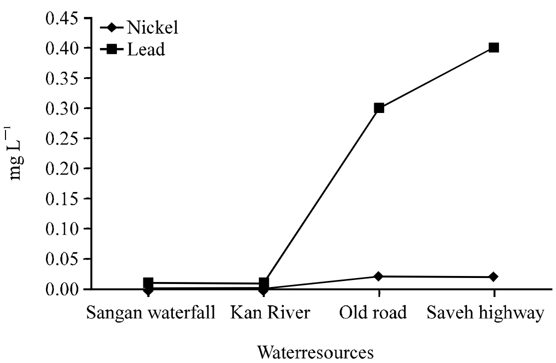


Fig. 8: Changes in Pb, Ni and Zn in Western watercourse in 23 October to 21 November

Table 4: ANOVA test study of significance relationship between elements

Elements	Sum of squares	Degree of freedom	Mean square	F-values	Significance level
pb					
Between groups	0.001	1.000	0.001	0.051	0.825
Within groups	0.389	14.000	0.028	-	-
Total	0.391	15.000	-	-	-
Cd					
Between groups	0.000	1.000	0.000	1.000	0.334
Within groups	0.000	14.000	0.000	-	-
Total	0.000	15.000	-	-	-
Ni					
Between groups	0.000	1.000	0.000	0.084	0.776
Within groups	0.001	14.000	0.000	-	-
Total	0.001	15.000	-	-	-

Table 5: The mean of elements

Group statistics

Groups	N	Mean	The mean standard deviation	Standard deviation error
Cd				
23 July to 22 August	8	0.0263	0.00354	0.00125
23 October to 21 November	8	0.0238	0.00000	0.00000
Ni				
23 July to 22 August	8	0.0125	0.00886	0.00313
23 October to 21 November	8	0.0113	0.00835	0.00295
Pb				
23 July to 22 August	8	0.1375	0.17912	0.06333
23 October to 21 November	8	0.1063	0.15334	0.05421

One-sample t-test

Cadmium: To show the proximity and significance of data by example means in Taiwan and Tunisia for Cadmium. According to Table 7, cadmium mean in water

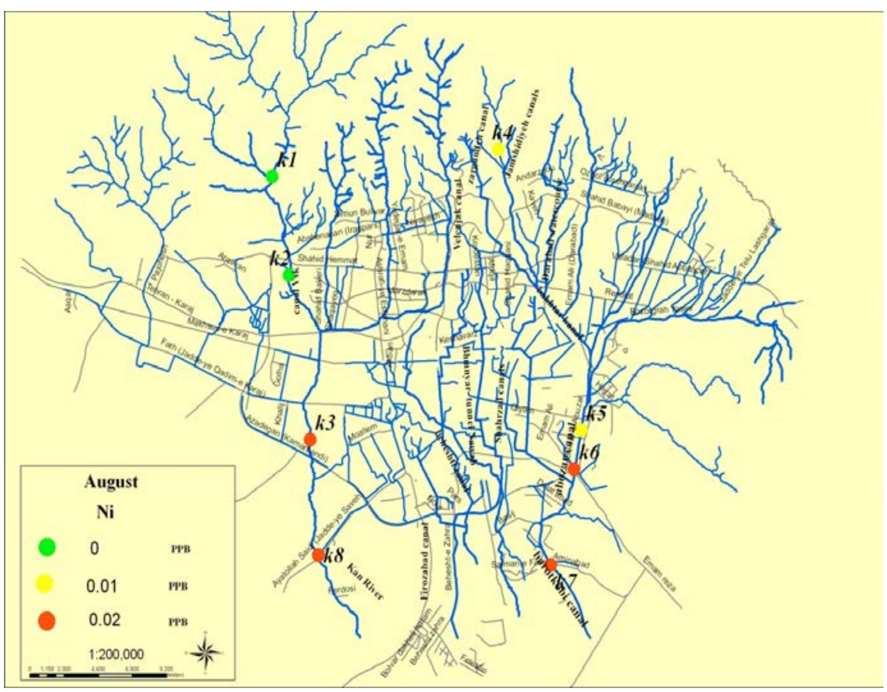


Fig. 9: Comparative map of the concentration of nickel in the studied watercourse

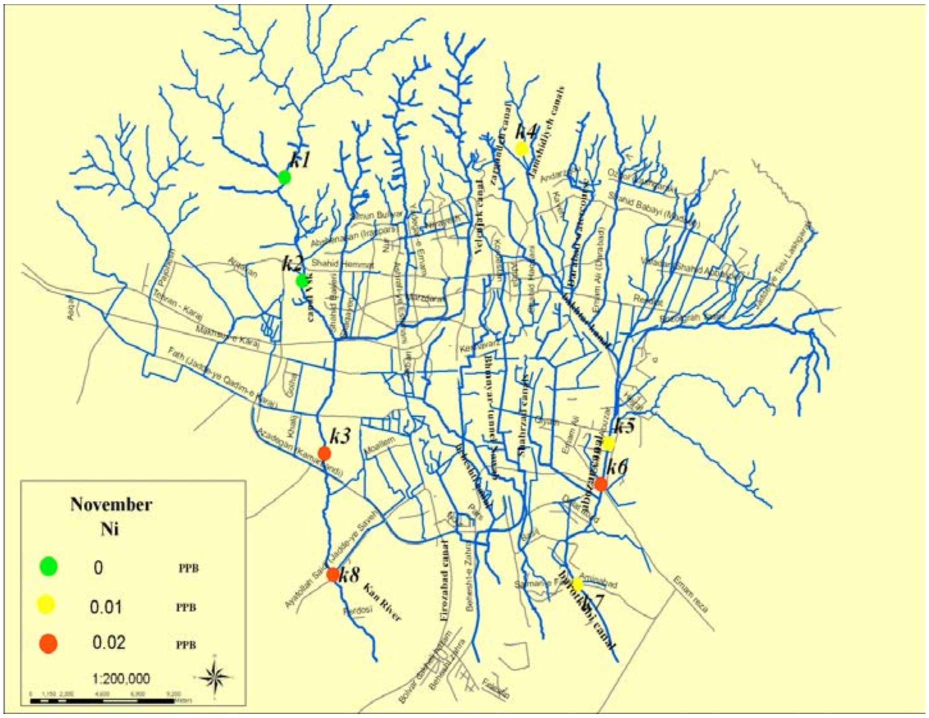


Fig. 10: Comparative map of the concentration of nickel in the studied watercourse

Table 6: t-test with two independent samples

	Independent samples test							95% confidence level	
Elements	F-values	Level of significance	t-values	Degrees of freedom	Level of significance	Mean difference	Standard deviation error difference	Low level	High level
Cd									
Similar variance	5.444	0.035	1.000	14	0.334	0.00250	0.00125	-0.00143	0.00393
Dissimilar variance	-	-	1.000	7	0.351	0.00250	0.00125	-0.00171	0.00421
Pb									
Similar variance	0.115	0.740	0.225	14	0.825	0.03120	0.08337	-0.16005	0.19755
Dissimilar variance	-	-	0.225	1.3675	0.825	0.03120	0.83370	-0.16045	0.19795
NNNi									
Similar variance	0.203	0.660	0.290	14	0.776	0.00125	0.00430	-0.00798	0.01048
Dissimilar variance	5.444	-	0.290	13.949	0.776	0.00125	0.00430	-0.00798	0.01048

Table 7: Cadmium mean in water samples at stations in 23 July to 22 August and 23 October 21 November

	One-sample statistics			
Element	N	Mean	The mean standard deviation	Standard deviation error
Cd	16	0.025	0.00250	0.00062

samples at stations in 23 July to 22 August and 23 October to 21 November is 0.025 that is 0.015 more than that of Taiwan and Tunisia standard.

With 95% confidence level and given the one-sample t-test (significance level = 0.000), we conclude that there is a significant difference between mean difference of cadmium in water samples and the mean concentration of cadmium in Taiwan and Tunisia standards. So, that with standard deviation of 0.00250 and degrees of freedom of 15 this difference is 0.015 (Table 8).

Table 8: Mean difference of cadmium in water samples and the mean concentration of cadmium in Taiwan and Tunisia standards

	One-sample test (the base value = 0.01)				95% confidence level	
Element	t-value	Degrees of freedom	Level of significance	Mean difference	Low level	High level
Cd	17	15	0.000	0.015	0.0093	0.0120

Table 9: The Mean cadmium in water samples in both 23 July to 22 August and 23 October to 21 November

	Sample statistics-one			
Element	N	Mean	The mean standard deviation	Standard deviation error
Cd	16	0.025	0.00250	0.00062

One-sample t-test to show the proximity and significance of data with the sample mean for the element cadmium in Saudi Arabia. According to Table 9, the mean cadmium in water samples in both 23 July to 22 August and 23 October to 21 November is about 0.025 that is 0.02 more than Saudi Arabia standard amount.

With 95% confidence level and given the one-sample t-test (significance level = 0.000), we conclude that there is a significant difference between mean difference of cadmium in water samples and the mean concentration of cadmium in Saudi Arabia standards. So, that with standard deviation of 0.00250 and degrees of freedom of 15 this difference is 0.02 (Table 10).

One-sample t-test to show the proximity and significance of data with the sample mean for the element cadmium in Hungary.

According to Table 9, the Mean cadmium in water samples in both 23 July to 22 August and 23 October to 21 November is about 0.025 that is 0.005 more than Hungary standard amount.

With 95% confidence level and given the one-sample t-test (significance level = 0.333), we conclude that there is no significant difference between mean difference of cadmium in water samples and the mean concentration of cadmium in Hungary (Table 11).

Table 10: Difference between mean difference of cadmium in water samples and the mean concentration of cadmium in Saudi Arabia standards

	One-sample test (the base value = 0.005)					
					95% confidence level	
Element	t-value	Degrees of freedom	Level of significance	Mean difference	Low level	High level
Cd	25	15	0.000	0.02	0.0143	0.0170

Lead: One-sample t-test to show the proximity and significance of data with the sample mean for the element lead in Taiwan and Saudi Arabia.

According to Table 12, the mean lead in water samples in both 23 July to 22 August and 23 October to 21 November is 0.1219 that is 0.0219 more than Taiwan and Saudi Arabia standard amount.

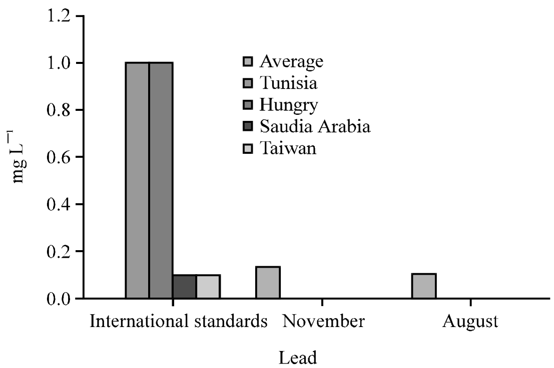


Fig. 11: The comparison of lead with international standards

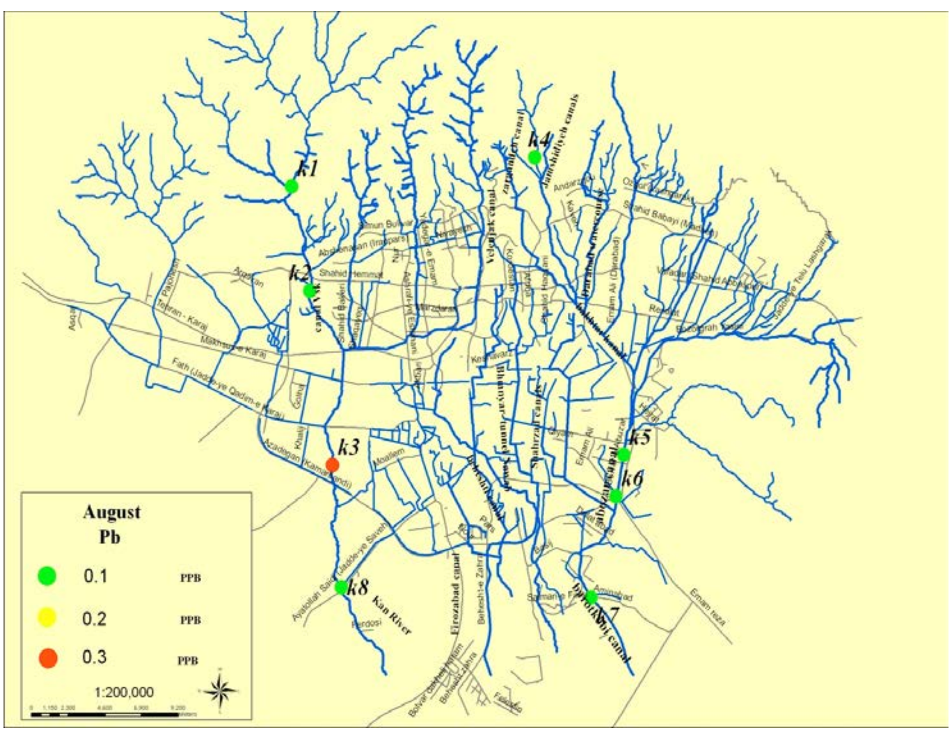


Fig. 12: Comparative map of the concentration of lead in the studied watercourse

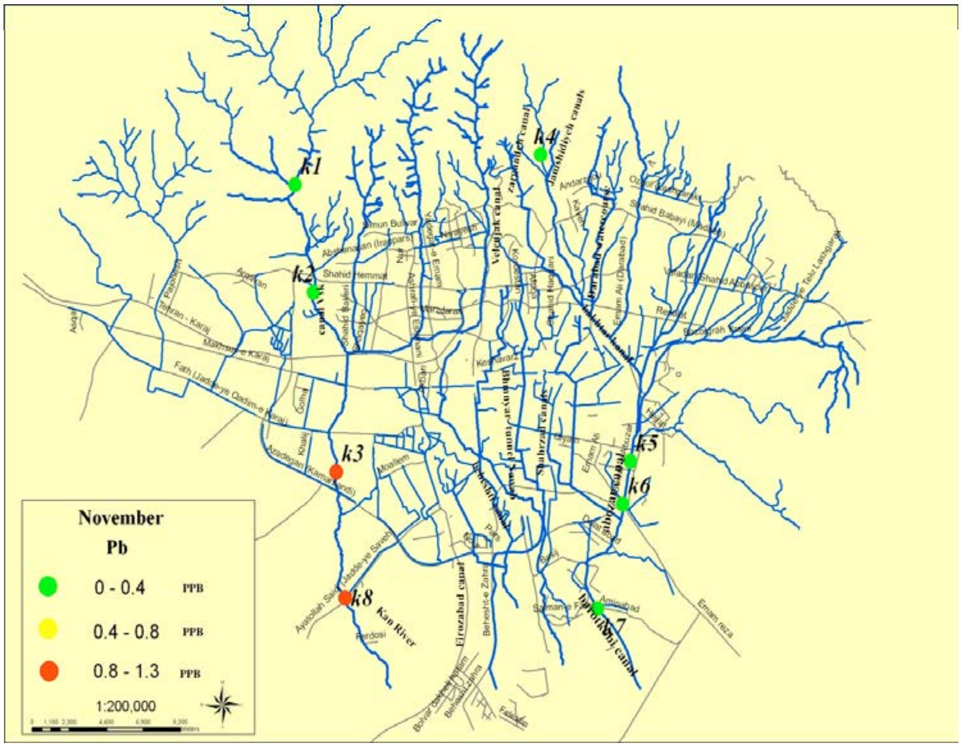


Fig. 13: Comparative map of the concentration of lead in the studied watercourse

Table 11: Mean difference of cadmium in water samples and the mean concentration of cadmium in Hungary

	One-sample test (the base value = 0.002)					
					95% confidence level	
Element	t-value	Degrees of freedom	Level of significance	Mean difference	Low level	High level
Cd	1	15	0.333	0.005	-0.0007	0.002

Table 12: The Mean cadmium in water samples in both 23 July to 22 August and 23 October to 21 November

	One-sample statistics			
Element	N	Mean	The mean standard deviation	Standard deviation error
Pb	16	0.1219	0.16137	0.04034

Table 13: Mean difference of lead in water samples and the mean concentration of lead in Taiwan and Saudi Arabia standards

	One-sample test (the base value = 0.1)					
					95% confidence level	
Element	t-value	Degree of freedom	Level of significance	Mean difference	Low level	High level
Pb	17	15	0.704	0.0219	-0.0704	0.1016

With 95% confidence level and given the one-sample t-test (significance level = 0.704), we conclude that there is no significant difference between mean difference of lead in water samples and the mean concentration of lead in Taiwan and Saudi Arabia standards. So, that with standard deviation of 0.11565 and degrees of freedom of 15 this difference is 0.01563 (Table 13).

Table 14: The mean lead in water samples in both 23 July to 22 August and 23 October to 21 November

	14 one-sample statistics			
Element	N	Mean	The mean standard deviation	Standard deviation error
Pb	16	0.1219	0.16137	0.04034

Table 15: Difference between mean difference of lead in water samples and the mean concentration of lead in Hungary and Tunisia standards

	One-sample test (the base value = 1)					
					95% confidence level	
Element	t-value	Degrees of freedom	Level of significance	Mean difference	Low level	High level
Pb	-21.922	15	0.000	-0.8781	-0.9704	-0.7984

One-sample t-test to show the proximity and significance of data with the sample mean for the element lead in Hungary and Tunisia.

According to Table 14, the mean lead in water samples in both 23 July to 22 August and 23 October to 21 November is 0.1219 that is 0.8781 more than Hungary and Tunisia standard amount.

With 95% confidence level and given the one-sample t-test (significance level = 0.000), we conclude that there is a significant difference between mean difference of lead in water samples and the mean concentration of lead in Hungary and Tunisia standards. So, that with standard deviation of 0.16137 and degrees of freedom of 15 this difference is 0.8781 (Table 15).

Table 16: The mean nickel in water samples in both 23 July to 22 August and 23 October to 21 November

	One-sample statistics			
Element	N	Mean	The mean standard deviation	Standard deviation error
Ni	16	0.0119	0.00834	0.00209

Table 17: Difference between mean difference of nickel in water samples and the mean concentration of lead in Tunisia standards

	One-sample test (the base value = 0.2)					
					95% confidence level	
Element	t-value	Degree of freedom	Level of significance	Mean difference	Low level	High level
Ni	-90.21	15	0.000	-0.48813	-0.1926	-0.01837

Table 18: Significant difference between mean difference of nickel in water samples and the mean concentration of lead in Taiwan standards

	One-sample test (the base value = 0.5)					
					95% confidence level	
Element	t-value	Degree of freedom	Level of significance	Mean difference	Low level	High level
Ni	-234.066	15	0.000	-0.48813	-0.4926	-0.4837

Nickel: One-sample t-test to show the proximity and significance of data with the sample mean for the element nickel in Tunisia.

According to Table 16, the mean nickel in water samples in both 23 July to 22 August and 23 October to 21 November is 0.0119 that is 0.18813 less than Tunisia standard amount.

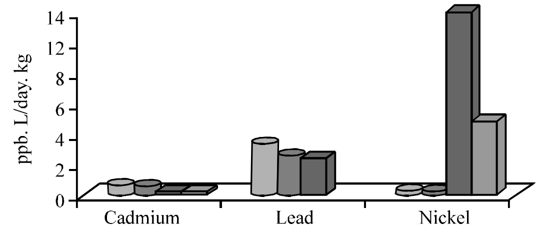
With 95% confidence level and given the one-sample t-test (significance level = 0.000), we conclude that there is a significant difference between mean difference of nickel in water samples and the mean concentration of lead in Tunisia standards. So, that with standard deviation of 0.00834 and degrees of freedom of 15 this difference is 0.18813.

One-sample t-test to show the proximity and significance of data with the sample mean for the element nickel in Taiwan.

According to Table 17, the mean nickel in water samples in both 23 July to 22 August and 23 October to 21 November is 0.03 that is 0.48813 less than Taiwan standard amount.

With 95% confidence level and given the one-sample t-test (significance level = 0.000), we conclude that there is a significant difference between mean difference of nickel in water samples and the mean concentration of lead in Taiwan standards. So, that with standard deviation of 0.00834 and degrees of freedom of 15 this difference is 0.48813 (Table 18).

The results of applying Acceptable Daily Intake (ADI): ADI index was calculated to determine the health risk of the consumers in water samples taking into consideration the considerable concentration of lead in water chain and



	Cadmium	Lead	Nickel
November	0.75	3.93	0.36
August	0.6785	3.036	0.33
Taiwan	0.285	2.86	14
Tunisia	0.285		5.7

Fig. 14: Pb, Ni and Cd ADI index chart

login lead to the consumer's body. Acceptable Daily Intake (ADI) Index is defined as follows in accordance with EPA guidelines and authoritative references:

$$ADI = \frac{C_s\ (ppb) \times \text{Drinking water volume}\ (L\ day^{-1})}{\text{Body weight (kg)}}$$

In the above equation, C_s is concentration of contaminant in drinking water. Also, to calculate the allowable amount of the above index the allowable standards can be used instead of C_s in equation. The term "drinking water volume" indicates the average amount water consumption of a person in liters of per a day. In the above equation, the term "body weight" is the average weight of a person in kilograms (Marcus, 1986; Sun *et al*., 2010). It should be noted that in some references, the average amount of water consumed per adult person is considered to be 2 L day^{-1} with this is 1 L day^{-1} for children. The average adult human and children weight are considered to be 70 and 10 kg, respectively (Fig. 14).

CONCLUSION

Generally, concentrations of heavy metals were higher in 23 July to 22 August than in 23 October to 21 November and Pb and Ni had a favorable situation while cadmium was higher than other countries standard. In order to prevent increasing the concentration of these elements and environmental pollution it is necessary to take serious measures in the treatment and transmission of floods through optimal channels while avoiding the use of untreated runoff in agricultural irrigation.

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