Assessment of Heavy Metals in Zohreh River, Iran

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Abstract

Zohreh River is one of the main water sources in south of Khuzestan, Iran. Due to importance of heavy metals on water quality, metal index (MI), pollution index (PI), heavy metal pollution index (HPI) and contamination index (Cd) were used to evaluate this river quality. For this purpose, water samples were collected during each season at 11 stations and seven heavy metals [mercury (Hg), cadmium (Cd), chromium (Cr), manganese (Mn), nickel (Ni), lead (Pb) and zinc (Zn)] were determined. In this study, standard values for each metal were extracted from international standards [United States Environmental Protection Agency (EPA) and World Health Organization (WHO)] and some national guidelines (Iran, Iraq, Egypt, Jordan, Lebanon and India). Results showed that Hg, Cd, Cr, and Zn concentrations were below the highest permissible value using all suggested guidelines while other metals showed low to high values based on used guidelines at some stations. MI was in the range of 1.01-2.88, 0.75-2.29 and 1.91-8.03 during spring, summer and winter, respectively. High values of PI (3.03), HPI (803) and Cd (2.03) were found during spring, winter and winter, respectively. The lowest values for mentioned indexes were found during spring (0.38), summer (75) and summer (-4.66), respectively. Comparison between selected indexes indicated that MI index showed normal values compared with other indexes. In addition, the guideline suggested by Lebanon revealed high quality for this river compared with other standards. Consequently, Zohreh River showed low quality for drinking uses during winter while this river showed high quality during other seasons.

Key Words: Metal Index, Pollution Index, Water Quality

Introduction

Rivers from the ancient times have been the main water sources, especially in flat plain, so maintaining its quality is important. Anthropogenic influences such as urban, industrial and agriculture activities degrade rivers (Carpenter *et al*., 1998; Jarvie *et al*., 1998). River pollution is one of the most important issues in developing countries, because maintenance of water quality did not developed with their growing (Sundaray *et al*., 2006; Karbassi *et al*., 2007; Akoto *et al*., 2008; Ahmad *et al*., 2010). Regarding to importance of this subject, many studies were conducted (Tayfur *et al*., 2008; Houben *et al*., 2009; Ketata *et al*., 2011).

Heavy metals like Hg, Cd, Cr and Pb are among the most common environmental pollutants, and their occurrence in waters and biota indicate the presence of natural or anthropogenic sources (Abdullah, 2013a). These pollutants were derived from urban and agricultural runoff, chemical fertilizers, pesticides and soil leaching (Hatje *et al*., 1998; Amman *et al*., 2002; Nouri *et al*., 2006; Nouri *et al*., 2008).

Trace metals (Mn, Ni and Zn) such as heavy metals have high pollution potential (Gueu *et al*., 2007; Lee *et al*., 2007; Adams *et al*., 2008; Vinodhini and Narayanan, 2008). Although trace metals are essential as micronutrients for the life processes in animals and plants (Kar *et al*., 2008; Suthar and Singh, 2008; Aktar *et al*., 2010) but their accumulation in human body cause damage to some organs (Lee *et al*., 2007; Lohani *et al*., 2008). The concentration of the metals in unaffected environments is very low and is mostly derived from the mineralogy and the weathering (Karbassi *et al*., 2008). The rivers have been polluted by these metals because of either natural or anthropogenic sources (Bem *et al*., 2003; Wong *et al*., 2003; Adaikpoh *et al*., 2005; Akoto *et al*., 2008). Heavy metal assessment have been the topics of interest for researchers like: Edet and Offiong (2002), Geriesh *et al.* (2004), El-Sayed (2008), Abdullah (2013a), Khalifa (2014) and Goher *et al*. (2014).

Zohreh River is one the most important rivers in Khuzestan, Iran, with a total length of nearly 275km. Today it is the source of drinking water supply for a great number of people especially in Kheriabad basin. Due to its importance, this study is to ascertain the concentration of heavy and trace metal in Zohreh River and assessment of the metal contamination using different indexes.

Materials and Methods

The study area is situated between latitude of 30° 20’-30° 40’ N and longitude 49° 47’-50° 15’ E covering an area of about 5000 ha. Fig 1 shows location of the study area in Khuzestan province, Iran. Water samples were obtained from 11 stations (Table 1) which are shown in Fig 1. Sampling was divided into four times consist of: spring, summer, autumn and winter. Then, samples were transported to the laboratory and were analyzed according to Iranian National Standard (ISIRI, 2005; ISIRI, 2010). The measured parameters include mercury (Hg), cadmium (Cd), chromium (Cr), manganese (Mn), nickel (Ni), lead (Pb) and zinc (Zn). River discharge in each sampling was also determined.

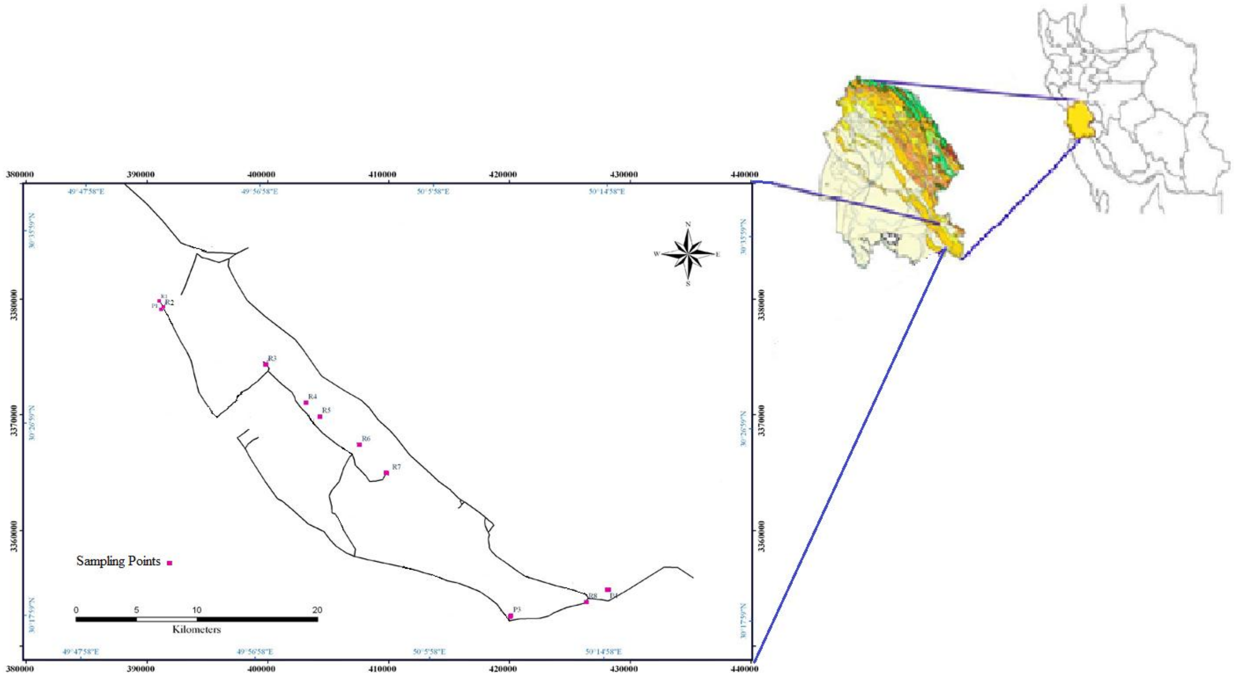

Fig 1: Location of study area, sampling points are ashown as red squares

Table 1: Properties of sample locations in Zohreh River

Code	UTM		Locatons
	Latitude	Longitude	
R1	**3379545**	**392093**	**Upstream**
R2	**3379391**	**391668**	**Soormeghdad bridge**
R3	**3374349**	**399867**	**Cham karteh village**
R4	**3371050**	**404318**	**Longir village**
R5	**3369855**	**403334**	**Longirate village**
R6	**33674140**	**407603**	**Salameh village**
R7	**33649671**	**410132**	**Gavkadeh village**
R8	**3353801**	**426385**	**Downstrem**
P1	**3378875**	**426385**	**Asphalt factory**
P3	**3352641**	**420138**	**Asphalt factory**
P4	**3354882**	**428131**	**Edible oil factory**

In order to classify of Zohreh River, the metal index (MI), pollution index (PI), heavy metal pollution index (HPI) and contamination index (Cd) were applied (Edet and Offiong, 2002; Reza and Sing, 2010; Abdullah, 2013a). These indexes are shown in Equations 1-4, respectively:

$$MI = \sum_{i=1}^{n} \frac{C_i}{MAC_i} \quad (1)$$

$$PI = \frac{\sqrt{\left(\frac{C_i}{S_i}\right)^2_{\max} + \left(\frac{C_i}{S_i}\right)^2_{\min}}}{2} \quad (2)$$

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

$$where: \quad (3)$$

$$Q_i = 100\frac{V_i}{S_i}$$

$$W_i = \frac{k}{S_i}$$

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

$$where: \quad (4)$$

$$C_{fi} = \frac{C_{Ai}}{C_{Ni}} - 1$$

Which C_i is mean concentration of each metal in µg.l^{-1}, MAC_i is maximum allowable concentration in µg.l^{-1}, S_i is recommended standard for the ith parameter in µg.l^{-1}, V_i is monitored value of the ith parameter in µg.l^{-1}, k is the constant of proportionality, C_{Ai} is analytical value for the ith parameter in µg.l^{-1}, C_{Ni} is upper permissible concentration of the ith parameter in µg.l^{-1}.
MI classified into six categories (Table 2). Generally, the critical pollution index value for HPI is 100 (Backan *et al*., 2010; Reza and Singh, 2010). PI categorized into 5 class (Table 3) and Cd grouped into 3 categories as follows: low (Cd <1), medium (Cd =1-3) and high (3<Cd) (Edet and Offiong, 2002; Goher *et al*., 2014).

Table 2: Categories of metal index (Lyulko *et al*., 2001; Caerio *et al*., 2005)

Class	MI value	Class
1	**<0.3**	**Very pure**
2	**0.3-1**	**Pure**
3	**1-2**	**Slightly affected**
4	**2-4**	**Moderately affected**
5	**4-6**	**Strongly affected**
6	**>6**	**Seriously affected**

Standard value for each parameter were extracted from EPA (2009), WHO (2011), drinking water standard of Iran (ISIRI), Iraq, Egypt, Jordan, Lebanon and India (IS 10500, 1993; WHO, 2006; Egyptian drinking water quality standards, 2007; Ministry of Planning and Development

Cooperation, 2009; ISIRI, 2010). Minitab 16 software was used for determination of correlation coefficient (r) between the measured parameters.

Table 3: Categories of water pollution index (Guher *et al*., 2014)

Class	PI value	Class
1	<1	No effect
2	1-2	Slightly affected
3	2-3	Moderately affected
4	3-5	Strongly affected
5	>5	Seriously affected

Results and Discussion

The standard deviation (SD), minimum (Min), maximum (Max) and mean value of individual metals for each season are represented in Table 4. Maximum and minimum variations were found in manganese (Mn) and mercury (Hg), respectively. Cd, Cr, Ni, Pb and Zn were varied in the range of 0.5-1, 2.5-5, 2.5-54, 2.5-45 and 1-122 µg.l^{-1}, respectively. Hg concentration in each season was 0.5 µg.l^{-1}. Maximum and minimum concentrations of Ni were in winter and spring, respectively. Concentrations of other parameter in autumn were not detected. Ni is positively correlated with Pb and Mn in winter and spring, respectively. Pb is also positively correlated with Zn during spring. There was no correlation between river discharge and the monitored metals.

Table 4: Statistical variation among various heavy metals

Metals	Min	Max	SD	Winter	Spring	Summer	Autumn
				Mean			
Hg (µg.l^{-1})	0.5	0.5	0	0.5	0.5	0.5	0.5
Cd (µg.l^{-1})	0.5	1	±0.23	1	0.5	0.5	ND*
Cr (µg.l^{-1})	2.5	5	±1.18	5	2.5	2.5	ND
Mn (µg.l^{-1})	0.5	999	±346.73	490	133	134	ND
Ni (µg.l^{-1})	2.5	54	±16.58	33	8	2.5	10
Pb (µg.l^{-1})	2.5	45	±13.48	26.5	9.5	2.5	ND
Zn (µg.l^{-1})	1	122	±25.99	37.5	34.5	33	ND

*** ND: not detected**

The concentrations of Hg, Cd, Cr and Zn were found below the highest permissible value of the mentioned standards. While the concentration of Mn during winter was detected above the permissible value based on national standard of Iran (ISIRI), Egypt and Jordan except at three stations (P1, P3 and P4). P1 showed high Mn concentrations during spring and summer. There was also high Mn concentration in P3 during spring based on Iran, Egypt and Jordan national standard. The Ni concentrations were below the permissible value during spring and summer. Although concentration of Ni was recorded in the range of 5-54, it is below the critical value based on ISIRI and Jordan national standard. Pb concentrations were below the permissible value based on national standard of Egypt and Lebanon. Based on the other standards all stations during spring and summer and P1 during winter were below the critical value. The results showed that in the most of selected stations, water was found appropriate quality for drinking usage. It may be assigned to the purification of factories sewage before it is drained into the river.

MI values during spring for each station are shown in Fig 2. Stations R1, R2, R4 and R7 were pure (0.3<MI<1). Similar results cited by Abdullah (2013b). Stations R3 and P1 were slightly (1<MI<2) and seriously (6<MI) affected, respectively. The results agreed with Amadi *et al*. (2012) about slightly affected of River Chanchaga. Other stations were moderately affected (2<MI<4). Similar results reported by Goher *et al.* (2014) for evaluating the pollution status of Ismailia Canal.

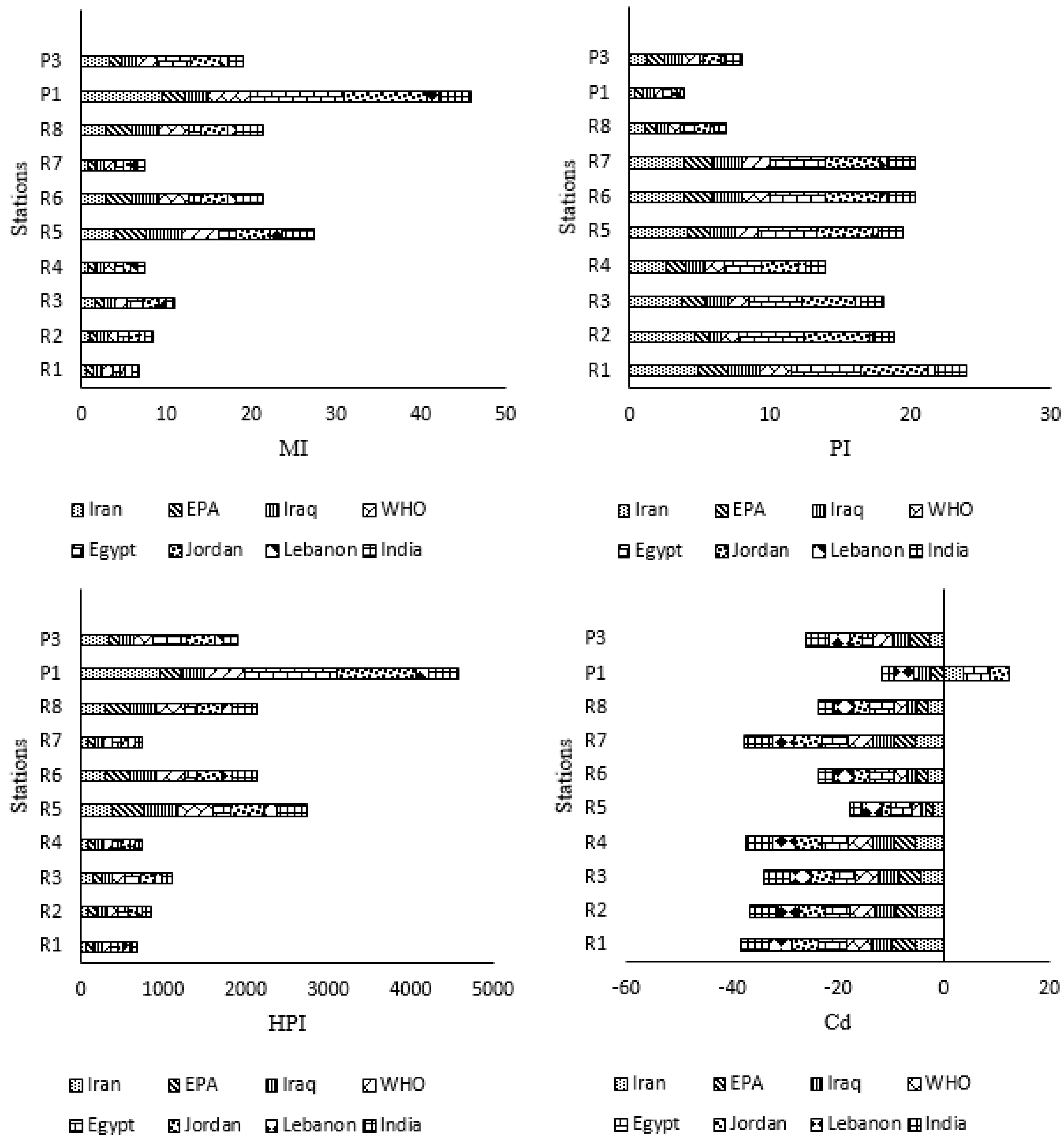

Fig. 2: Comparison of four heavy metal indexes in spring

MI values obtained by EPA standard showed similar to ISIRI except at stations P1 (2.54) and P3 (1.44). It may be due to high Ni concentrations in mentioned stations. Although metals concentration at each station were different but limited value of Ni concentration according to

ISIRI is 3.5 times more than EPA, which cause great differences between mentioned stations. Other standards indicated different degree of pollution compared with ISIRI and EPA. Mean MI values of Zohreh River were 2.71, 1.82, 2.48, 2.09, 2.59, 2.88, 1.01, 2.00 based on ISIRI, EPA, WHO, Iraq, Egypt, Jordan, Lebanon and India standard, respectively (Fig. 3). The most high quality stations were obtained by uses of Lebanon national standard.

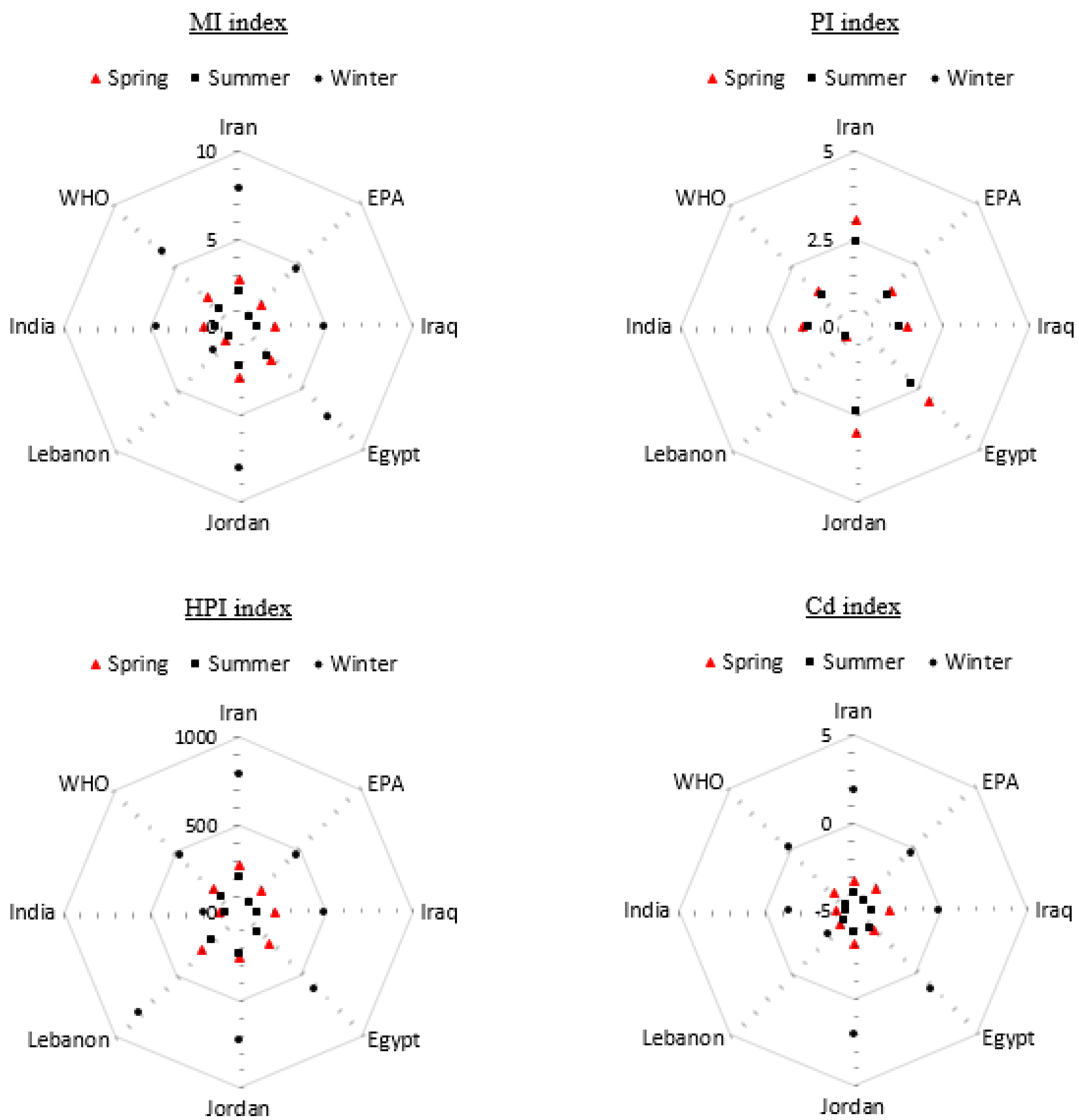

Fig 3: Mean value of each index during selected seaosons

PI was in the range of 0.33-4.82, 0.67-2.25, 0.67-2.25, 0.67-2.25, 0.25-4.82, 0.33-4.82, 0.25-0.45 and 0.25-2.25 based on ISIRI, EPA, WHO, Iraq, Egypt, Jordan, Lebanon and India standard, respectively. It showed no effect to strongly affected at the stations. According to mean PI values, Lebanon standard (0.38) showed the highest quality of Zohreh River. The lowest quality obtained by using ISIRI and Jordan standard (3.03). HPI values were more than 100 using all guidelines which represented strong pollution effects at all stations that agreed with the results reported by Ameh and Akpah (2011) and Abdullah (2013a). The HPI for Zohreh River showed values between from 101 to 288. Cd index showed slight pollution effect at some stations. This index revealed high pollution effects at Station P1 using ISIRI, Egypt and Jordan standard. Mean Cd values were less than zero at all stations based on Fig. 3.

Fig. 4 illustrated the value of MI, PI, HPI and Cd for each station using eight guidelines during summer. MI values ranged between 0.60-10.57 using ISIRI. Based on Table 2 the stations P1 and R4 were seriously and moderately affected, respectively. Other stations were pure. Comparison of other standards showed that MI values were pure based on EPA and Lebanon national standard. All stations were in the range of 1-2 based on WHO guideline except at station P1. The range of mean MI was 0.75 (Lebanon standard)-2.29 (Egypt standard). PI values ranged between 0.33-4.82 based on ISIRI. While station P1 had the lowest values among other stations, station R1 recorded high value of PI. Mean values of PI were in between 0.34 (Lebanon standard)-2.41 (ISIRI and Jordan standard). Lebanon guideline showed PI values in the range of 0-1. It seemed Lebanon standard was the most conservative guideline among the others.

The HPI values were found to be above the critical value of 100 at all stations based on ISIRI. HPI values were 82 and 75 by using WHO and Lebanon guideline, respectively. Other standards showed HPI values above 100. Station R4 and station P1 had minimum and maximum values of HPI, respectively. Cd index denoted negative values at many stations. Only station P1 indicated positive Cd (Cd>3) based on guideline suggested by ISIRI, Egypt and Jordan. Mean values of Cd index were negative which showed high quality of the River using all guidelines.

MI, PI, HPI and Cd did not compute during autumn because of not detected metals in the season, although these indexes were used to estimate the metal pollution during winter. MI index showed moderately affected at stations P1, P3 and P4 based on ISIRI (Fig. 5). Station R8 was strongly affected according to MI. This index denoted seriously affected at other stations. These results were found in agreement with Lyulko *et al*. (2001), Caerio *et al*. (2005) and Abdullah (2013a). Lebanon standard showed the lowest mean value of MI (1.91), while the highest mean value of MI obtained by using Jordan standard (8.03). PI was in the range of 0.33-4.66, 0.67-2.05, 0.67-2.05, 0.67-2.05, 0.25-4.66, 0.33-4.66, 0.25-0.47 and 0.25-2.05 using guideline suggested by ISIRI, EPA, WHO, Iraq, Egypt, Jordan, Lebanon and India standard, respectively. Based on the mean values of PI index, Zohreh River showed no effect (Lebanon standard), slightly affected (EPA, WHO, Iraq and India standard) and moderately affected (ISIRI, Egypt and Jordan standard). According to HPI index, all stations along this river showed high pollution for drinking usage. Cd index indicated the high pollution at stations R1, R2, R3, R4, R5 and R6 based on ISIRI (Cd>3). Cd index was in the range of -2.50-2.09, -2.20-2.39, -3.66—2.43 and 4.57-1.39 using guideline suggested by EPA, Iraq, Lebanon and India national standard, respectively. Other guidelines showed slight to strong pollution effects at the stations.

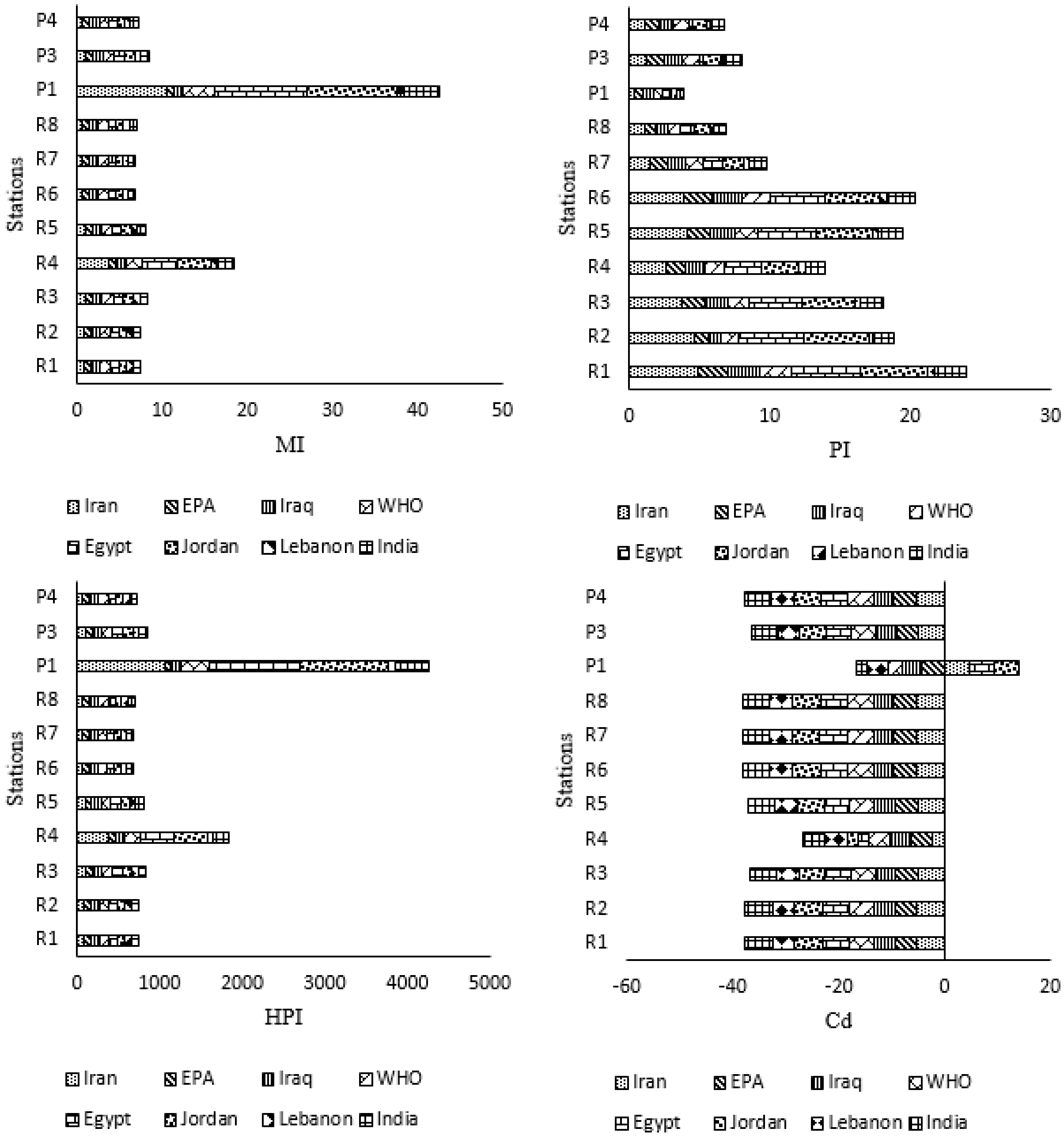

Fig 4: Comparison of four heavy metal indexes in summer

The results revealed that the mentioned indexes showed very different quality for Zohreh River. Accroding to Cd values, all stations denoted high quality for this river but HPI values showed low quality. Zohreh River quality based on PI values had better quality than this river based on MI values. It may be attributed to the related equations. PI index consider only maximum and minimum proportionality for all metals. It seems can not represent the effect of all metals on water quality. On the other hand, high concentration of any metals had great effect on PI values. In the case of MI index, there were lower values due to use the sum of all metals proportionality. On the other hand, HPI index uses a coefficient (*Wi*) at the numerator and denominator, which cause the value increases in comparison, when a simple ratio (V_i/S_i) uses. The concentrations ratio (C_i/S_i) changed into negative value by using Cd index. Quality categories for Cd index also cause to reach high quality for this river.

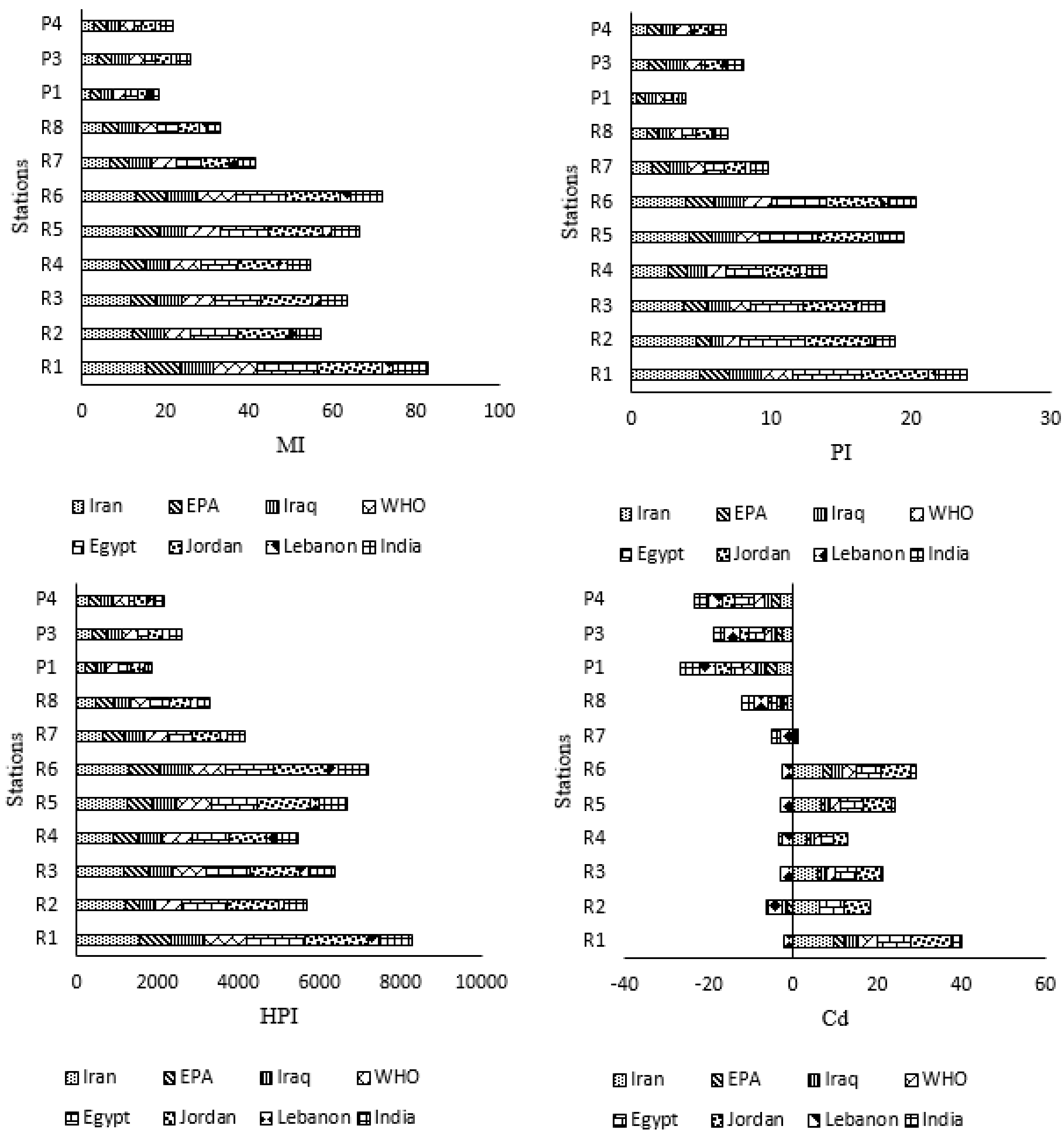

Fig 5: Comparison of four heavy metal indexes in winter

Conclusion

According to the results, Hg, Cd, Cr, and Zn were found below the highest permissible value using all suggested guidelines while other metals showed low to high values based on used guidelines at some stations. Zohreh River quality was moderately, slightly, moderately and slightly affected based on MI, PI, HPI and Cd values during spring, respectively. Results showed that Zohreh River quality was slightly affected based on MI, PI and Cd values during summer. HPI index revealed moderately affected of this river. MI, PI, HPI and Cd were moderately, slightly, strongly and moderately affected during winter. Zohreh River showed low quality during winter. It may be due to the precipitation and land erosion during winter (Ameh and Akpah, 2011) with respect to the "no correlation" between river discharge and the metals. The comparison between water quality using each metal and four metal pollution indexes (MI, PI, HPI and Cd) revealed that MI index showed normal values. Although PI index almost showed the same values but this index was sensitive to the minimum and maximum concentrations of the metals. Cd index indicated high quality for this river while HPI index showed low quality.

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