

Applied Heavy Metals Pollution Index (HPI) as a Water Pollution Indicator of Shatt Al-Arab River, Basrah-Iraq

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Abstract Five stations were selected at the middle part of Shatt Al-Arab river to determine the monthly variation of seven eco-toxic elements (Cd^{+2} , Cu^{+2} , Fe^{+2} , Mn^{+2} , Ni^{+2} , Pb^{+2} and Zn^{+2}) concentrations and their distribution as dissolved and particulate (exchangeable and residual) phases during the low tide period from December, 2012 to November, 2013. Heavy Metals Pollution Index (HPI) was applied to determine the pollution of Shatt Al-Arab water. Results showed that the concentrations of the previous metals as dissolved phase were (3.01; 2.35; 89.45; 4.48; 9.51; 43.67 and 7.58) $\mu\text{g/l}$, respectively, whereas in the exchangeable phase of particulate were (48.56; 53.22; 8968.76; 1748.58; 120.14; 271.52; 243.16) $\mu\text{g/g}$ dry weight respectively and in the residual phase of particulate were (57.59; 88.68; 21571.74; 365.90; 163.39; 388.44 and 219.42) $\mu\text{g/g}$ dry weight respectively. The results indicated that mean HPI values were found to be above the critical pollution index value of 100. HPI values for the presence study were ranged from 130.41 to 196.97 referred to polluted water caused by the world impermissible values of dissolved Pb, Fe and Cd.

Keywords Shatt Al-Arab water; HPI; Heavy metals pollution; Indices

Introduction

Heavy metals is a term generally taken to include the metallic elements with an atomic weight greater than 40, which have specific gravity greater than 5 g/cm^3 , but excluding the alkaline earth metals, alkali metals, lanthanides and actinides. All heavy metals exist in surface waters in colloidal, particulate, and dissolved phases. The dissolved metals have size below $0.45 \mu\text{m}$ and found as free ions or unionized organometallic chelates or complexes, or as colloids.

Heavy metals are among the most common environmental pollutants because of their toxicity, persistence and non-degradability in the environment (Majhi and Biswal, 2016), and their occurrence in water and biota indicate the presence of natural or anthropogenic sources (Balakrishnan and Ramu, 2016). Industrial processes, domestic sewages, agricultural fertilizers are the main source of metal pollution. In addition, metallic compounds are used as pigments in paint and dye manufacture, plastic, rubber, and paper; and many others. The prevalence of heavy metals in domestic formulations, such as cosmetic or cleansing agents, is frequently overlooked. Some forms of intensive agriculture give rise to severe metal pollution (Abel, 2002). The partitioning of metals between dissolved and suspended particulate matter determines their ultimate fate in the aquatic environment (Al-Khafaji et al., 2011).

The most important heavy metals from the point of view of water pollution are lead, cadmium, iron, zinc, copper, nickel and manganese. Some of these metals (e.g. copper, zinc and iron) are essential trace elements to living organisms and play an important roles in the functioning of critical enzyme systems, but become toxic at higher concentrations. Others, such as lead and cadmium, have no known biological function, and may be toxic even at trace levels to exposure (Al-Hejuje, 2014). Heavy metal exposure causes serious health problems, including reduced growth and development, cancer, organ damage, nervous system damage, and in extreme cases death (Alani et al., 2014). Heavy metals, like Cd and Pb are toxic even at low concentrations, can bio-accumulated and

biomagnificated through the food chain and are not degradable by decomposers organisms (Al-Hejuje, 1997).

In future to protect water bodies from pollution, continuous monitoring is necessary to avoid further pollution. For water bodies it is necessary to find out some pollution monitoring tools (Chougule et al., 2009; Yankey et al., 2013). Heavy metal pollution indices are a useful and a relatively easy way to assess the composite of overall heavy metal pollution (Al-Hejuje, 2014). Several methods have been previously proposed such HPI: heavy metals pollution index (Mohan et al., 1996), MPI: metal pollution index (Meybeck et al., 2004), and HEI: heavy metal evaluation index (Bhuiyan et al., 2010) to calculate the overall water pollution with heavy metals. The heavy metal pollution index (HPI) is a method of rating that shows the composite influence of individual heavy metal on the overall quality of water (Reza and Singh, 2010; Balakrishnan and Ramu, 2016).

The main goal of the present study is to determine the temporal and spatial variations of heavy metals at the Shatt Al-Arab River, and also apply HPI as an effective tool to assess the water pollution with heavy metals and its suitability for different purposes. HPI describes as a bridge between professionals and laymen or the decision makers.

1 Materials and Methods

Water sample (5 L) were collected from each of five stations along the middle part of Shatt Al-Arab river, Southern of Iraq during Dec., 2012 -Nov., 2013 period at the following coordinates: 30.36 623 N and 47.45 662 E (station 1); 30.34 915 N and 47.46 368 E (station 2); 30.33 755 N and 47.47 563 E (station 3); 30.30 376 N and 47.51 328 E (station 4); and 30.27 251 N and 48.02 810 E (station 5). Water samples were collected at least 20 -30 cm under the water surface at the middle of the river using polyethylene bottles and preserved cooling until reach the lab.

In the laboratory, water samples (5 L) were filtered as soon as possible through pre-washed (HCl 0.5 N) and pre-weighted Millipore membrane filters (0.45 μ m pore size). The filtrate was considered as dissolved phase, while those retained on the surface of filters were considered as particulate phase. The filtrate was then pre-concentrated using chelating ion exchange resin (Purolite-C-100 resin in hydrogen form); about 5 L of filtrate was pass through activated ion exchange column with a flow rate of about 8 ml/min. The column was then washed with 100 ml of deionized water and the bounded heavy metals were eluted using 50 mL of HNO₃ (2 N). The elutes were collected in 100 ml clean Polyethylene Tri Fluro Ethane (PTFE) containers ,allowed on hot plate at 70 °C until the sample volume reduced below 25 ml. The sample volume was up to 25 mL mark with deionized water and stored in tightly stopper polyethylene vials ready for analysis of the metals using flame atomic absorption spectrophotometer (FAAS).

The filters were dried in oven at 60 °C to constant weights and their weights recorded to obtain the values of the total suspended matter. The exchangeable heavy metals were extracted using 30 ml HCl (0.5 N) overnight in an orbital shaker with 300 rpm. The solution was centrifuged at 5000 rpm for 20 minute, then the supernatant was filtered using pre-cleaned filter paper (Watman No. 1) to remove some of the suspended matters. The filtrate was decanted and stored in tightly stopper polyethylene vials to be ready for analysis (Chester and Voutsinou, 1981).

The metals in residual phase of the particulate matter was extracted according to Sturgeon, et al. (1982), where the above mentioned steps was washed by 40 mL deionized water, centrifuge for 20 minutes. Then samples were digested with 5 mL concentrated HNO₃ acid in PTFE vessels at 70 °C on hot plate near dryness state. The digestion was further proceeded with 1:1 mixture of concentrated HClO₄ and HF acids. The residue was dissolved in 30 mL of HCl (0.5 N), allowed on hot plate at 70 °C, then made up to 30 mL with deionized water ,and filtered using pre-cleaned filter paper (Watman No. 1). The samples were stored in tightly stopper polyethylene vials to be ready for analysis by FAAS.

1.1 Heavy metal pollution index (HPI)

The Heavy Metal Pollution Index (HPI) is a method of rating that shows the composite influence of individual

heavy metal on the overall quality of water (Reza and Singh, 2010). HPI in water was developed by assigning weight or rating (W_i) for each selected element. The weighing value was between zero and one, reflecting the relative importance of individual quality considerations.

$$W_i = K / S_i$$

Where W_i is the unit of weightage, k is the constant of proportionality ($k=1$), and S_i is the recommended standard for i th parameter.

The sub index (Q_i) of the i th parameter was calculated according to Reza and Singh (2010):

$$Q_i = \frac{|M_i - I_i|}{S_i - I_i} \times 100$$

Where M_i is the monitored value of heavy metal of i th parameter in $\mu\text{g/l}$, I_i is the maximum desirable value (ideal) of i th parameter, S_i refers to the standard or permissible limit for i th parameter.

The HPI model (Mohan et al., 1996) was calculated as:

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

Critical pollution index value is 100. The higher HPI value causes the greater damage to health.

1.2 Statistical analysis

Analysis Of Variance was applied by Minitab ver.16 software and Relative Least Significant Differences (RLSD) values were calculated to identify the existence of temporal and spatial significant differences. Principal Components Analysis (PCA) was done using Canoco ver.4.53 in order to get an overall assessment of the possible relations among environmental variables.

2 Results and Discussion

During visitation to the area, people were seen washing their cars, washing sheep and cattle in Shatt Al-Arab River, irrigating their farms with the polluted water. Hence, consumers of milk, meat products, and vegetables may be at risk of chemical poisoning and health complications arising from the dangerous metals pollutants.

The metal speciation (dissolved, particulate) can provide informations about the complex interactions among components in an aquatic environment.

The concentrations of cadmium in dissolved phase ranged from (2.88 $\mu\text{g/L}$) at station 5 to (3.08 $\mu\text{g/L}$) at station 2 (Table 1). Whereas in particulate phase, the concentrations in the exchangeable phase ranged from (28.42 $\mu\text{g/g}$ dry weight) at station 5 to (56.47 $\mu\text{g/g}$ dry weight) at station 4, the residual phase of particulate ranged from (31.93 $\mu\text{g/g}$ dry weight) at station 5 to (69.64 $\mu\text{g/g}$ dry weight) at station 4. Relative Least Significant Differences showed non-significant differences ($P>0.05$) were found among the cadmium concentrations (as dissolve or as particulate) at different stations.

Copper concentrations as dissolved ranged from (2.14 $\mu\text{g/L}$) at station 5 to (2.58 $\mu\text{g/L}$) at station 1 (Table 1). Non-significant differences ($P>0.05$) were found among the concentrations at different stations. While in particulate phase, the concentrations in the exchangeable phase ranged from (22.74 $\mu\text{g/g}$ dry weight) at station 5 to (67.10 $\mu\text{g/g}$ dry weight) at station 1, and significant differences ($P<0.01$) were found among the concentrations at different stations. The copper concentrations in the residual phase of particulate ranged from (60.80 $\mu\text{g/g}$ dry weight) at station 5 to (107.60 $\mu\text{g/g}$ dry weight) at station 1, and non-significant differences ($P>0.05$) were found among the residual concentrations at different stations.

Table 1 The concentrations of heavy elements in dissolved and particulate phases at the studied stations during the studied periods

Stations	Heavy elements	Dissolved phase($\mu\text{g/l}$)	Particulate phase ($\mu\text{g/g}$ dry weight)	
		Mean \pm SD	Exchangeable Mean \pm SD	Residual Mean \pm SD
Station 1	Cd	3.06 \pm 1.82	53.51 \pm 63.21	64.61 \pm 83.69
	Cu	2.58 \pm 0.84	67.10 \pm 31.15	107.60 \pm 226.30
	Fe	145.68 \pm 108.39	9510.0 \pm 3640.0	23945.0 \pm 8872.0
	Mn	4.98 \pm 1.46	1480.2 \pm 442.0	423.3 \pm 121.9
	Ni	10.45 \pm 2.15	132.38 \pm 79.83	194.83 \pm 84.94
	Pb	46.26 \pm 8.68	312.60 \pm 193.0	444.60 \pm 512.9
	Zn	8.20 \pm 3.69	245.40 \pm 211.9	246.40 \pm 146.6
Station 2	Cd	3.08 \pm 1.81	54.30 \pm 66.25	61.76 \pm 81.19
	Cu	2.44 \pm 0.8	56.54 \pm 15.5	88.20 \pm 179.7
	Fe	107.91 \pm 64.15	9505.0 \pm 3996.0	24181.0 \pm 5099.0
	Mn	4.79 \pm 1.29	1866.8 \pm 633.0	371.1 \pm 90.8
	Ni	10.18 \pm 1.28	129.84 \pm 81.83	174.91 \pm 63.77
	Pb	46.55 \pm 7.70	268.6 \pm 173.6	383.7 \pm 368.2
	Zn	8.73 \pm 5.24	385.3 \pm 205.2	233.2 \pm 109.6
Station 3	Cd	2.95 \pm 1.68	48.81 \pm 47.52	59.48 \pm 63.13
	Cu	2.28 \pm 0.74	61.06 \pm 26.49	85.7 \pm 149.5
	Fe	88.21 \pm 66.96	10107.0 \pm 4850.0	22331.0 \pm 4810.0
	Mn	4.09 \pm 1.46	1956.8 \pm 679.9	374.2 \pm 90.5
	Ni	9.47 \pm 1.65	135.17 \pm 78.98	172.31 \pm 76.91
	Pb	40.91 \pm 9.44	303.6 \pm 176.6	440.5 \pm 444.7
	Zn	5.92 \pm 1.54	232.8 \pm 105.5	233.4 \pm 106.0
Station 4	Cd	3.07 \pm 1.81	56.47 \pm 53.96	69.64 \pm 68.46
	Cu	2.29 \pm 0.90	57.27 \pm 37.80	101.4 \pm 207.5
	Fe	63.69 \pm 43.01	9419.0 \pm 4134.0	18667.0 \pm 7889.0
	Mn	4.575 \pm 1.474	2396.5 \pm 1041.0	334.4 \pm 134.1
	Ni	9.07 \pm 1.93	120.42 \pm 85.69	126.49 \pm 86.19
	Pb	42.55 \pm 6.91	321.1 \pm 111.6	509.3 \pm 462.6
	Zn	9.65 \pm 16.87	234.1 \pm 101.3	254.2 \pm 138.8
Station 5	Cd	2.88 \pm 1.54	28.42 \pm 29.29	31.93 \pm 35.25
	Cu	2.14 \pm 0.84	22.74 \pm 9.46	60.8 \pm 101.5
	Fe	41.75 \pm 25.77	6111.0 \pm 3322.0	18428.0 \pm 7933.0
	Mn	3.97 \pm 1.28	954.1 \pm 373.5	325.2 \pm 137.7
	Ni	8.39 \pm 2.07	81.99 \pm 49.42	146.55 \pm 48.36
	Pb	42.08 \pm 9.04	144.6 \pm 61.10	159.8 \pm 144.50
	Zn	5.427 \pm 3.5	107.0 \pm 78.80	127.4 \pm 61.30

Note: mean \pm Standard deviation (SD)

The concentrations of iron in dissolved phase ranged from (41.75 $\mu\text{g/L}$) at station 5 to (145.68 $\mu\text{g/L}$) at station 1 (Table 1). Significant differences ($P < 0.01$) were found among the concentrations at different stations. In the exchangeable phase of particulate the concentration ranged from (6111.0 $\mu\text{g/g}$ dry weight) at station 5 to (10107.0 $\mu\text{g/g}$ dry weight) at station 3. In the residual phase of particulate ranged from (18428.0 $\mu\text{g/g}$ dry weight) at station 5 to (24181.0 $\mu\text{g/g}$ dry weight) at station 2. Non-significant differences ($P > 0.05$) were found among the concentrations of iron in the exchangeable or residual phases of particulate at different stations.

The concentrations of manganese in dissolved phase ranged from (3.97 $\mu\text{g/L}$) at station 5 to (4.98 $\mu\text{g/L}$) at station 1 (Table 1). Non-significant differences ($P > 0.05$) were found among the dissolved concentrations at different stations.

In particulate phase, the concentrations in the exchangeable phase ranged from (954.1 $\mu\text{g/g}$ dry weight) at station 5 to (2396.5 $\mu\text{g/g}$ dry weight) at station 4. Significant differences ($P < 0.01$) were found among the concentrations at different stations. In the residual phase of the particulate ranged from (325.2 $\mu\text{g/g}$ dry weight) at station 5 to (423.3 $\mu\text{g/g}$ dry weight) at station 1. Non-significant differences ($P > 0.05$) were found among the residual concentrations at different stations.

Nickel concentration in the dissolved phase ranged from (8.39 $\mu\text{g/L}$) at station 5 to (10.45 $\mu\text{g/L}$) at station 1 (Table 1). In particulate phase, the concentrations in the exchangeable phase ranged from (81.99 $\mu\text{g/g}$ dry weight) at station 5 to (135.17 $\mu\text{g/g}$ dry weight) at station 3. The nickel concentrations in the residual phase of particulate ranged from (126.49 $\mu\text{g/g}$ dry weight) at station 4 to (194.83 $\mu\text{g/g}$ dry weight) at station 1. Non-significant differences ($P > 0.05$) were found among the concentrations of nickel (as dissolve or as particulate) at different stations.

The concentrations of lead in dissolved phase ranged from (40.91 $\mu\text{g/L}$) at station 3 to (46.55 $\mu\text{g/L}$) at station 2 (Table 1). Non-significant differences ($P > 0.05$) were found among the dissolved concentrations at different stations. In particulate phase, the concentrations in the exchangeable phase ranged from (144.6 $\mu\text{g/g}$ dry weight) at station 5 to (321.1 $\mu\text{g/g}$ dry weight) at station 4. Significant differences ($P < 0.05$) were found among the concentrations at different stations, while in the residual phase of particulate ranged from (159.8 $\mu\text{g/g}$ dry weight) at station 5 to (509.3 $\mu\text{g/g}$ dry weight) at station 4. Non-significant differences ($P > 0.05$) were found among the residual concentrations at different stations.

The concentrations of zinc in dissolved phase ranged from (5.43 $\mu\text{g/L}$) at station 5 to (9.65 $\mu\text{g/L}$) at station 4 (Table 1). Non-significant differences ($P > 0.05$) were found among the dissolved concentrations at different stations. In particulate phase, the concentrations in the exchangeable phase ranged from (107.0 $\mu\text{g/g}$ dry weight) at station 5 to (385.3 $\mu\text{g/g}$ dry weight) at station 2. Significant differences ($P < 0.01$) were found among the concentrations at different stations, whereas in the residual phase of particulate ranged from (127.4 $\mu\text{g/g}$ dry weight) at station 5 to (254.2 $\mu\text{g/g}$ dry weight) at station 4 and non-significant differences ($P > 0.05$) were found among the concentrations at different stations.

In the present study the concentrations of Pb, Cd and Fe in dissolved phase at most stations exceeded the highest permissible limits of drinking water, and this finding was in agreement with Al-Saffie (2005) who found elevated in Pb concentrations at Shatt Al-Arab river and Hassan (2007) who found elevation in Cd and Pb concentrations at Shatt Al-Arab river. The concentrations of other metals (Ni, Mn, Cu, and Zn) were below the permissible limits of drinking water according to the WHO (2011) (Table 2). The present finding was in agreement with Mastoi et al. (2008) who found that the main source of high level of Cd in water is the runoff from the agricultural fields rich in chemical fertilizers. The spatial elevated concentrations could be related to land-based point source discharges caused by rapid urbanization and economic development in Basrah city center, this finding was in agreement with Al-Hejuje (1997) and Zhang et al. (2009), or may be due to a wide range of anthropogenic impacts linked to variations in population density, wastewater discharges and industrial activities. The river is extensively used for washing vehicle and the wastewater is drained back into the river, the vehicle emission which can travel for a long distance from the source of emission by atmospheric transport, traffic sources, and cities are the main sources of contaminations of heavy metals in the river (Song et al., 2010; Manoj et al., 2012). The fluctuation in the concentrations of heavy metals could be attributed to the interactions between multi factors that affect the concentrations of dissolved metals, such as the unequal amount s of sewage discharged, the phytoplankton and aquatic plants densities which absorbed or adsorbed the ionic metals, the sand storms occurring, and the fuel burn emissions specially during Summer as a result of electrical power generation machines that released large amounts of metals, especially lead compounds, into the river.

The mean concentrations of all the studied heavy metals in particulate phase were higher than those in dissolved phase. This finding was in agreement with Al-Khafaji (1996); Al-Hejuje (1997) and Hassan et al. (2010). Most of heavy metals in particulate phase positively correlated with those in dissolved phase and this could be attributed to

the same sources and the ability of suspended particulate to accumulate these metals from the surrounding water. Suspended solid is the same as the sediments that can scavenge and enrich the metals input into water (Song et al., 2010). This could be attributed to the ability of the particulate matter (especially the living phytoplankton) to concentrate the heavy elements in their bodies, or may be due to the considerable variations in partitioning between water and particulate matter. However, the concentrations of heavy metals in particulate matter mostly depend on many factors such as wastewater discharge, seasonal loads and the nature of basin. Also, sewage and seepage from agricultural lands, the disposal of industrial and municipal effluent could change the concentrations of heavy metals in the particulate matters (Taobi et al., 2000).

Table 2 The World and the Iraqi Permissible values for heavy metals in water as compared with the present study

Parameters	Units	WHO (2004, 2011) for drinking and domestic purposes	Ayers and Westcot (1985) for Irrigation water resources	Iraqi systems for rivers maintains (2011)	US-EPA (2012)	Present study		
						Dissolved	Exchangeable Particulate (µg/g dry weight)	Residual particulate (µg/g dry weight)
Cadmium	µg/l	3	10	5	5	3.01	48.56	57.59
Copper	µg/l	2000	200	50	1000	2.35	53.22	88.68
Iron	µg/l	50	5000	300	300	89.45	8968.76	21571.74
Manganese	µg/l	400	200	100	50	4.48	1748.58	365.90
Nickel	µg/l	70	200	50	-	9.51	120.14	163.39
Lead	µg/l	10	5000	50	-	43.67	271.52	388.44
Zinc	µg/l	3000	2000	500	5000	7.58	243.16	219.42

3 The Heavy Metals Pollution Index (HPI)

The lowest mean value of HPI (130.41) was found at station 5 in summer, while the highest mean value (196.97) was found at station 1 in winter (Table 3). ANOVA test showed non-significant differences ($P > 0.05$) were found among stations or among seasons. Generally, the water was polluted with heavy metals along the studied period at all the studied stations. This could be attributed to high concentrations of Pb, Cd, and Fe in dissolved phase which exceeded the permissible limits in drinking water, and the low concentrations of Cu, Mn and Zn which were below the permissible limits.

High positive correlation between HPI and its correlated metals is illustrated in Figure 1.

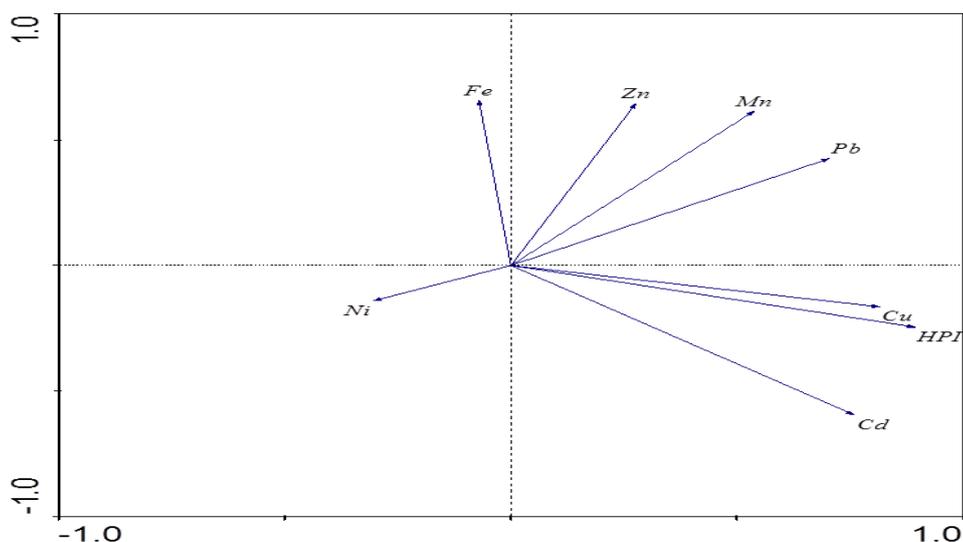


Figure 1 The Principal Components Analysis (PCA) between HPI and its correlated heavy metals

Table 3 The HPI values and the water pollution descriptions at the studied stations during the studied periods

Stations	Season	$\sum W_i * Q_i$	HPI Value	Descriptions of water pollution
Station 1	Winter	97.19	196.97	polluted
	Spring	88.38	179.12	polluted
	Summer	73.14	148.23	polluted
	Autumn	87.76	177.86	polluted
Station 2	Winter	87.49	177.31	polluted
	Spring	89.50	181.37	polluted
	Summer	71.20	144.29	polluted
	Autumn	94.10	190.71	polluted
Station 3	Winter	68.82	139.46	polluted
	Spring	81.69	165.54	polluted
	Summer	70.26	142.39	polluted
	Autumn	89.78	181.94	polluted
Station 4	Winter	89.18	180.72	polluted
	Spring	79.12	160.34	polluted
	Summer	66.95	135.67	polluted
	Autumn	83.30	168.82	polluted
Station 5	Winter	77.77	157.59	polluted
	Spring	83.35	168.92	polluted
	Summer	64.35	130.41	polluted
	Autumn	79.19	160.48	polluted

Note: $\sum W_i = 0.493452$

4 Conclusion

In the present study, the mean heavy metal pollution index (HPI) of Shatt Al-Arab River were found above the critical index value 100, according to impermissible values of dissolved Pb, Fe and Cd. which indicates that are represented as surface water pollution with respect to heavy metals.

Authors' contributions

Conceived and designed the experiments: AL-Saad H.T., Al-Hejuje M. and Hussain N. Analysed the data: Al-Hejuje M. Wrote the first draft of the manuscript: Al-Hejuje M. Contributed to the writing of the manuscript: AL-Saad H.T., Al-Hejuje M. and Hussain N. Agree with manuscript results and conclusions: AL-Saad H.T., Al-Hejuje M. and Hussain N. Jointly developed the structure and arguments for the paper: AL-Saad H.T., Al-Hejuje M. and Hussain N. Made critical revisions and approved final version: Al-Hejuje M., AL-Saad H.T. and Hussain N. authors reviewed and approved of the final manuscript.

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