



# EVALUATION OF HAZARDOUS AND METAL POLLUTION INDECES OF RIVERS THAT SUPPLY DUKAN RESERVIOR, KURDISTAN, NORTHEAST IRAQ

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## Abstract

The study aims were to reveal the monthly water quality variations in rivers that supplies Dukan reservoir, and to analysis the water pollution in terms of heavy metal total content. Recently, several numerical water quality indices were developed as an interpretive tool for metal pollution assessment, the mostly tools used were Heavy Metal Pollution Index (HPI), Heavy Metal Evaluation Index (HEI) and Contamination Index ( $C_d$ ). The HPI was in the ranges of (42.10 to 69.75), (18.87 to 61.27), (31.74 to 60.70), (33.05 to 60.17), (35.21 to 60.93) and (37.70 to 62.05) during August, November, February, March, April and May respectively, the range of monthly average values of HPI were (42.70 to 48.09) with mean  $\pm$ SD (44.96  $\pm$ 10.63) and falls under high degree of pollution. Highest values of HEI (72.15) and  $C_d$  (65.15) were found during August, while the smallest value of (38.81) and (31.81) during May for HEI and  $C_d$  were founded, respectively, and the range of monthly average with mean  $\pm$ SD of HEI and  $C_d$  were (48.55 to 55.48) (51.13  $\pm$ 10.48) and (41.55 to 48.81) (44.29  $\pm$ 9.69), respectively and fall under high degree of pollution. The overall heavy metal mean concentration values were obtained within the highest permissible limit for Fe (0.252), Cu (0.010), Zn (0.148) and Mn (0.004) mg L<sup>-1</sup>. However, the whole mean concentrations of Pb (0.049), Cd (0.105), and Cr (0.510) mg L<sup>-1</sup> were observed to be above the highest permissible limit values of (WHO) World Health Organization and (IQS) Iraqi Quality Standard.

**Key words** : Degree of pollution, water quality, contamination, anthropogenic activities.

## Introduction

Heavy metals come into the rivers from very different sources; whether natural or anthropogenic, the entry may be as a consequence of its direct discharges into water ecosystems or through with indirect paths like dry and wet deposition and land run-off (Adaikpoh *et al.*, 2005 and Akoto *et al.*, 2008). The agricultural drain water comprises pesticides and fertilizers and out flowing of industrial activities and runoff in extra to sewage effluents entry huge amounts of heavy metals and inorganic anions into the sediment and water bodies (ECDG, 2002). At the same time, river water quality has affected by seasonal agricultural activity, atmospheric deposit and storm water runoff fluctuation (Cidu and Biddau, 2007).

An anthropogenic activity like rapid urbanization and larger agricultural runoff has become a threat problem for quality of surface water around the world (Yadav *et*

*al.*, 2014). At the present time, and throughout the world, the water quality sources were diminished, especially due to the growth and development of population and economic. Innumerable and various wastes, hazardous contaminants and emanations were released straightly into the environment (Senila *et al.*, 2012 and Islam, 2015). Metal pollution indices are an important device for appraisal quality of water and have been employed successfully around the world (Bhuiyan *et al.*, 2010). The contamination of the outer face of water by metals is a serious ecological problem (Kar *et al.*, 2008 and Nair *et al.*, 2010).

In Iraq like other countries, river pollution levels are no longer inside the boundaries for ingestion, and the statistical distribution avails of water do not concord with the demands. Regarding the importance of this subject, this research was conducted out. In urban area's rivers have metal contamination problems due to the entry of untreated domestic and industrial wastes out flowing inside

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the water bodies (Sekabira *et al.*, 2010). Heavy metals can enter river systems, principally from the point and non-point sources which add vast quantities of inorganic ions and heavy metals (Pandey and Singh, 2017). Heavy metals like Fe, Cu, Zn, Mn, and Cr are requisite keeps assorted biochemical and physiological single-valued function in living organisms, when they are in low concentrations, all the same, they get toxic when transcending certain threshold concentrations (Jaishankar *et al.*, 2014). Although nonessential metals are dangerous even at highly low concentration like Cd and Pb (Paul, 2012). Metal contamination evaluation in the rivers is important because the heavy metals threat aquatic life, human wellness and the environment due to their biomagnifications and perniciousness (Ahmed *et al.*, 2015 and Ali *et al.*, 2016).

## Materials and Methods

### Description of Study Site

Iraqi Kurdistan region is a mountainous land locates, where Syria, Turkey and Iran meet. It has connected of high mountains like Taurus and Zagros mountains, which

schemes a pair of huge arch of about 3000 to 4000 meters elevation and includes an area of approximately 165 000 km<sup>2</sup> (Fig. 1). Kurdistan is bounded to the north by Taurus Mountain in Turkey, to the North West by Syrian, and to the southwest, and south by Hamreen mountain of Iraq (Maulood and Hinton, 1978a).

Dukan Lake is a large reservoir in the Iraqi Kurdistan region, covers an area of about 25000 hectare that is fed by some large and small rivers. The study area is situated between (36° 14' 31" to 35° 41' 03") north and (45° 32' 29" to 44° 36' 34") east. The elevation ranges between (412 to 868) meters over sea level and it is located to the south of Ranya town, about 60 kilometers northwest of Sulaimanyah city is located northern of Iraq, between latitude (35° 31' 26" to 35° 35' 37" N) and longitude (45° 28' 48" to 45° 22' 10" E). It covers all rivers and tributaries flow into the Dukan reservoir. Many tributaries enter the Dukan reservoir from its northwestern part of reservoir.

A series of shorter streams combine the Dukan reservoir in Ranya plain. The Qalachwan River, which flows northward and joins the Lesser Zab River from

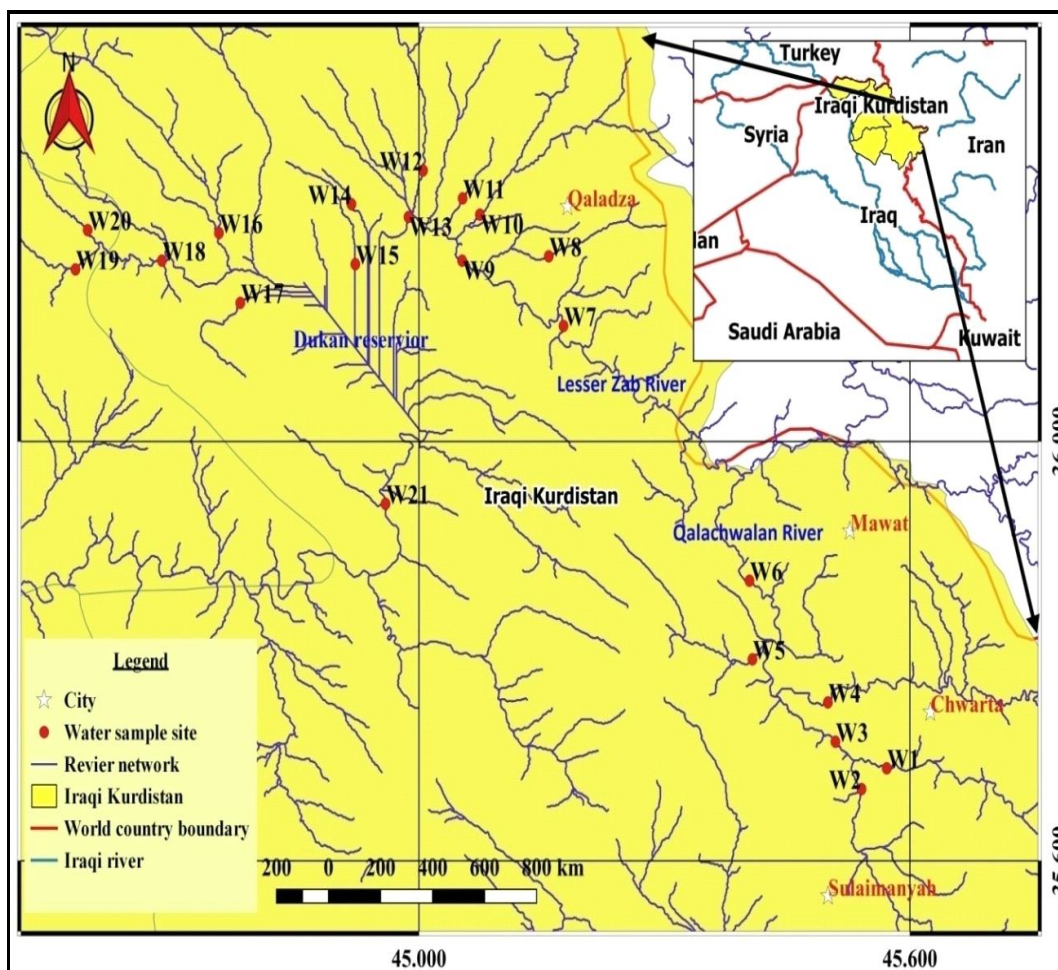


Fig. 1: Map of the studied area with the assignation of water sampling sites.

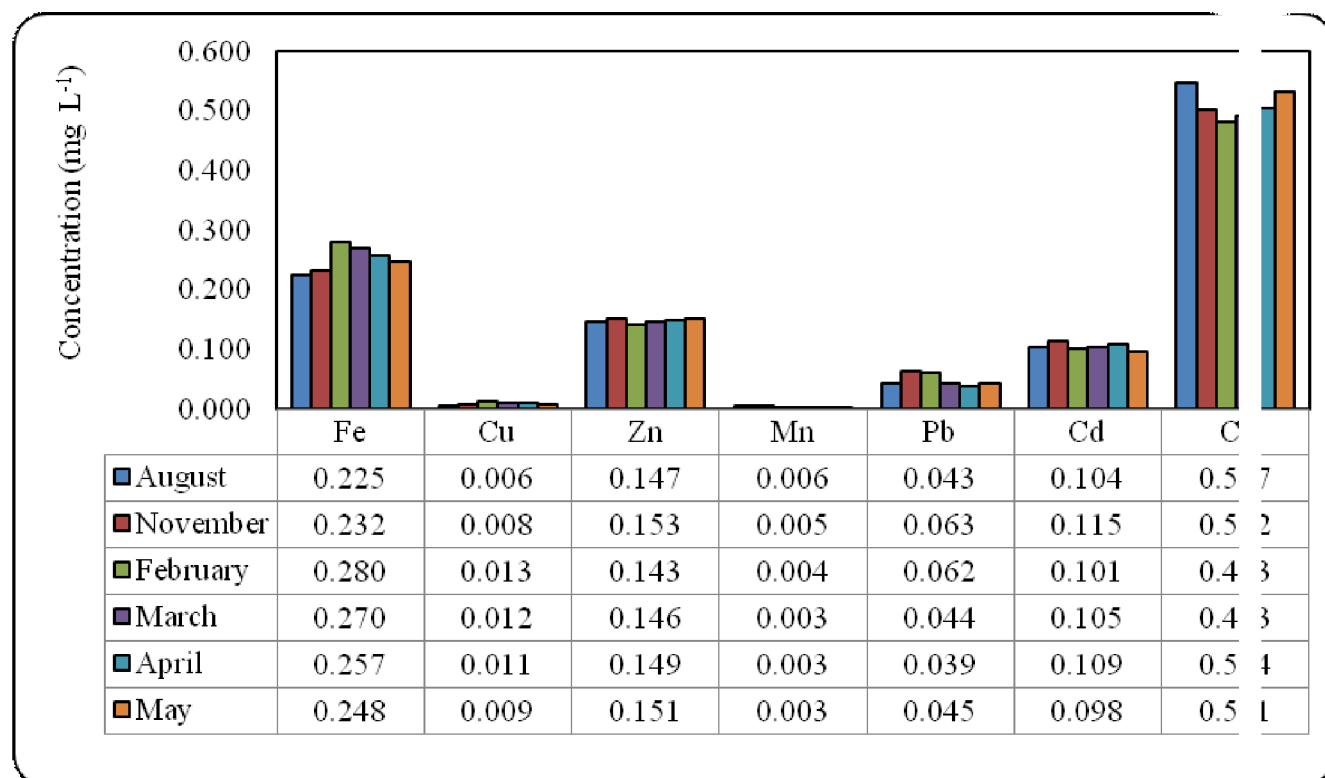
**Table 1:** Details of sampling sites.

Site codes	Sampling sites	Elevation (m)	Latitude	Longitude
W1	Joga-Sur	849	35°41'46"	045°32'29"
W2	Mawakan	868	35°41'03"	045°31'49"
W3	Shakha-Sur	836	35°42'49"	045°30'32"
W4	Siwayl	832	35°45'04"	045°29'59"
W5	Kuna-Masi	792	35°47'32"	045°24'27"
W6	Qashan	736	35°52'02"	045°24'14"
W7	Kawe	537	36°06'37"	045°10'36"
W8	Hallsho	604	36°10'36"	045°09'31"
W9	Sndollan	501	36°10'21"	045°03'10"
W10	Zharawa	501	36°12'59"	045°04'28"
W11	Dolabafra	523	36°13'55"	045°03'12"
W12	Doli-Shahidan	506	36°14'31"	044°59'56"
W13	Darbany-Ranya	493	36°12'51"	044°59'14"
W14	Bosken	514	36°13'35"	044°55'03"
W15	Dukan-Lake	501	36°10'9"	044°55'20"
W16	Qarani-Agha	506	36°11'56"	044°45'20"
W17	Khdran	540	36°07'56"	044°46'54"
W18	Hizop	531	36°10'19"	044°41'10"
W19	Smaquli	625	36°10'09"	044°37'16"
W20	Jali	592	36°11'23"	044°36'34"
W21	Qashqoli	412	35°55'31"	044°57'42"

the Iranian-Iraqi border near an area called Du Choman (Two Rivers) and with tributaries enter the reservoir. The Qalachwalan River and its branches draw off areas around the cities of Penjwin, Chwarta and Mawat. Qalachwalan-Lesser Zab River moves straight numerous villages, towns, and agricultural regions where potential artificial pollution sources could impress its quality of water, in the fact of, the causes of natural pollution such as erosion, spring waters and weathering of outcrops. The area has a semi-arid climate and a mean yearly precipitation about (700 to 800) mm with the maximum of temperature in summer and a minimum temperature in winter and more than (85 %) of the yearly rainfall fall during the four months (February to May).

### Data Collection and Analysis

The water samples (W) were gathered for the duration of (August 2016 to May 2017) in six different months of the year from twenty one sites on the major streams and its tributaries that fed Dukan reservoir, which was shown in (Fig. 1) and (Table 1). Based on the land use pattern differences, including agricultural and residential areas, the sampling sites were selected. Sampling was separated into six field visits during Summer, Autumn, Winter, and Spring, the monthly sampling were chosen situated on the hydrological regime of the area was studied and it was affected by seasonal variations due to rainfall specimen.


**Fig. 2:** Monthly mean changes in the value of metals (mg L<sup>-1</sup>) over the duration of study.

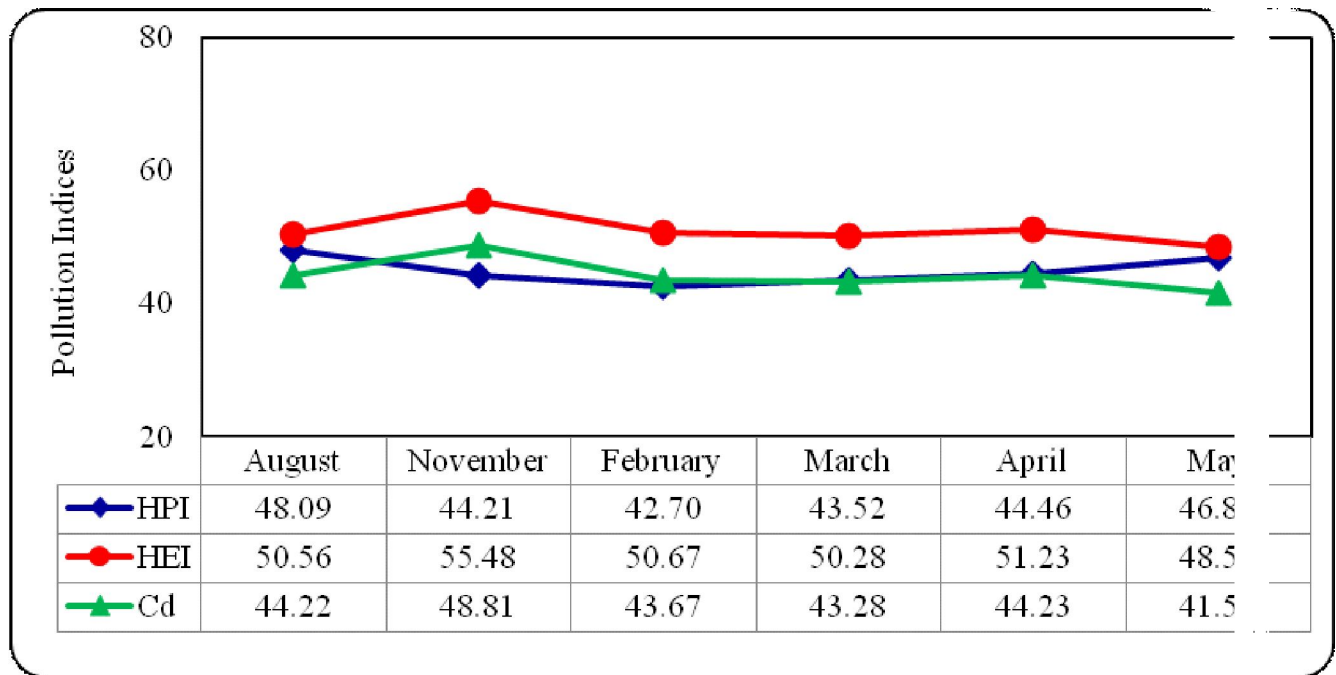


Fig. 3: Comparative studies of pollution evaluation indices.

Table 2: Monthly variation of HPI in studied sites over the duration of study.

Site codes	Months						Mean	±SD
	August	November	February	March	April	May		
W1	44.57	41.82	41.02	41.34	41.79	42.44	42.16	1.28
W2	56.75	51.32	50.08	50.66	51.45	53.29	52.26	2.45
W3	54.35	45.87	44.83	45.68	47.13	50.79	48.11	3.71
W4	52.55	40.62	38.47	39.86	40.89	42.79	42.53	5.11
W5	50.49	35.07	31.74	33.05	35.21	39.54	37.52	6.88
W6	46.04	35.85	35.12	35.97	36.14	37.70	37.80	4.12
W7	56.15	60.18	44.04	44.47	45.60	46.09	49.42	6.93
W8	No	43.76	42.88	43.64	44.05	44.87	36.53	17.91
W9	42.79	39.36	38.29	39.46	39.91	40.52	40.05	1.53
W10	No	37.38	36.80	37.18	37.54	38.72	31.27	15.33
W11	42.10	No	38.21	38.65	39.41	40.02	33.06	16.25
W12	53.37	48.74	47.28	47.99	49.25	50.57	49.53	2.19
W13	63.92	57.41	55.78	54.88	53.91	55.78	56.95	3.61
W14	69.75	61.27	60.70	60.17	60.93	62.05	62.48	3.62
W15	57.45	18.87	42.98	44.95	46.19	51.73	43.70	13.25
W16	52.94	60.49	32.74	35.76	39.09	45.82	44.47	10.70
W17	51.58	44.77	43.46	44.21	44.99	46.65	45.94	2.96
W18	52.42	42.04	39.18	41.31	43.08	45.49	43.92	4.65
W19	52.93	43.44	42.09	42.76	44.38	45.99	45.26	4.00
W20	54.04	60.17	42.84	43.18	43.47	47.95	48.61	7.11
W21	55.80	59.88	48.07	48.65	49.28	53.89	52.60	4.74
Mean	48.09	44.21	42.70	43.52	44.46	46.80	44.96	
±SD	16.94	14.61	6.95	6.41	6.13	6.22		10.63

No: No flows were recorded at those times in the rivers.

**Table 3:** Monthly variation of HEI in studied sites over the period of study.

Site codes	Months						Mean	±SD
	August	November	February	March	April	May		
W1	51.36	55.72	49.42	50.00	48.65	44.39	49.92	3.69
W2	60.19	61.17	50.87	49.86	53.05	46.36	53.58	5.91
W3	57.07	57.01	47.12	47.13	49.48	43.53	50.22	5.61
W4	53.36	56.34	46.01	47.25	49.75	44.96	49.61	4.46
W5	53.88	52.95	43.89	44.76	45.60	46.14	47.87	4.37
W6	54.12	54.12	48.64	49.56	50.79	48.67	50.98	2.55
W7	53.70	61.33	50.06	51.85	51.78	47.86	52.76	4.64
W8	No	53.33	46.95	45.91	47.03	43.47	39.45	19.60
W9	54.97	60.37	54.23	51.24	51.72	49.67	53.70	3.81
W10	No	57.23	52.74	52.29	52.46	49.71	44.07	21.73
W11	44.34	No	42.54	41.32	42.26	38.81	34.88	17.18
W12	65.13	65.14	55.99	55.97	56.81	54.83	58.98	4.81
W13	58.05	61.64	55.73	54.75	54.44	54.52	56.52	2.85
W14	72.15	71.31	70.05	65.48	65.88	64.46	68.22	3.33
W15	56.57	51.13	51.23	53.05	53.42	50.47	52.64	2.24
W16	59.97	66.79	50.27	51.43	54.13	53.24	55.97	6.27
W17	51.79	53.40	49.92	47.13	47.61	46.22	49.35	2.84
W18	47.79	51.44	43.82	43.83	45.30	41.43	45.60	3.54
W19	53.50	53.56	48.71	47.79	48.72	47.58	49.98	2.79
W20	55.20	59.32	49.18	49.01	50.32	47.79	51.80	4.50
W21	58.52	61.76	56.68	56.32	56.56	55.32	57.53	2.32
Mean	50.56	55.48	50.67	50.28	51.23	48.55	51.13	
±SD	17.61	13.77	6.45	5.74	5.35	6.09		10.48

**Table 4:** Monthly variation of  $C_d$  in studied sites over the period of study.

Site codes	Months						Mean	±SD
	August	November	February	March	April	May		
W1	44.36	48.72	42.42	43.00	41.65	37.39	42.92	3.69
W2	53.19	54.17	43.87	42.86	46.05	39.36	46.58	5.91
W3	50.07	50.01	40.12	40.13	42.48	36.53	43.22	5.61
W4	46.36	49.34	39.01	40.25	42.75	37.96	42.61	4.46
W5	46.88	45.95	36.89	37.76	38.60	39.14	40.87	4.37
W6	47.12	47.12	41.64	42.56	43.79	41.67	43.98	2.55
W7	46.70	54.33	43.06	44.85	44.78	40.86	45.76	4.64
W8	No	46.33	39.95	38.91	40.03	36.47	33.61	16.79
W9	47.97	53.37	47.23	44.24	44.72	42.67	46.70	3.81
W10	No	50.23	45.74	45.29	45.46	42.71	38.24	18.89
W11	37.34	No	35.54	34.32	35.26	31.81	29.05	14.34
W12	58.13	58.14	48.99	48.97	49.81	47.83	51.98	4.81
W13	51.05	54.64	48.73	47.75	47.44	47.52	49.52	2.85
W14	65.15	64.31	63.05	58.48	58.88	57.46	61.22	3.33
W15	49.57	44.13	44.23	46.05	46.42	43.47	45.64	2.24
W16	52.97	59.79	43.27	44.43	47.13	46.24	48.97	6.27
W17	44.79	46.40	42.92	40.13	40.61	39.22	42.35	2.84
W18	40.79	44.44	36.82	36.83	38.30	34.43	38.60	3.54
W19	46.50	46.56	41.71	40.79	41.72	40.58	42.98	2.79
W20	48.20	52.32	42.18	42.01	43.32	40.79	44.80	4.50
W21	51.52	54.76	49.68	49.32	49.56	48.32	50.53	2.32
Mean	44.22	48.81	43.67	43.28	44.23	41.55	44.29	
±SD	15.68	12.42	6.45	5.74	5.35	6.09		9.69

The heavy metals were tested by using the analytical methodologies as per (APHA, 2005). The gathered water samples directly forwarded to the laboratory for doing analysis by placing in a cooler at 4 °C. The collected samples were filtered with Millipore filtration unit, filter paper (pore size 0.45 µm) and to minimize adsorption and precipitation metals on the walls of the bottles the samples were preserved by correcting the pH below 2 with nitric acid as described the standard procedure. The heavy metals concentrations, iron (Fe), copper (Cu), zinc (Zn), manganese (Mn), lead (Pb), cadmium (Cd), and chromium (Cr) were determined using Inductively Coupled Plasma Optical Emission Spectrometer (ICP-OES) Optima 2100 DV Series (Perkin-Elmer). It comes with WinLab32 Software which optimizes the workflow and accuracy.

#### Pollution Evaluation Indices

In this study, three various pollution indices, viz. (HPI) heavy metal pollution index, (HEI) heavy metal evaluation index and ( $C_d$ ) degree of contamination. The quality of water for drinking so well irrigation purposes were evaluated by using these indices. The HPI and HEI techniques equip a whole characteristic about the water with consider to heavy metals. On the other side, in the ( $C_d$ ) method, by computing of the extent of pollution the quality of water was measured. Many researchers were used those indices successfully (Edet and Offiong, 2002, Prasad and Mondal, 2008, Zhang *et al.*, 2009, Giri *et al.*, 2010, Virha *et al.*, 2011, Kumar *et al.* 2012, Dý'az *et al.*, 2013, Tiwari *et al.*, 2014, Panigrahy *et al.*, 2015, Mohammad *et al.*, 2015 and Salam, 2016).

**Table 5:** Categories of metal indices and degree of pollution according to sources.

Index method	Category	Degree of pollution	Sources
HPI	<15	Low	(Edet and Offiong, 2002; Giri and Singh, 2014)
	15–30	Medium	
	>30	High	
HEI	<10	Low	(Edet and Offiong, 2002)
	10–20	Medium	
	>20	High	
C <sub>d</sub>	<1	Low	(Edet and Offiong, 2002; Goher <i>et al.</i> , 2014)
	1–3	Medium	
	>3	High	

### Heavy Metal Pollution Index (HPI)

HPI was developed by calculating a rating ( $W_i$ ) for each picked parameter. The rating is value between (0 to 1) and its choice devolve on the importance of separate quality considerations or it can be defined as conversely comparable to the standard allowable rate (Reddy, 1995 and Mohan *et al.*, 1996). In calculating the HPI for the present water quality data, the standard allowable rate ( $S_i$ ) and highest acceptable value ( $I_i$ ) for any parameter were taken from the WHO and IQS. (Mohan *et al.*, 1996) determined the HPI by using the equation below (Eq.1):

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

Where  $Q_i$  is the sub-index of the  $i$ -th parameter.  $W_i$  is the unit rating of the  $i$ -th parameter and  $n$  is the amount of parameters studied. The sub-index ( $Q_i$ ) is estimated by expression below (Eq.2):

$$Q_i = \sum_{i=1}^n \left[ \frac{M_i(-)I_i}{S_i - I_i} \right] * 100 \quad (\text{Eq. 2})$$

**Table 6:** Correlation analysis of different metal concentration and indices values.

	HPI	HEI	C <sub>d</sub>	Fe	Cu	Zn	Mn	Pb	Cd	Cr
HPI	1									
HEI	0.797	1								
C <sub>d</sub>	0.789	0.997	1							
Fe	0.531	0.642	0.623	1						
Cu	0.135	0.195	0.172	0.348	1					
Zn	0.756	0.776	0.760	0.630	0.194	1				
Mn	0.424	0.410	0.435	0.348	0.020	0.445	1			
Pb	0.177	0.443	0.436	0.228	0.141	0.272	0.011	1		
Cd	0.702	0.970	0.971	0.617	0.176	0.723	0.407	0.286	1	
Cr	1.000	0.794	0.786	0.521	0.132	0.753	0.421	0.176	0.698	1

Where, ( $M_i$ ) observed value of heavy metal, ( $I_i$ ) ideal and ( $S_i$ ) standard values of the  $i$ -th parameter, respectively. The signal (-) evidences numerical variances of the two values, ignoring the algebraic signal.

### Heavy Metal Evaluation Index (HEI)

Similar to HPI, HEI assigns an overall water quality based on (Edet and Offiong, 2002) with noticed to heavy metals and it is expressed as follow (Eq.3):

$$HEI = \sum_{i=1}^n \frac{H_{ci}}{H_{maci}} \quad (\text{Eq. 3})$$

Where  $H_{ci}$  is the observed value of the  $i$ -th parameter and  $H_{maci}$  the maximum proper concentration of the  $i$ -th parameter.

### Degree of Contamination (C<sub>d</sub>)

$C_d$  summarizes the compound effects or degree of contamination of several parameters considered potentially harmful to domestic water (Backman *et al.*, 1997).  $C_d$  is a sum of the contamination factors of the separate parameters that exceed their respective allowable values and calculated as follows (Eq.4 and Eq.5):

$$Cd = \sum_{i=1}^n C_{fi} \quad (\text{Eq. 4})$$

Where,

$$C_{fi} = \frac{CA_i}{C_{Ni}} - 1 \quad (\text{Eq. 5})$$

Where  $C_{fi}$ ,  $C_{Ai}$  and  $C_{Ni}$  depict contamination agent, analytical rate and over allowable concentration of the  $i$ -th element, respectively ( $N$  indicates the 'normative value').

### Statistical analysis

To test the differences and the correlation matrix between sites and periods for studied heavy metals and indices, the XLSTAT software at 95% confidence level was used. All the studied data were statistically analyzed by (ANOVA) analysis of variance means were compared using Duncan's multiple comparisons tests.

### Results

Seven heavy metals in river and tributaries were analyzed during six months, and have been used to calculate the HPI, HEI and  $C_d$  (Table 2, 3 and

**Table 7:** Monthly variation of Fe in water ( $\text{mg L}^{-1}$ ) in studied sites over the duration of study.

Site codes	Months						Mean	$\pm$ SD
	August	November	February	March	April	May		
W1	0.231	0.241	0.271	0.262	0.268	0.250	0.254	0.016
W2	0.227	0.213	0.279	0.265	0.268	0.239	0.249	0.026
W3	0.243	0.226	0.266	0.259	0.244	0.247	0.248	0.014
W4	0.218	0.215	0.225	0.222	0.218	0.211	0.218	0.005
W5	0.231	0.221	0.249	0.251	0.242	0.234	0.238	0.011
W6	0.226	0.219	0.240	0.235	0.088	0.228	0.206	0.058
W7	0.232	0.246	0.297	0.295	0.295	0.247	0.269	0.030
W8	No	0.181	0.213	0.206	0.194	0.175	0.162	0.080
W9	0.318	0.305	0.294	0.272	0.279	0.281	0.292	0.018
W10	No	0.314	0.326	0.302	0.309	0.292	0.257	0.127
W11	0.214	No	0.259	0.263	0.253	0.219	0.201	0.101
W12	0.269	0.262	0.339	0.347	0.329	0.300	0.308	0.036
W13	0.243	0.251	0.332	0.319	0.313	0.261	0.287	0.039
W14	0.389	0.382	0.336	0.303	0.292	0.326	0.338	0.040
W15	0.196	0.212	0.182	0.208	0.213	0.204	0.203	0.012
W16	0.308	0.301	0.335	0.253	0.264	0.313	0.296	0.031
W17	0.211	0.203	0.236	0.226	0.225	0.190	0.215	0.017
W18	0.273	0.224	0.337	0.321	0.296	0.286	0.290	0.040
W19	0.234	0.228	0.283	0.270	0.257	0.241	0.252	0.022
W20	0.259	0.242	0.306	0.302	0.279	0.260	0.275	0.026
W21	0.195	0.187	0.270	0.294	0.268	0.198	0.235	0.047
Mean	0.225	0.232	0.280	0.270	0.257	0.248	0.252	
$\pm$ SD	0.086	0.070	0.045	0.038	0.051	0.041		0.061
IQS (2009) Guideline value							0.3 $\text{mg L}^{-1}$	
WHO (2018) Guideline value							None set	

4). The result of the concentrations studied metals in the studied area such as Fe, Cu, Zn, Mn, Pb, Cd, and Cr with standard deviation ( $\pm$ SD), mean, maximum, and the minimum values and compared with (IQS) and (WHO) guidelines have been shown in (Appendix: Table 7 to 13). The metal concentrations were different between sampling sites and months, except in the situation of Mn and Cu where differences in concentrations were not so large.

Generally the concentrations of metals were ranged (0.088 to 0.389), (0.002 to 0.016), (0.112 to 0.223), (0.001 to 0.067), (0.006 to 0.091), (0.074 to 0.153) and (0.211 to 0.790)  $\text{mg L}^{-1}$  for Fe, Cu, Zn, Mn, Pb, Cd and Cr respectively (Appendix: Table 7 to 13). The average monthly metal concentration values for whole studied months ranged with mean  $\pm$ SD were (0.225 to 0.280) (0.252  $\pm$  0.061), (0.006 to 0.013) (0.010  $\pm$  0.004), (0.143 to 0.153) (0.148  $\pm$  0.032), (0.003 to 0.006) (0.004  $\pm$  0.009), (0.039 to 0.063) (0.049  $\pm$  0.019), (0.098 to 0.115) (0.105

$\pm$ 0.023) and (0.483 to 0.547) (0.510  $\pm$  0.121)  $\text{mg L}^{-1}$  for Fe, Cu, Zn, Mn, Pb, Cd and Cr respectively as shown in (Fig. 2) and (Appendix: Table 7 to 13).

From the fig.2, it has been illustrated that the mean heavy metal concentrations such as Cu, Zn and Mn were well below the desirable standard limits of water for drinking in all sites around the duration of study (Appendix: Table 8, 9 and 10). However, at many sites, the mean Fe concentrations were upon the desirable standard limits of water for drinking around the duration of study (Appendix: Table 7). While the mean Pb, Cd and Cr concentrations were found more than the highest desirable limits of the mentioned standard guidelines at whole the studied sites (Appendix: Table 11, 12 and 13) and need steady checking to see malicious increases.

The metal pollution indices in all over the whole studied period were ranged from lowest to highest (18.87 to 69.75), (38.81 to 72.15) and (31.81 to 65.15) for (HPI,

**Table 8:** Monthly variation of Cu in water (mg L<sup>-1</sup>) in studied sites over the duration of study.

Site codes	Months						Mean	±SD
	August	November	February	March	April	May		
W1	0.009	0.008	0.013	0.011	0.010	0.009	0.010	0.002
W2	0.004	0.007	0.013	0.011	0.011	0.009	0.009	0.003
W3	0.005	0.008	0.014	0.012	0.011	0.010	0.010	0.003
W4	0.009	0.008	0.015	0.013	0.012	0.010	0.011	0.003
W5	0.003	0.007	0.009	0.009	0.008	0.008	0.007	0.002
W6	0.002	0.008	0.012	0.011	0.011	0.009	0.009	0.004
W7	0.007	0.011	0.014	0.012	0.010	0.008	0.010	0.003
W8	No	0.008	0.012	0.011	0.009	0.008	0.008	0.004
W9	0.007	0.009	0.013	0.011	0.009	0.006	0.009	0.003
W10	No	0.009	0.013	0.012	0.012	0.010	0.009	0.005
W11	0.007	No	0.013	0.011	0.010	0.008	0.008	0.005
W12	0.005	0.011	0.014	0.012	0.010	0.007	0.010	0.003
W13	0.010	0.010	0.015	0.013	0.012	0.007	0.011	0.003
W14	0.007	0.008	0.016	0.014	0.012	0.008	0.011	0.004
W15	0.009	0.010	0.013	0.012	0.011	0.008	0.011	0.002
W16	0.006	0.009	0.014	0.012	0.011	0.009	0.010	0.003
W17	0.009	0.008	0.014	0.012	0.010	0.008	0.010	0.002
W18	0.006	0.010	0.013	0.013	0.012	0.010	0.011	0.003
W19	0.006	0.009	0.014	0.012	0.011	0.009	0.010	0.003
W20	0.005	0.007	0.014	0.014	0.013	0.010	0.011	0.004
W21	0.009	0.010	0.014	0.013	0.012	0.009	0.011	0.002
Mean	0.006	0.008	0.013	0.012	0.011	0.009	0.010	
±SD	0.004	0.004	0.004	0.004	0.004	0.003		0.004
IQS (2009) Guideline value						1 mg L <sup>-1</sup>		
WHO (2018) Guideline value						2 mg L <sup>-1</sup>		

HEI and  $C_d$ ) have portrayed in (Table 2, 3 and 4) respectively. While the average monthly metal pollution indices value for whole studied months were ranged with mean ±SD (42.70 to 48.09) (44.96 ±10.63), (48.55 to 55.48) (51.13 ±10.48) and (41.55 to 48.81) (44.29 ±9.69) for (HPI, HEI and  $C_d$ ) respectively as schemed in (Fig.3) and (Table 2, 3 and 4).

The highest HPI value 69.75 was observed at sampling site (W14-Bosken) during August, and the lowest value 18.87 was recorded at sampling site (W15-Dukan-Lake) during February, as shown in (Table 2). The highest concentrations for metals were measured in sampling site (W14-Bosken), which implies the highest value for HPI. The result of indices showed that the HPI for all the sites were under the critical restriction of 100 expected water for drinking by (Prasad and Singita, 2008; Prasad and Mondal, 2008). The level of contamination is undesirable above this value. The HPI calculated with mean concentration values of whole metals, in addition

to whole sampling sites is 44.96, which is also well below the critical threshold value of 100, the whole quality of water in respect to metals downfall in the high class (HPI > 30) (Table 5).

The HEI used for a better realizing of pollution indices. The highest HEI value 72.15 was observed at sampling site (W14-Bosken) and the lowest value 38.81 was recorded at sampling site (W11-Dolabafra), (Table 3). The mean HEI value was 51.13 of all metals. By following the method of (Edet and Offiong, 2002), the criteria expected HEI for the samples are as: low, medium and high. The current level of HEI exhibits that the quality of water downfalls into high region of pollution (HEI > 20) as shown in (Table 5).

The  $C_d$  was used by (Al-Ami *et al.*, 1987) as a reference to estimate the degree of metal pollution.  $C_d$  may be categorized into three groups. According to  $C_d$  the highest value 65.15 was obtained at sampling site (W14-Bosken), while the lowest  $C_d$  value 31.81 was



**Table 9:** Monthly variation of Zn in water (mg L<sup>-1</sup>) in studied sites over the duration of study.

Site codes	Months						Mean	±SD
	August	November	February	March	April	May		
W1	0.143	0.148	0.125	0.127	0.131	0.134	0.135	0.009
W2	0.179	0.182	0.162	0.163	0.167	0.169	0.170	0.008
W3	0.148	0.157	0.132	0.137	0.139	0.141	0.142	0.009
W4	0.155	0.156	0.136	0.138	0.139	0.144	0.145	0.009
W5	0.134	0.144	0.112	0.117	0.120	0.123	0.125	0.012
W6	0.146	0.146	0.131	0.135	0.136	0.138	0.139	0.006
W7	0.164	0.161	0.148	0.152	0.156	0.157	0.156	0.006
W8	No	0.126	0.117	0.119	0.122	0.125	0.102	0.050
W9	0.173	0.171	0.154	0.157	0.159	0.162	0.163	0.008
W10	No	0.137	0.126	0.129	0.132	0.135	0.110	0.054
W11	0.150	No	0.131	0.134	0.137	0.139	0.115	0.057
W12	0.161	0.157	0.143	0.147	0.149	0.152	0.152	0.007
W13	0.154	0.154	0.139	0.142	0.144	0.146	0.147	0.006
W14	0.223	0.220	0.207	0.209	0.211	0.213	0.214	0.006
W15	0.156	0.152	0.139	0.141	0.143	0.146	0.146	0.007
W16	0.150	0.150	0.136	0.141	0.143	0.144	0.144	0.005
W17	0.165	0.163	0.151	0.153	0.158	0.157	0.158	0.005
W18	0.171	0.174	0.155	0.158	0.161	0.164	0.164	0.007
W19	0.169	0.172	0.145	0.149	0.153	0.159	0.158	0.011
W20	0.196	0.200	0.174	0.178	0.181	0.185	0.186	0.010
W21	0.151	0.148	0.134	0.137	0.140	0.141	0.142	0.006
Mean	0.147	0.153	0.143	0.146	0.149	0.151	0.148	
±SD	0.052	0.041	0.022	0.022	0.022	0.022		0.032

IQS (2009) Guideline value 3 mg L<sup>-1</sup>  
 WHO (2018) Guideline value None set

obtained at sampling site (W11-Dolabafra) as shown in (Table 4). The studied region was found to have high degree of contamination, as the C<sub>d</sub> average value 44.29 indicates of all metals. The results of indices showed that the value of C<sub>d</sub> beat 3, recommending that water is extremely polluted depending on (Table 5).

In order to distinguish the main contributing parameters to the pollution indices, a correlation was carried out between pollution indices and heavy metal parameters as shown in (Table 6). This suggests that Fe, Zn, Cd, and Cr were the key contributing parameters. HPI, HEI and C<sub>d</sub> show high positive correlations with Fe (0.531, 0.642, and 0.623), Zn (0.756, 0.776, and 0.760), Cd (0.702, 0.970, and 0.971) and Cr (1.000, 0.794, and 0.786). Further, HPI shows low correlation with Cu (0.135) and Pb (0.177). The correlation between HEI and C<sub>d</sub> is very high (0.997) and their results demonstrated similar trends at different sampling sites (Fig. 3). However, HPI is high correlated with HEI (0.797) and with C<sub>d</sub> (0.789). Thus, positive relationships between metal concentrations can be observed, such as Zn/ Fe, Cd/Fe,

Cd/Zn, and, Cr/Fe, Cr/Zn, and Cr/Cd.

### Discussion

Heavy metals are commonly present at lowly concentrations in aquatic habitats however their concentrations may be raised due to anthropogenic stimulus like wastes from municipal, application of fertilizer and pesticides, and industrial effluents (Ntakirutimana *et al.*, 2013). The numerous anthropogenic actions duplicated with land-use shape around these sites must have co-operated to the pollution situation of Pb, Cr and Cd in the study area. The metal loads especially (Pb, Cr and Cd) could also increase due to run-offs into these sites because (Karouna-Renier and Sparling, 2001) have reputed that run-offs away from developed/built-up can bring up metal concentrations in water bodies.

The low of heavy metal concentrations in the surface water may be through dilution, adsorption, and precipitation. However, at many sites, the mean Fe concentrations were upon the desirable limits for drinking water. While the mean Pb, Cd and Cr concentrations

**Table 10:** Monthly variation of Mn in water (mg L<sup>-1</sup>) in studied sites over the duration of study.

Site codes	Months						Mean	±SD
	August	November	February	March	April	May		
W1	0.002	0.002	0.001	0.001	0.001	0.001	0.001	0.001
W2	0.004	0.002	0.002	0.002	0.002	0.002	0.002	0.001
W3	0.002	0.002	0.001	0.001	0.001	0.001	0.001	0.001
W4	0.003	0.002	0.003	0.002	0.002	0.002	0.002	0.001
W5	0.001	0.002	0.002	0.002	0.002	0.001	0.002	0.001
W6	0.003	0.002	0.002	0.002	0.002	0.002	0.002	0.000
W7	0.003	0.002	0.003	0.002	0.003	0.002	0.003	0.001
W8	No	0.001	0.002	0.001	0.001	0.001	0.001	0.001
W9	0.004	0.002	0.003	0.002	0.001	0.001	0.002	0.001
W10	No	0.001	0.002	0.001	0.001	0.001	0.001	0.001
W11	0.001	No	0.002	0.001	0.001	0.001	0.001	0.001
W12	0.003	0.002	0.005	0.002	0.002	0.002	0.003	0.001
W13	0.006	0.004	0.006	0.006	0.005	0.002	0.005	0.002
W14	0.067	0.052	0.033	0.023	0.021	0.018	0.036	0.020
W15	0.004	0.002	0.004	0.002	0.003	0.003	0.003	0.001
W16	0.004	0.003	0.005	0.003	0.003	0.003	0.004	0.001
W17	0.005	0.004	0.002	0.002	0.001	0.001	0.003	0.002
W18	0.005	0.004	0.003	0.002	0.002	0.002	0.003	0.001
W19	0.002	0.002	0.003	0.002	0.002	0.002	0.002	0.000
W20	0.006	0.003	0.002	0.002	0.001	0.001	0.003	0.002
W21	0.007	0.016	0.005	0.006	0.007	0.006	0.008	0.004
Mean	0.006	0.005	0.004	0.003	0.003	0.003	0.004	
±SD	0.014	0.011	0.007	0.005	0.005	0.004		0.009

IQS (2009) Guideline value

0.1 mg L<sup>-1</sup>

WHO (2018) Guideline value

No value established in the fourth edition,  
previously 0.4 mg L<sup>-1</sup>

have been found over than the highest desirable limits because of anthropogenic input. Those high values of some metal could be a suitable symbol of geological compound of rocks and earth influence.

In general, the level of Fe was higher throughout the long rain period across all sites. The highest amount of Fe during August at sampling site (W14-Bosken) this may be attributed to the high evaporation and intense anthropogenic activities (agriculture and high degree of human activities) in summer (Olias *et al.*, 2004), while the smallest rate was recorded in April at sampling site (W6-Qashan). The diluting effect owing to heavy rainfall therefore of rainy season resulted in the sequential reduction of Fe concentration and later on dilutes the river pollutants. The low rates of Cu denote that there is no important source of pollution. The apply of phosphate fertilizers is known to increase Cu levels in rivers from runoffs. The source of high concentration of Mn may be because of agricultural actions taking place in the area with the main source from organic fertilizers. The abnormal concentration of the Pb might be for the increase

amount of agricultural, untreated domestic and urban wastewaters (Yilmaz and Sadikoglu, 2011) discharged into the water nearby the study area that can pose a hazard to humans which depends on water for drinking and household goals as it can cause cancer. The Cd concentrations stay at fairly high levels in the area due to excess enters of contaminated waters that drain from the dumps (Nnabo, 2015).

It was found which the metal concentrations at site (W14-Bosken) situated downstream of the general wastewater were higher than concentrations measured at other sites. This was due to the exposure of site (W14) to the various sorts of pollution such as sewage, animal waste and chemicals used in agricultural, because this site was placed close to populous areas. The highest concentrations for metals were measured in sample site (W14-Bosken), which implies the highest value for HPI, HEI and C<sub>d</sub>. The maximum mean rate of HEI and C<sub>d</sub> was obtained in November while the maximum average value of HPI was in August. However, the HEI and C<sub>d</sub> show similar curves at the most sampling sites. It can be

**Table 11:** Monthly variation of Pb in water (mg L<sup>-1</sup>) in studied sites over the duration of study.

Site codes	Months						Mean	±SD
	August	November	February	March	April	May		
W1	0.031	0.064	0.062	0.054	0.026	0.019	0.043	0.020
W2	0.078	0.084	0.072	0.051	0.041	0.044	0.062	0.019
W3	0.072	0.068	0.057	0.042	0.036	0.028	0.051	0.018
W4	0.043	0.077	0.055	0.051	0.047	0.055	0.055	0.012
W5	0.076	0.079	0.072	0.061	0.058	0.087	0.072	0.011
W6	0.052	0.069	0.062	0.056	0.062	0.070	0.062	0.007
W7	0.021	0.071	0.054	0.051	0.041	0.052	0.048	0.017
W8	No	0.064	0.048	0.026	0.020	0.023	0.030	0.023
W9	0.052	0.091	0.079	0.037	0.034	0.042	0.056	0.024
W10	No	0.074	0.070	0.042	0.036	0.043	0.044	0.027
W11	0.037	No	0.070	0.040	0.038	0.043	0.038	0.022
W12	0.084	0.075	0.038	0.026	0.022	0.030	0.046	0.027
W13	0.033	0.067	0.056	0.042	0.038	0.046	0.047	0.013
W14	0.055	0.050	0.077	0.027	0.023	0.032	0.044	0.021
W15	0.031	0.045	0.058	0.051	0.045	0.043	0.046	0.009
W16	0.049	0.080	0.041	0.038	0.047	0.048	0.051	0.015
W17	0.043	0.055	0.079	0.043	0.036	0.046	0.050	0.015
W18	0.006	0.051	0.065	0.044	0.032	0.038	0.039	0.020
W19	0.053	0.059	0.062	0.045	0.041	0.053	0.052	0.008
W20	0.050	0.061	0.061	0.052	0.045	0.050	0.053	0.006
W21	0.031	0.044	0.065	0.046	0.041	0.050	0.046	0.011
Mean	0.043	0.063	0.062	0.044	0.039	0.045	0.049	
±SD	0.025	0.020	0.013	0.012	0.012	0.017		0.019

IQS (2009) Guideline value 0.01 mg L<sup>-1</sup>  
 WHO (2018) Guideline value 0.01 mg L<sup>-1</sup>

clearly observed that the calculated HPI, HEI and C<sub>d</sub> were found to be more in the dry season than in the wet season. It indicates that the rivers/streams are more amount of waste in the dry season and have less dilution of water that reduced the self sustained.

### Conclusion

According to the obtained results, the concentration of Fe, Cu, Zn, and Mn were obtained below the highest permissible value of suggested guideline standards, while additional metals Pb, Cd, and Cr were revealed high rates and outside limit. The correlation coefficient indicates low and high positive correlation of these metals among them and with pollution indices. Rivers/streams water quality was high affected based on HPI, HEI, and C<sub>d</sub> values. The sampling sites fall in the high grade of contamination classes as per HPI, HEI, and C<sub>d</sub> classifications. The highest values of mentioned indices recorded in sampling sit (W14-Bosken) because it's close to the farmland, villages dump wastes, highway, and the residential area, it's understandable that this pollution is caused by the spill of leachate from the farmland, dump

mound, and air pollution. The mean values for the HPI, HEI and C<sub>d</sub> in dry seasons were higher than of wet seasons, and increasing rainfall magnitudes lead to rising the levels of river water and subsequent decrease the heavy metals concentrations in water due to rainfall dilution effect.

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**Table 12:** Monthly variation of Cd in water (mg L<sup>-1</sup>) in studied sites over the duration of study.

Site codes	Months						Mean	±SD
	August	November	February	March	April	May		
W1	0.112	0.117	0.099	0.103	0.107	0.096	0.106	0.008
W2	0.116	0.121	0.094	0.097	0.109	0.087	0.104	0.013
W3	0.110	0.117	0.091	0.095	0.103	0.085	0.100	0.012
W4	0.109	0.116	0.093	0.097	0.105	0.087	0.101	0.011
W5	0.102	0.109	0.086	0.091	0.093	0.083	0.094	0.010
W6	0.113	0.115	0.101	0.105	0.108	0.097	0.107	0.007
W7	0.114	0.119	0.101	0.107	0.109	0.094	0.107	0.009
W8	No	0.109	0.095	0.098	0.103	0.091	0.083	0.041
W9	0.117	0.124	0.110	0.113	0.115	0.106	0.114	0.006
W10	No	0.121	0.109	0.116	0.118	0.107	0.095	0.047
W11	0.091	No	0.078	0.083	0.086	0.074	0.069	0.034
W12	0.131	0.137	0.121	0.124	0.127	0.118	0.126	0.007
W13	0.118	0.123	0.109	0.111	0.112	0.109	0.114	0.006
W14	0.148	0.153	0.142	0.144	0.146	0.138	0.145	0.005
W15	0.119	0.125	0.105	0.111	0.113	0.101	0.112	0.009
W16	0.126	0.132	0.113	0.116	0.119	0.111	0.120	0.008
W17	0.105	0.111	0.094	0.096	0.099	0.091	0.099	0.007
W18	0.103	0.108	0.082	0.087	0.094	0.079	0.092	0.012
W19	0.106	0.111	0.096	0.098	0.101	0.093	0.101	0.007
W20	0.111	0.116	0.097	0.099	0.105	0.093	0.104	0.009
W21	0.126	0.129	0.115	0.119	0.121	0.112	0.120	0.006
Mean	0.104	0.115	0.101	0.105	0.109	0.098	0.105	
±SD	0.036	0.029	0.016	0.016	0.014	0.016		0.023

IQS (2009) Guideline value 0.003 mg L<sup>-1</sup>

WHO (2018) Guideline value 0.003 mg L<sup>-1</sup>

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**Table 13:** Monthly variation of Cr in water (mg L<sup>-1</sup>) in studied sites over the duration of study.

Site codes	Months						Mean	±SD
	August	November	February	March	April	May		
W1	0.506	0.474	0.464	0.468	0.473	0.481	0.478	0.015
W2	0.646	0.584	0.568	0.575	0.584	0.606	0.594	0.029
W3	0.618	0.521	0.508	0.518	0.535	0.577	0.546	0.043
W4	0.598	0.461	0.436	0.452	0.464	0.486	0.483	0.059
W5	0.574	0.397	0.358	0.373	0.398	0.448	0.425	0.079
W6	0.523	0.406	0.397	0.407	0.413	0.427	0.429	0.047
W7	0.639	0.685	0.498	0.503	0.516	0.523	0.561	0.080
W8	No	0.498	0.487	0.496	0.501	0.511	0.416	0.204
W9	0.483	0.444	0.432	0.446	0.451	0.458	0.452	0.017
W10	No	0.421	0.414	0.419	0.423	0.437	0.352	0.173
W11	0.478	No	0.432	0.437	0.446	0.454	0.375	0.184
W12	0.606	0.553	0.534	0.542	0.557	0.573	0.561	0.026
W13	0.728	0.653	0.632	0.622	0.611	0.634	0.647	0.042
W14	0.790	0.693	0.688	0.683	0.692	0.704	0.708	0.041
W15	0.655	0.211	0.489	0.511	0.525	0.589	0.497	0.152
W16	0.600	0.687	0.367	0.404	0.442	0.518	0.503	0.123
W17	0.587	0.509	0.493	0.502	0.511	0.531	0.522	0.034
W18	0.595	0.477	0.441	0.466	0.487	0.515	0.497	0.054
W19	0.602	0.493	0.476	0.484	0.503	0.522	0.513	0.046
W20	0.614	0.685	0.484	0.488	0.492	0.544	0.551	0.082
W21	0.636	0.683	0.545	0.551	0.559	0.614	0.598	0.056
Mean	0.547	0.502	0.483	0.493	0.504	0.531	0.510	
±SD	0.193	0.167	0.080	0.073	0.070	0.071		0.121

 IQS (2009) Guideline value 0.05 mg L<sup>-1</sup>

 WHO (2018) Guideline value 0.05 mg L<sup>-1</sup>

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