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Assessment of Heavy Metals Pollution in the Sediments of Euphrates River, Iraq

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ABSTRACT

Fourteen bed sediments samples were collected from the Euphrates River in order to determine concentrations, seasonal, spatial and contamination assessment of heavy metals such as Pb, Cd, Zn, Cu, Ni, Co, Fe, Mn and Cr. The mean concentrations are as follows: 2249.47 mg/kg for Fe, 228.18 mg/kg for Mn, 67.08 mg/kg for Ni, 58.4 mg/kg for Cr, 48.00 mg/kg for Zn, 28.16 mg/kg for Co, 22.56 mg/kg for Pb, 18.91 mg/kg for Cu and 1.87 mg/kg for Cd. To assess metal contamination in sediments, sediment quality guidelines were applied. The mean concentration of Cd, Cu, Ni, Fe, Mn, and Cr exceeded the USEPA guideline. The metal contamination in the sediments was also evaluated by appling enrichment factor (EF), contamination factor (CF), geo-accumulation index (Igeo) and pollution load index (PLI). Based on enrichment factor (EF), the Euphrates River sediments have very high enrichment for Pb, extremely high for Cd, moderate for Zn, significant to very high for Ni, very high to extremely high for Co, moderate to significant for Mn and significant to very high for Cr. According to contamination factor (CF), Cd and Cr are responsible for very high contamination. According to Igeo, the Euphrates River sediments are moderately to strongly polluted by Cd. Based on PLI, all sampling sites suggest no overall pollution of site quality.

Keywords: Heavy Metals; Euphrates; River Sediments; Pollution; Iraq

1. Introduction

River sediments are a major carrier of heavy metals in the aquatic environment. Sediments are mixture of several components of mineral species as well as organic debris, represent as ultimate sink for heavy metals discharged into environment [1,2]. Chemical leaching of bedrocks, water drainage basins and runoff from banks are the primary sources of heavy metals [3]. Mining operations, disposal of industrial wastes and applications of biocides for pest are other anthropogenic sources [4]. Heavy metals are serious pollutants because of their toxicity, persistence and nondegradability in the environment [5-8]. Polluted sediments, in turn, can act as sources of heavy metals, imparting them into the water and debasing water quality [9,10]. To date, many researchers have conducted extensive surveys of heavy metal contamination in sediments [3,11-13]. The results demonstrated that accumulation of heavy metals has occurred in sediments of different regions. Limited surveys have been undertaken to study distribution of heavy metals in the Euphrates River sediments [14-16]

The aim of this work is to assess concentrations of the heavy metals and degree of contamination in the Euphrates River sediments.

2. Materials and Methods

2.1. Study Area

The Euphrates River is one of the most important rivers in the world. Along with the Tigris River, it provided much of the water that supported the development of ancient Mesopotamian culture. Euphrates River rise in the highlands of Turkey and it is formed the Karasu and Murat tributary rivers. Euphrates enters Iraq at AlQaim city. During its passage through Iraq, the river crosses more than 1000 km.The water resources in Iraq are concentrated to the Euphrates and Tigris Rivers. The study area is bounded by latitudes (33°26'N to 34°22'N) and Longitudes (41°8'N to 43°20'E), **Figure 1**. The climate of Iraq in summer, is dry and extremely hot with a shade temperature of 43°C during July and August, dropping at night to 26°C. The winter in Iraq is cold and rainy. Average annual rainfall is estimated at 154 mm but it ranges from less than 100 mm in central plain and southern desert in Iraq to 1200 mm in the north and north-east mountainous regions, which have Mediterranean climate. The climate of the western desert, including the study

Figure 1. Location map of study area.

area, is characterized by hot summer and cold winter. This region also receives brief violent rainstorms in the winter that usually total of 10 cm per year.

2.2. Sampling Collection and Analysis

Fourteen sampling sites were chosen for collection of sediments along the Euphrates River (**Figure 2**, **Table 1**). Sampling sites were localized exactly by GPS (Garmin) locator. Auger tube was used for sediment sampling. The sediments samples were collected in winter and spring 2012. The samples were placed in polyethylene bags and transported to the laboratory under frozen condition (at 4˚C). The samples were dried in the laboratory at 104˚C for forty eight hours, ground to a fine powder and sieved through 106μm stainless steel mesh wire. The samples were then stored in a polyethylene container ready for digestion and analysis. Closed vessel microwave assisted acid digestion technique under high temperature and pressure has become routine [17], which avoids the external contamination and requires shorter time and smaller quantities of acids, thus improving detection limits and overall accuracy of the analytical method [18]. 0.5gram of sediment sample was put into the reference vessel. Then 25 ml of mixture (HCL:H_2SO_4:HNO_3, 3:2:2) were added to reaction vessel which was inserted into the microwave unit. The digested solution was cooled and filtered. The filtered sample was then made up to 50ml with distilled water and stored in a special containers. We used AAS (Atomic Absorption Spectrometry) instrument (Phoenix - 986) to detect and measure heavy metal content in the sediment samples.

2.3. Assessment of Metal Contamination

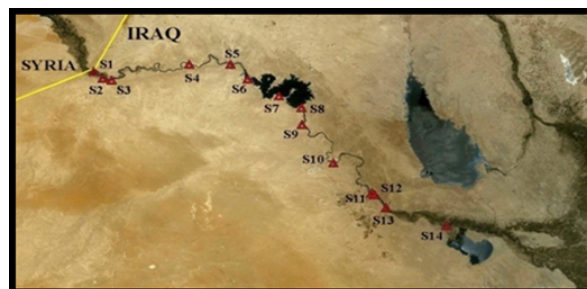To evaluate the degree of contamination in the sediments,

Figure 2. Sampling sites map.

Table 1. Details of sampling locations of Euphrates River.

Site No.	Name of Site	Location	
		Latitude-N	Longitude-E
S1	Albagoz	34˚25'22.7"	41˚01'08.0"
S2	Almanee	34˚22'53.6"	41˚04'23.2"
S3	Alphosphate	34˚22'0.39"	41˚08'02.3"
S4	Jbab	34˚28'09.1"	41˚38'29.4"
S5	Rawa	34˚28'24.2"	41˚54'38.5"
S6	Alkaser	34˚22'42.1"	42˚01'05.9"
S7	Before Haditha Dam	34˚17'01.5"	42˚13'22.8"
S8	After Haditha Dam	34˚11'30.7"	42˚22'18.4"
S9	Hajlan	34˚05'18.6"	42˚22'08.1"
S10	Albaghdadi	33˚51'35.1"	42˚31'58.4"
S11	Hit	33˚39'12.0"	42˚49'01.6"
S12	Aldowara	33˚38'27.3"	42˚49'59.9"
S13	Almohamadi	33˚33'51.3"	42˚45'07.3"
S14	Ramadi	33˚26'23.3"	43˚17'53.5"

we used four parameters: Enrichment Factor (EF), Contamination Factor (CF), Pollution Load Index (PLI) and Geo-accumulation Index (I_{geo}).

Enrichment Factor (EF)

The enrichment factor (EF) of metals is a useful indicator reflecting the status and degree of environmental contamination [19]. The EF calculations compare each value with a given background level, either from the local site, using older deposits formed under similar conditions, but without anthropogenic impact, or from a regional or global average composition [20,21]. The EF was calculated using the method proposed by [22] as follows:

$$EF = (Me/Fe)_{sample} / (Me/Fe)_{background} \qquad (1)$$

where (Me/Fe) sample is the metal to Fe ratio in the sample of interest; (Me/Fe)background is the natural

background value of metal to Fe ratio. As we do not have metal background values for our study area, we used the values from surface world rocks [23]. Iron was chosen as the element of normalization because natural sources (1.5%) vastly dominate its input [24]. Enrichment factor categories are listed in **Table 2**.

Contamination Factor (CF)

The level of contamination of sediment by metal is expressed in terms of a contamination factor (CF) calculated as:

$$CF = C_m Sample/C_m Background \qquad (2)$$

where, C_m Sample is the concentration of a given metal in river sediment, and C_m Background is value of the metal equals to the world surface rock average given by [23]. CF values for describing the contamination level are shown in **Table 3**.

Pollution Load Index (PLI)

Pollution load index (PLI), for a particular site, has been evaluated following the method proposed by [25]. This parameter is expressed as:

$$PLI = \left(CF_1 \times CF_2 \times CF_3 \times \cdots CF_n\right)^{1/n} \qquad (3)$$

where, n is the number of metals.

Geo-accumulation Index (I_{geo})

Enrichment of metal concentration above baseline concentrations was calculated using the method proposed by [26], termed the geo-accumulation index (I_{geo}). Geo-accumulation index is expressed as follows:

$$I_{geo} = Log_2 \left[C_m Sample/\left(1.5 \times C_m Background\right) \right] \qquad (4)$$

where C_m Sample is the measured concentration of element n in the sediment sample and B_m Background is the geochemical background value ([world surface rock average given by [23]). The factor 1.5 is introduced to include possible variation of the background values due to lithogenic effect. Muller [27] proposed seven grades or classes of the geo-accumulation index. These classes are given in **Table 4**. The overall total geo-accumulation index (I_{tot}) is defined as the sum of I_{geo} for all trace elements obtain from the site [28]. The number of toxic elements determined in a sediment sample and their respective I_{geo} value would influence the I_{tot}.

Table 2. Enrichment factor (EF) categories (Mmolawa *et al*. 2011).

Enrichment factor (EF)	Enrichment factor (EF) Categories
EF < 2	Deficiency to minimal enrichment
2 ≤ EF < 5	Moderate enrichment
5 ≤ EF < 20	Significant enrichment
20 ≤ EF < 40	Very high enrichment
EF ≥ 40	Extremely high enrichment

Table 3. Contamination factor (CF) and level of contamination (Hakanson, 1980).

Contamination Factor (CF)	Contamination Level
Cf < 1	Low contamination
1 ≤ Cf < 3	Moderate contamination
3 ≤ Cf < 6	Considerable contamination
Cf > 6	Very high contamination

Table 4. Muller's classification for geo-accumulation index (I_{geo}).

I_{geo} Value	Class	Sediment Quality
≤0	0	Unpolluted
0 - 1	1	From unpolluted to moderately polluted
1 - 2	2	Moderately polluted
2 - 3	3	From moderately to strongly polluted
3 - 4	4	Strongly polluted
4 - 5	5	From strongly to extremely polluted
>6	6	Extremely

3. Results and Discussion

The descriptive statistics of the data set pertaining to the Euphrates River sediments, geochemical background concentration and sediment quality guidelines are presented in **Table 5**. Intermetallic correlation, seasonal and spatial variations were delineated in **Table 6** and shown in **Figures 3** and **4**. Results of this study were compared with the other previous local and global studies, **Table 7**.

The enrichment factor (EF) is a convenient measure of geochemical trends and is used for making comparisons between areas [22]. The EF values of heavy metals in the Euphrates River sediments were listed and **Table 8** and shown in **Figure 5**.

The contamination factor (CF) was used to determine the contamination status of sediments of Euphrates River. The calculated CF for various heavy metals in sediments of Euphrates River is presented in **Table 9** and shown in **Figure 6**.

The PLI provides simple but comparative means for assessing a site quality, where a value of PLI < 1 denotes perfection; PLI = 1 presents that only baseline levels of pollutants are presented and PLI > 1 would indicate deterioration of site quality [25] The PLI values for heavy metals in the Euphrates River sediments are listed in **Table 10** and shown in **Figure 7**.

The geo-accumulation index (I_{geo}) was used to determine the pollution level of sediments. The calculated I_{geo} values, based on the world surface rock average, are presented in

Table 5. Concentration of heavy metals in the sediments samples of Euphrates river during the study period.

| Metal | Minimum | Maximum | Mean | Standard deviation | Geochemical Background | | WHO[3] SQG* | USEPA[4] SQG* | CCME[5] SQG* |
					World[1] surface rock average	Mean shale concentration			
Pb	8.02	32.69	22.56	7.37	16	20	-	40	35
Cd	0.87	2.35	1.87	0.45	0.2	0.3	6	0.6	0.6
Zn	14.96	130.25	48.00	31.25	127	95	123	110	123
Cu	10.35	30.52	18.91	5.59	32	11.2	25	16	35.7
Ni	39.98	103.98	67.08	19.36	49	68	20	16	-
Co	21.88	38.73	28.16	4.91	13	29	-	-	-
Fe	928.7	3441.05	2249.47	571.18	35900	46700	-	30	-
Mn	136.05	312.11	228.18	56.13	750	850	-	30	-
Cr	36.45	120.11	58.40	21.73	71	90	25	25	37.3

Values are in milligram per Kilogram (mg/kg); [1]Martin and Meybeck [23]; [2]Venkatesha Raju [3]; [3]WHO [32]; [4]USEPA [33]; [5]CCME [17]; *Sediment quality guidelines.

Table 6. Pearson's correlation coefficient of heavy metals in Euphrates River sediments.

Metal	Pb	Cd	Zn	Cu	Ni	Co	Fe	Mn	Cr
Pb	1.000								
Cd	0.436	1.000							
Zn	0.515	0.374	1.000						
Cu	0.519	**0.598**	**0.758**	1.000					
Ni	0.380	0.487	0.387	**0.683**	1.000				
Co	0.472	0.032	0.577	0.234	0.053	1.000			
Fe	**0.610**	0.522	**0.595**	**0.617**	0.318	0.084	1.000		
Mn	0.047	**0.699**	−0.086	0.401	0.342	−0.485	0.208	1.00	
Cr	0.441	**0.580**	**0.808**	**0.574**	0.421	**0.668**	0.451	−0.035	1.00

Marked correlations are significant at $p < 0.05$.

Table 11 and the variations are shown in **Figure 8**.

The concentration of Pb varied from 8.02 to 32.69 mg/kg, and mean value was 22.56 mg/kg. It was more than the world surface rock average and the shale concentration as a background level. In comparison with sediment quality guideline, the mean value did not exceed the limits, and this result shows that the Euphrates River sediments are not polluted by Pb. Pb expressed a strong positive correlation with Fe at 0.05 level. The strong correlation indicates that the two elements have common sources. In general, Pb concentrations in sediments were high during the spring than winter (**Figure 3(a)**). Pb concentration varies between 8.02 mg/kg at S6 and 32.69 mg/kg at S1, **Figure 4(a)**. High values of Pb concentration at S7, S8 (Haditha Dam), S12 (Heet city) and S14 (Ramadi city) as well as S1 (AlQaim city) might

be due to increased human activity since these are township areas. Pb concentration was in a good agreement to that reported in study of [14] for the upper region of Euphrates River (same study area) and study of [29] for the Euphrates River profile in Iraq (**Table 7**). It was less than that recorded by [15] for two stations in Heet and Ramadi cities. It was also less than the world rivers average [23].

The EF values for Pb in Euphrates River sediments were ranged from 9.35 to 35.97. The EF values for Pb were found to be greater than 20 in most of sampling sites (**Table 8**), suggesting that these sites are classified as very high enrichment for Pb. Rabee *et al*. [15] found that the EF values for Pb in two stations in Heet and Ramadi cities are 5.4 and 6.20, respectively. They classified these stations as significant enrichment for Pb. The

Table 7. Concentrations of heavy metals in the Euphrates river sediments (in mg/kg) in comparison to other local studies, for other rivers and world river sediments averages.

River/Date of sampling/ Location	Pb	Cd	Zn	Cu	Ni	Co	Fe	Mn	Cr	Reference
Euphrates 1997 Iraq	19.5	0.08	30	24.6	125	-	-	450	-	[14]
Euphrates 2008 Iraq	39.1	0.73	-	46.6	29.1	-	-	302.75	-	[15]
Euphrates 1998 Iraq	19.5	3.6	91.16	45.25	182.91	48.6	-	-	119.4	[29]
Euphrates 2004-2005 Iraq	0.59	11.2	67.66	14.14	0.37	8.24	661.7	37.7	0.47	[16]
Tigris Iraq	43.4	-	54.6	25.5	155.3	44.9	-	-	865.4	[34]
Tigris 1993 Iraq	17.9 - 30.6	0.1 - 1.7	8.3 - 47.1	17.4 - 28.9	105.4 - 125.5	-	-	451.3 - 565.6	-	[35]
Tigris 2008 Iraq	7 - 90	0.3 - 1.3	-	5 - 55	6 - 30	-	-	166 - 426	-	[36]
Yangtze 2005 China	49.19	0.98	230.39	60.03	41.86				108.00	[13]
Tapti India	-	-	1.17 - 6.06	0.52 - 4.07	-	-	1.88 - 5.71	6 - 8.9	-	[37]
Buriganga Bangladesh	79.8	0.8	502.3	184.4	-	-	-	-	101.2	[38]
Cauvery 2007-2009 India	4.3	1.3	93.1	11.2	27.7	1.9	11144	176.3	38.9	[3]
World average	230.75	1.4	303	122.9	102.1	55.3	57405.9	975.3	126	[23]

Table 8. Enrichment ratio (ER) values of heavy metals in Euphrates river sediments.

Sampling Site	Pb	Cd	Zn	Cu	Ni	Co	Mn	Cr
S1	26.92	143.23	5.06	8.93	26.29	33.27	4.69	13.77
S2	16.66	167.90	5.37	12.51	33.61	26.66	6.28	11.84
S3	24.59	189.95	4.97	11.97	31.00	30.18	6.34	11.48
S4	24.84	183.99	4.61	9.70	18.15	34.87	7.09	11.46
S5	21.05	157.96	5.47	10.57	18.42	28.82	6.28	10.42
S6	9.35	141.84	2.43	6.64	15.22	39.42	4.94	13.87
S7	35.97	176.22	4.53	9.95	20.88	49.01	4.60	14.47
S8	18.60	80.33	4.73	6.79	13.15	20.88	2.56	6.04
S9	30.82	168.15	4.55	12.50	48.40	90.60	7.01	19.84
S10	27.82	103.70	7.55	9.02	19.62	38.58	3.91	11.20
S11	21.62	172.13	3.44	5.61	19.54	27.69	4.48	14.52
S12	22.72	145.53	10.87	9.34	20.26	34.60	4.01	15.78
S13	15.77	164.02	4.81	9.16	14.82	35.04	5.59	12.39
S14	23.12	146.61	12.90	12.00	22.27	37.49	3.23	21.28

Table 9. Contamination factor (CF) for the heavy metals of Euphrates river sediments.

Sampling Sites	Pb	Cd	Zn	Cu	Ni	Co	Fe	Mn	Cr
S1	2.04	10.45	0.37	0.65	1.93	2.42	0.072	0.342	1.00
S2	1.05	10.6	0.34	0.78	2.12	1.68	0.063	0.396	0.74
S3	1.43	11.05	0.29	0.69	1.80	1.75	0.058	0.374	0.66
S4	1.43	10.65	0.26	0.56	1.05	2.01	0.057	0.410	0.66
S5	1.39	10.45	0.36	0.69	1.21	1.90	0.066	0.416	0.68
S6	0.50	7.6	0.13	0.35	0.81	2.11	0.053	0.266	0.74
S7	2.01	9.85	0.25	0.55	1.16	2.74	0.055	0.257	0.80
S8	1.78	7.7	0.45	0.65	1.26	2.00	0.095	0.245	0.57
S9	0.79	4.35	0.11	0.32	1.25	2.34	0.025	0.181	0.51
S10	1.47	5.5	0.40	0.47	1.04	2.04	0.053	0.207	0.59
S11	1.47	11.75	0.23	0.38	1.33	1.89	0.068	0.306	0.99
S12	1.63	10.45	0.78	0.67	1.45	2.48	0.071	0.288	1.13
S13	0.87	9.05	0.26	0.50	0.94	1.93	0.055	0.308	0.68
S14	1.83	11.65	1.02	0.95	1.77	2.97	0.079	0.257	1.69
Mean	1.40	9.36	0.37	0.58	1.36	2.16	0.062	0.30	0.81

Table 10. Geo-accumulation indices (I_{geo}) of heavy metals in Euphrates River sediments.

Sampling Sites	Pb	Cd	Zn	Cu	Ni	Co	Fe	Mn	Cr	I_{tot}
S1	0.44	2.79	−2.05	−1.21	0.35	0.69	−4.36	−2.13	−0.57	−6.05
S2	−0.51	2.81	−2.18	−0.94	0.49	0.16	−4.57	−1.92	−1.00	−7.66
S3	−0.07	2.87	−2.39	−1.12	0.26	0.22	−4.70	−2.00	−1.16	−8.09
S4	−0.06	2.82	−2.55	−1.43	−0.51	0.42	−4.69	−1.87	−1.17	−9.04
S5	−0.10	2.79	−2.05	−1.12	−0.30	0.34	−4.50	−1.85	−1.12	−7.91
S6	−1.60	2.33	−3.64	−2.12	−0.88	0.49	−4.80	−2.49	−1.01	−13.72
S7	0.42	2.71	−2.55	−1.43	−0.37	0.86	−4.74	−2.54	−0.89	−8.53
S8	0.25	2.35	−1.73	−1.21	−0.25	0.41	−3.96	−2.61	−1.37	−8.12
S9	−0.91	1.53	−3.83	−2.25	−0.26	0.64	−5.86	−3.05	−1.54	−15.52
S10	−0.03	1.87	−1.94	−1.68	−0.53	0.44	−4.82	−2.85	−1.33	−10.87
S11	−0.03	2.96	−2.73	−2.00	−0.18	0.33	−4.45	−2.29	−1.39	−9.78
S12	0.11	2.79	−0.94	−1.18	−0.04	0.72	−4.38	−2.38	−0.40	−5.70
S13	−0.78	2.59	−2.55	−1.59	−0.68	0.36	−4.76	−2.28	−1.13	−10.82
S14	0.28	2.95	−0.55	−0.66	0.85	0.98	−4.24	−2.54	0.17	−2.76

Table 11. Pollution load index (PLI) values for heavy metals in Euphrates river sediments.

PLI	Sampling Sites
0.94	S1
0.83	S2
0.80	S3
0.74	S4
0.81	S5
0.52	S6
0.77	S7
0.79	S8
0.45	S9
0.64	S10
0.75	S11
0.96	S12
0.65	S13
1.15	S14

CF values for Pb in Euphrates River sediments varied from 0.50 to 2.04 with a mean value of 1.4, **Table 9**. Most sampling sites has CF greater than 1 and less than 3. It was found that most sampling sites were moderately contaminated by Pb except S6, S9 and S13 face low contamination (**Table 3**). The I_{geo} values for Pb in majority of sampling sites were less than 0 (<0), except S1, S7 and S14 were less than 1 (<1), **Table 10**. According to Muller's classification (**Table 4**), the calculated I_{geo} values for Pb indicate sediment quality be considered as polluted for majority of sites and from unpolluted to moderately polluted for S1, S7 and S14.

Cd concentration varied between 0.87 and 2.35 mg/kg and mean value was 1.87 mg/kg. It was more than the world surface rock average and the mean shale concentration as a geochemical background level (**Table 5**). The mean value of Cd concentration did not exceed the WHO sediment quality guidelines and exceeded the USEPA guidelines. According to USEPA, Euphrates River sediments were polluted by Cd. Generally, Cd concentrations were highest during spring at downstream sites and highest during winter at upstream sites, **Figure 3(b)**. The mean value of Cd concentration has strong positive correlation with Mn at 0.05 level. It has also good positive
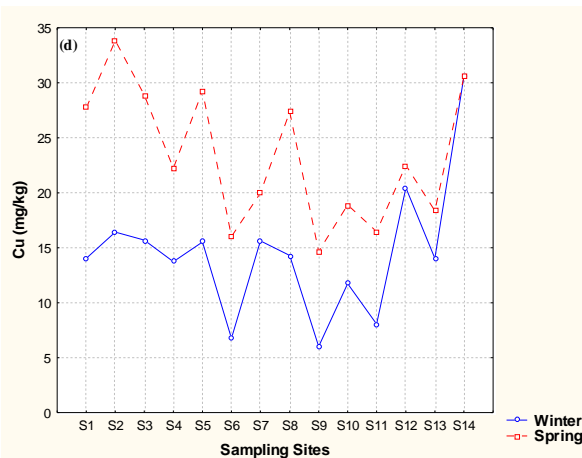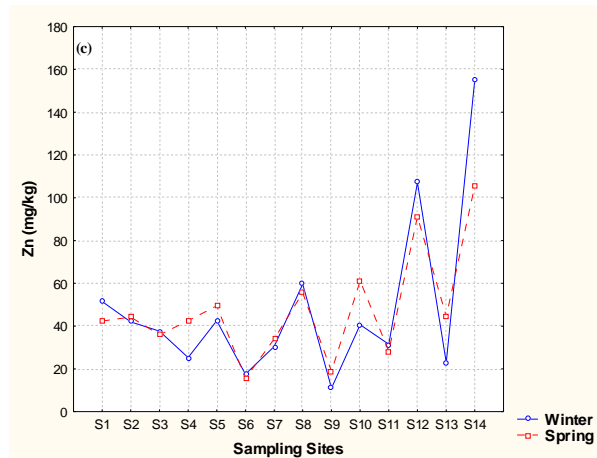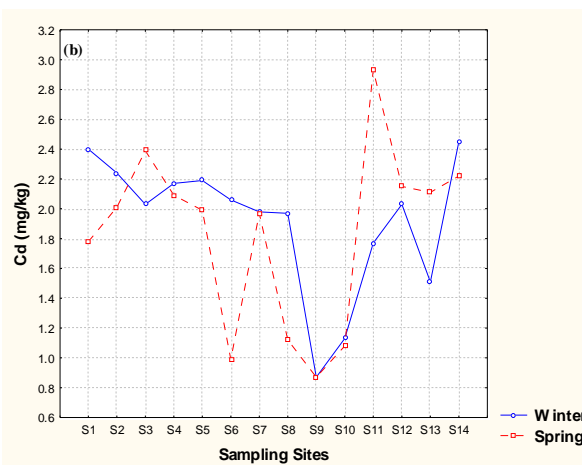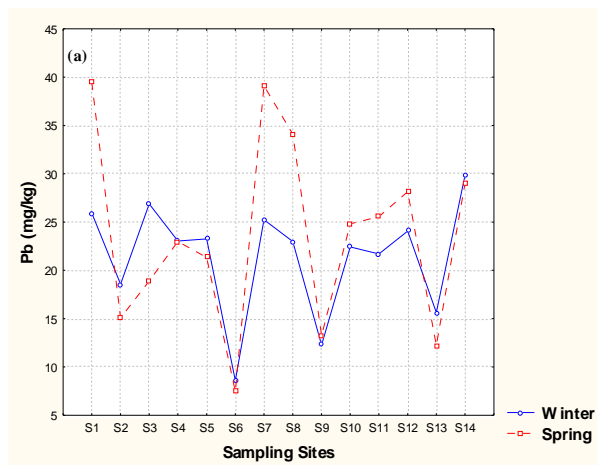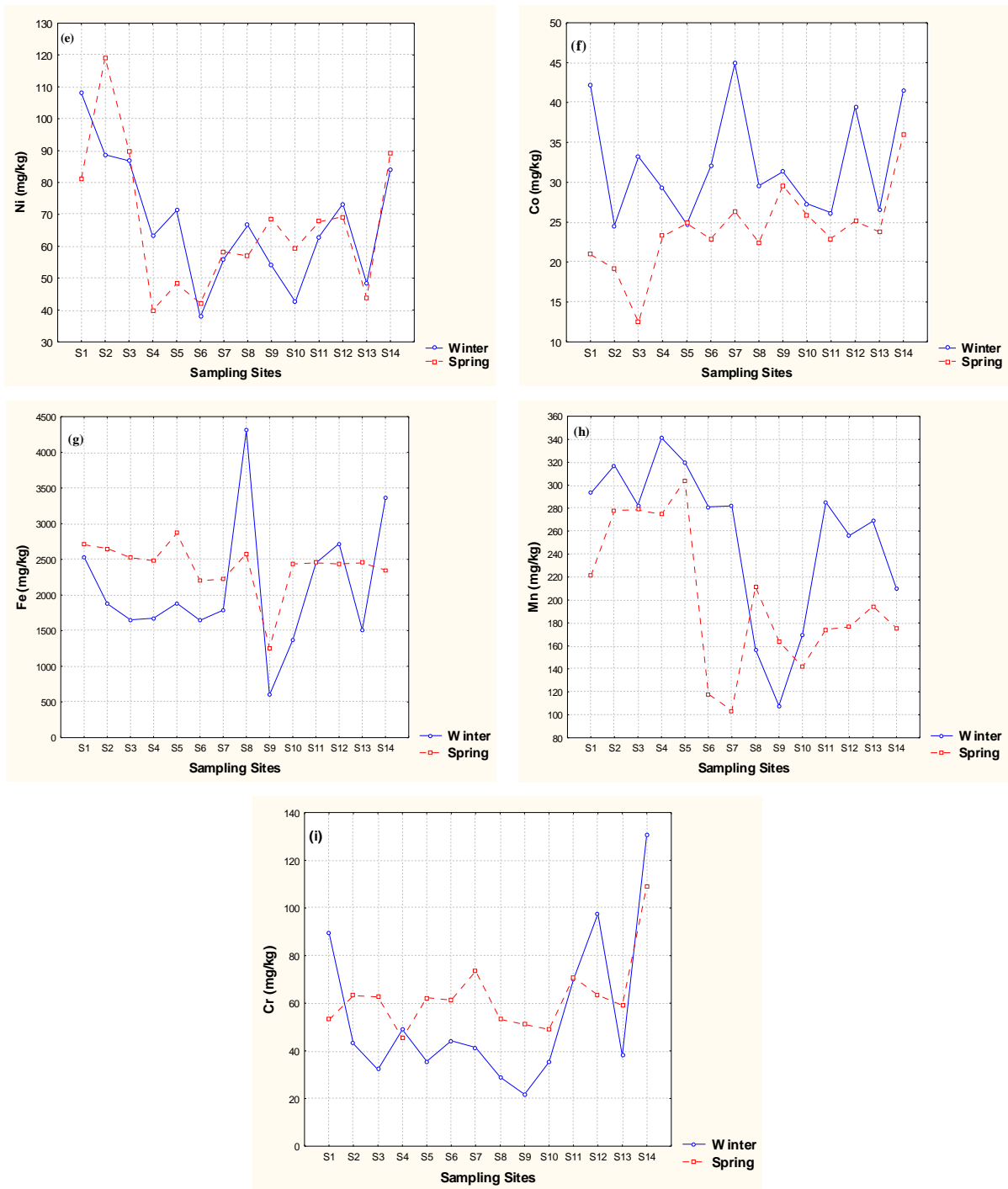
Figure 3. Seasonal and spatial variations of heavy metals in Euphrates river sediments.

correlation with Cu and Cr at 0.05 level. The good and strong positive correlations indicate that these heavy metals have common contamination sources. Spatial variation of Cd concentration was given in **Figure 4(b)**, the maximum value was 2.35 mg/kg at S11and the minimum value was 0.87 mg/kg at S9. High values, were recorded at S3 (near Phosphate Factory), S11 (Heet city) and S14 (Ramadi city). These high values may be attrib-

uted to the anthropogenic activities such as urbanization, industrialization and agricultural runoff. The mean value of Cd concentration was more than that assessed by [14] and by [15]. It was also more than that of the world rivers average [23]. It was less than that reported by [29]. Al-Bassam [30] suggested that anthropogenic sources may have significant role in the enrichment of Cd in the Euphrates River sediments. These sources include discharging of
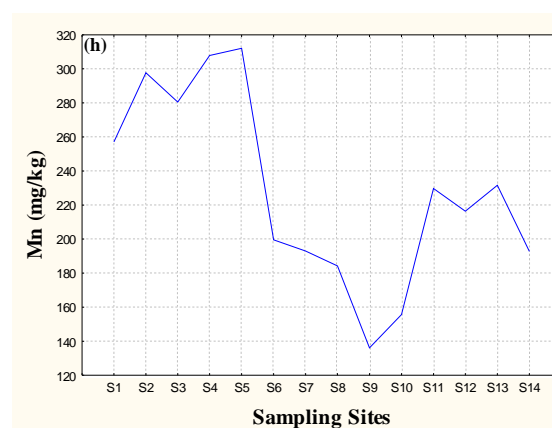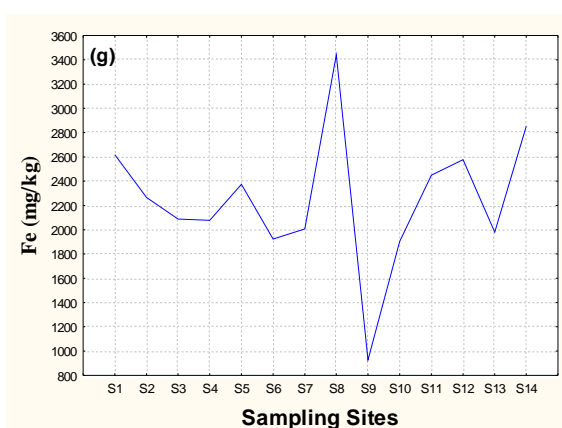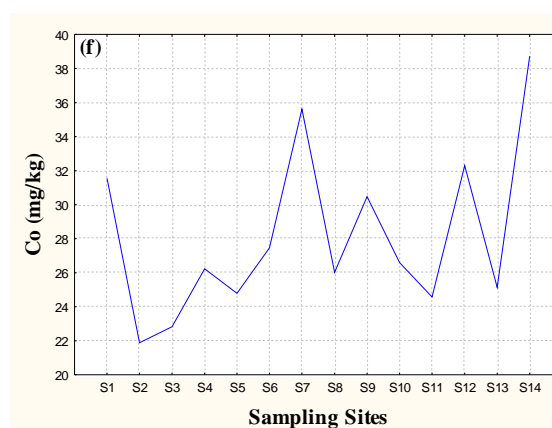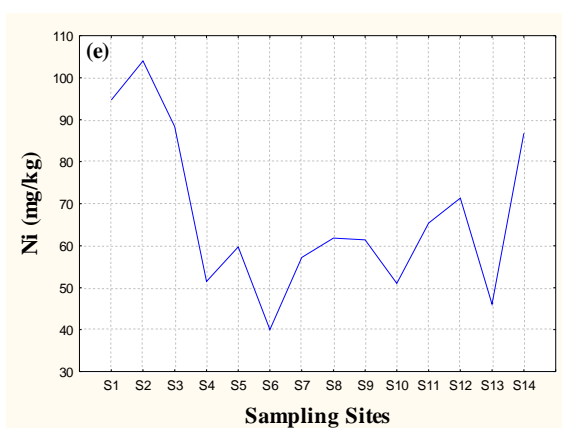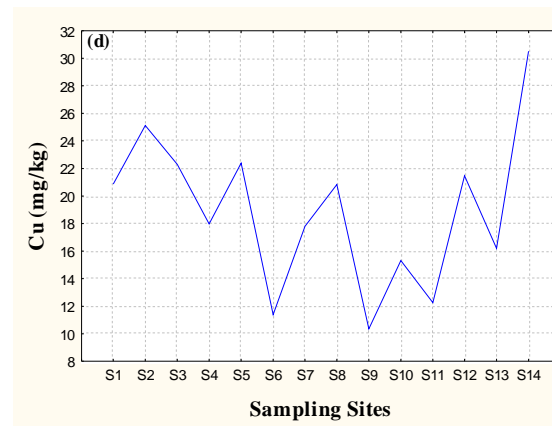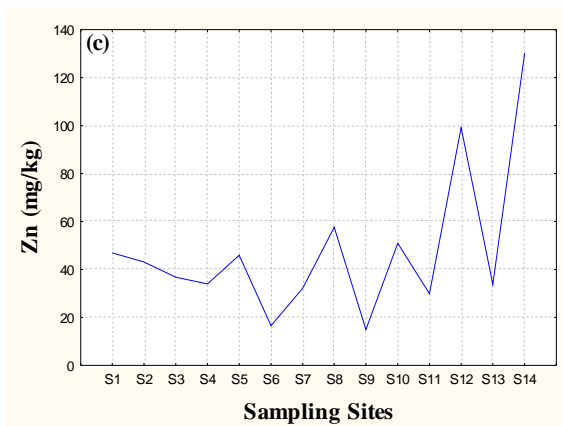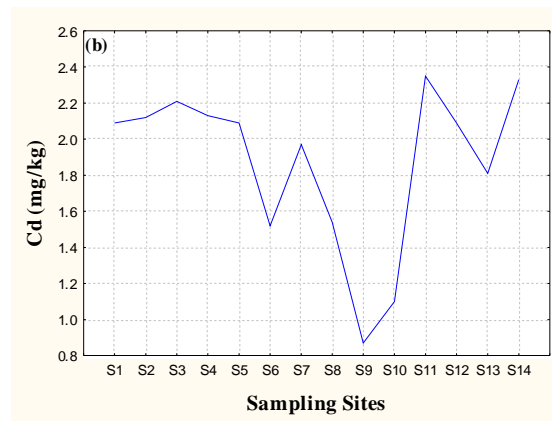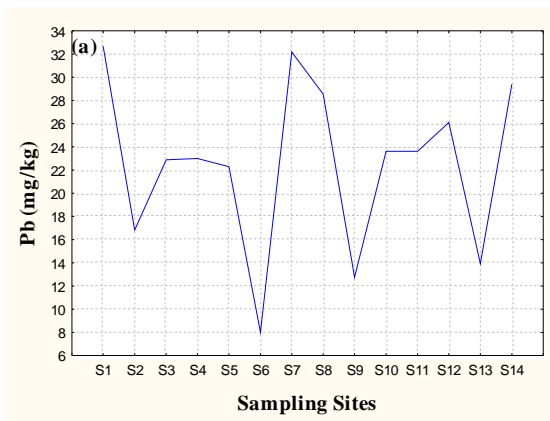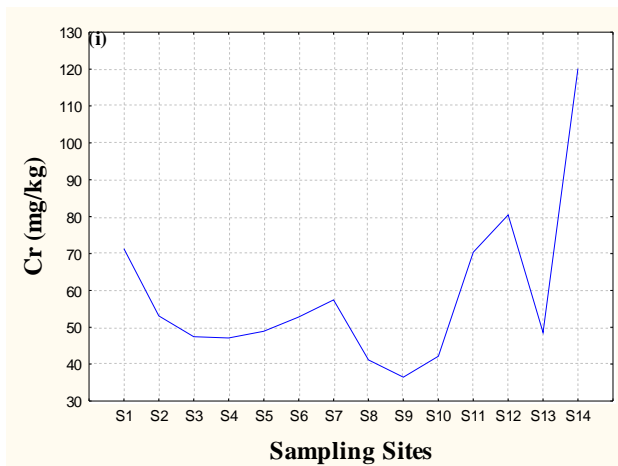
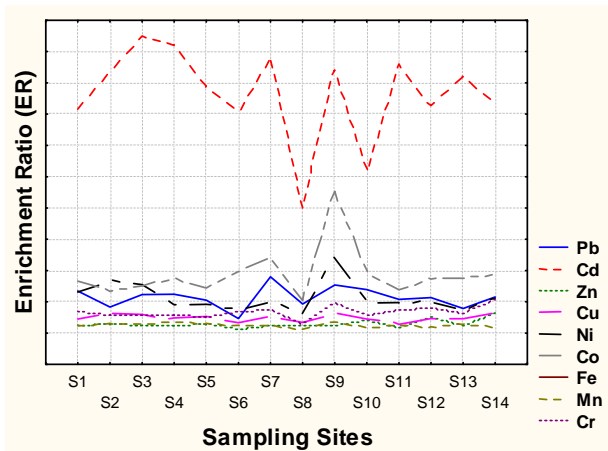**Figure 4. Spatial variation of heavy metals in Euphrates River sediments.**

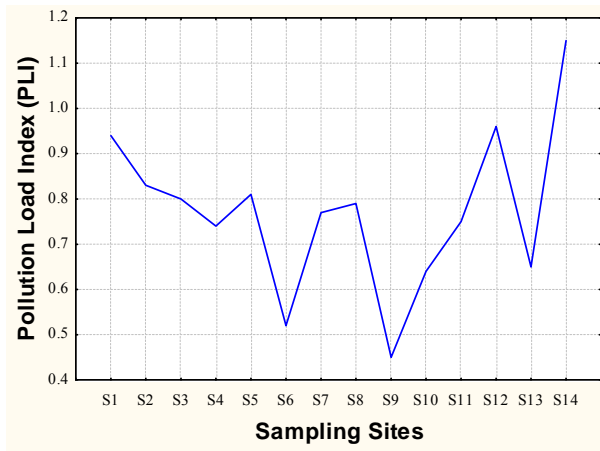**Figure 5. Enrichment ratio (ER) of heavy metals in Euphrates River sediments.**

Figure 7. Pollution load index values of sampling sites at Euphrates River.
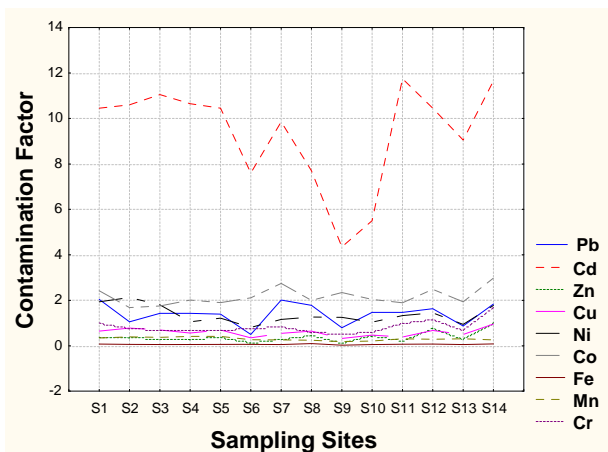

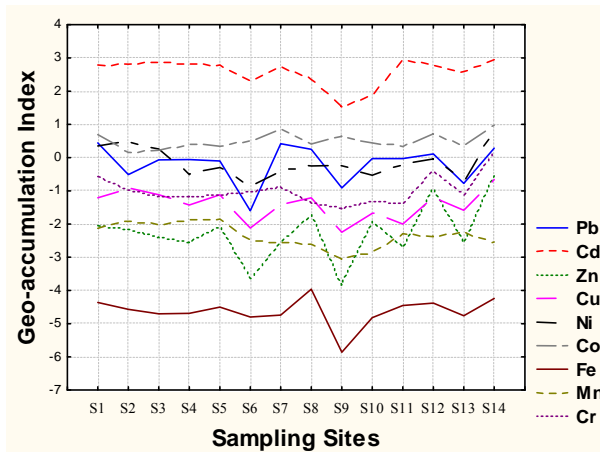**Figure 6. Contamination factor (CF) of heavy metals In Euphrates River sediments.**

Figure 8. Geo-accumulation indices (GIs) of heavy Metals in Euphrates River sediments.

irrigation water, rich in phosphate fertilizers, to the river and discharging untreated municipal heavy water to the river without treatment from highly populated cities.

The EF values for Cd in the Euphrates River Sediments varied between 80.70 to 189.95. The EF values of Cd were greater than 40 for all sampling sites, suggesting

that these sites are classified as extremely high enrichment (**Table 8**). The EF values for Cd in two stations in Heet and Ramadi cites are 8.60 and 5.80, respectively [15]. They classified these stations as significant enrichment for Cd.

The contamination factor (CF) values for Cd varied from 5.5 at S10 to 11.75 at S12 with a mean value of 9.36 (**Table 9**). All sampling sites has more than 6 (<6) except S10 less than 6 (6>). According to [31], all sampling sites were very high contaminated by Cd except S10 faces considerable contamination.

The I_{geo} values for Cd in Euphrates River sediments ranged from 1.53 to 2.96. All sampling sites has I_{geo} for Cd more than 2 and less than 3 ($2 < I_{geo} < 3$) except sites S9 and S10 more than 1 and less than 2 ($1 < I_{geo} < 2$). According to Muller's classification (**Table 4**), the I_{geo} values for Cd indicate that Euphrates River sediments are moderately to strongly polluted for most sampling sites and moderately polluted for S9 and S10. Rabee *et al.* [15] found that the I_{geo} values for Cd in the Euphrates River stations (Heet and Ramadi cities) indicate the sediments were unpolluted to moderately polluted.

Zn concentration ranged between 14.96 and 130.25 mg/kg. The mean value was 48 mg/kg. It was less than the world surface rock average and the mean shale background concentration as a geochemical background level (**Table 5**). In comparison, it was found that Zn mean value was below WHO, USEPA and CCME guidelines. According to sediment quality guidelines, Euphrates River sediments were unpolluted by Zn. Zn expressed strong positive correlation with Cu and Cr, and good positive correlation with Co and Fe at 0.05 level. There are not clear differences in Zn concentration between winter and spring, **Figure 3(c)**. Zn concentration varies between 14.96 at S9 and 130.25 at S14, **Figure 4(c)**. High values of Zn concentration were reported at S8 and S12. Zn concentration at S14 was more than sediment quality guidelines (**Table 5**). This indicates that Euphrates River sediments at S14 was polluted by Zn due to sewage water in Ramadi city. In comparison with previous studies (**Table 7**), We found that Zn concentration recorded in this study was near to that estimated by [14] and less than that assessed by [16,23,29].

The enrichment factor (EF) values for Zn in Euphrates River sediments ranged from 2.43 at S6 to 12.9 at S14. The EF values for majority of sampling sites were greater than 2 and less than 5 (**Table 8**), suggesting that these sites are classified as moderate enrichment for Zn. The other sites, S1, S2, S5, S10, S12, and S14) are classified as significant enrichment. These sites are in or near the township area.

The CF values for Zn in the Euphrates River sediments varied from 0.11 at S9 and 1.02 at S14 with mean value of 0.37 (**Table 9**). Most sampling sites has CF less than 1 except S14 more than 1. It was found that most sampling sites were classified as low contaminated and S14 faces moderate contamination.

The I_{geo} values for Zn in all sampling sites were less than 0 (<0), **Table 10**. These negative values indicate that the Euphrates River sediments in the study area are unpolluted by Zn.

Cu concentration varied from 10.35 to 30.52 mg/kg and 18.91 mg/kg mean concentration was found. Mean value was less than the world surface rock average and more than mean shale concentration as geochemical background level (**Table 5**). In comparison with sediment quality guidelines, the mean value did not exceed the WHO and CCME guidelines and exceeded the USEPA guidelines. According to USEPA, Euphrates River sediments have little pollution by Cu. Cu correlated significantly with Ni and Fe at 0.05 level. It has also good positive correlations. Due to correlations, these metals have common source.

Cu concentration mean was near to that reported by [14] for the same studied area and less than that estimated by [15] for downstream region of the study area. Al-Bassam and Al-Mukhtar [29] reported Cu concentration for number of sites in the study area, greater than recorded in this study. Cu mean value was also less than that of the world rivers average [23].

Higher concentration of Cu was found during spring than winter (**Figure 3(d)**). S14 showed higher concentration of Cu (30.52 mg/kg) and lowest concentration was 10.35 mg/kg at S9, **Figure 4(d)**. We found high concentrations for Cu at sites located in and near the population centers.

The enrichment factor (EF) values for Cu in Euphrates River sediments vary from 5.61 at S11 to 12.50 at S9 (**Table 8**). All sampling sites has EF values more than 5 and less than 20, suggesting that Euphrates River sediments are classified as significant enrichment for Cu. Rabee *et al.* [15] reported values for EF less than that estimated in this study for two sites in the downstream region of the study area.

The contamination factor (CF) for Cu in Euphrates River sediments ranged from 0.32 at S9 to 0.95 at S14 with a mean value of 0.58. The CF values for Cu were less than 1 (<1) at all sampling sites. According to [31], all sampling sites face low contamination by Cu.

The I_{geo} values for Cu at the sampling sites were negative. According to Muller's classification, Euphrates River sediments at all sampling sites were unpolluted. This result was in good agreement with results of [15].

The concentration of Ni value was between 39.98 and 103.98 mg/kg. Mean concentration was 67.08 mg/kg. Mean value greater than world surface rock average and less than mean shale concentration as background level. According to WHO and USEPA guidelines, Ni concen-

tration mean exceeded the guidelines suggesting that Euphrates River sediments are polluted by Ni. The seasonal variation of Ni is shown in **Figure 3(e)**. Ni concentrations of Euphrates River sediments vary between 39.98 mg/kg at S6 and 103.98 mg/kg at S2, **Figure 4(e)**. High concentrations were recorded at sampling sites in and near urbanization centers such as AlQaim (S1, S2, S3), Heet (S11, S12) and Ramadi (S14). In comparison with previous studies, Ni concentration mean value was less than reported by [14,29], **Table 7**. It was also more than estimated by [15]. Ni mean value was less than world rivers average.

The enrichment factor (EF) values for Ni in Euphrates River sediments range from 13.15 at S8 to 48.40 at S9, **Table 8**. Some sampling sites (S4, S5, S6, S8, S10, S11 S13) have EF for Ni more than 5 and less than 20. The Euphrates River sediments in as significant enrichment for Ni. Other sampling sites (S1, S2, S3, S7, S12, S14) have EF values for Ni more than 20 and less than 40 suggesting that Euphrates River sediments are classified as very high enrichment for Ni. Euphrates River sediments at S9 are classified as extremely high enrichment for Ni. Rabee *et al*. [15] classified Euphrates River sediments at two stations in Heet and Ramadi cities as moderately polluted for Ni.

The contamination factor (CF) values for Ni in Euphrates River sediments ranged from 0.81 at S6 to 2.12 at S2, with mean value of 1.36. Most sampling sites except S6 and S13 have CF more than 1 and less than 3. According to [31], most sampling sites are moderately contaminated and S6 and S13 face low contamination by Ni.

The I_{geo} values for Ni at all sampling sites were negative except S1, S2, S3, and S14 were positive. According to Muller's classification, Euphrates River sediments were unpolluted at most sites and from unpolluted to moderately polluted at other sites. This result was in good agreement with that of [15] for station at Heet city.

Co concentration ranged between 21.88 and 38.73 mg/kg. The mean value was 28.16 and 38.73 mg/kg. The mean value was 28.16 mg/kg. The general acceptance of Co is 4 - 20 mg/kg [3]. The mean value of Co concentration was more than the world surface rock average and near to the mean shale concentration as geochemical background level, **Table 5**. Co showed strong positive correlation with Cr at 0.05 level. Co concentrations in the sediments were highest during the winter than the spring, **Figure 3(f)**. Spatial variation of Co concentration was given in **Figure 4(f)**, and the maximum value was 38.73 mg/kg at S14 while the minimum value was 21.88 mg/kg at S2. As well as S14, high values were reported at S1, S7, S9 and S12. These sites locate in and near the urbanization centers, such as AlQaim, Haditha, Heet and Ramadi. The Co concentration value was less than that reported by [23,29]. It was also more than that the region

located at the downstream region of the study area [16].

The EF values for Co in Euphrates River sediments were from 20.88 at S8 and 90.60 at S9, **Table 8**. Most sampling sites have EF for Co more than 20 and less than 40, while S7 and S9 more than 40. According to Mmolawa *et al*. [12], Euphrates sediments at sampling sites are classified as very high to extremely high enrichment for Co.

The CF values for Co in Euphrates River sediments ranged from 1.68 at S2 to 2.74 at S7, with mean value of 2.16. At all sampling sites, the CF values for Co were more than 1 and less than 3. According to [31], all sampling sites were moderately contaminated by Co.

The I_{geo} values for Co at all sampling sites vary from 0.16 at S2 to 0.98 at S14, **Table 10**. According to Muller's classification, Euphrates sediments were from unpolluted to moderately polluted at all sampling sites.

The concentration of Fe in Euphrates River sediments varied from 928.7 mg/kg to 3441.05 mg/kg and mean value was 2249.47 mg/kg. The Fe mean value was less than world surface rock average and mean shale concentration as background level, **Table 5**. The mean value of Fe exceeded the USEPA sediment quality guidelines. Generally, during the spring, higher concentrations of Fe were observed, **Figure 3(g)**. Spatially, concentration of Fe in Euphrates River sediments ranged from 928.7 mg/kg at S9 to 3441.05 mg/kg at S8, **Figure 4(g)**. Fe concentration of Euphrates sediments was less than of the world rivers average [23] and more than that reported by [16].

The contamination factor (CF) values for Fe in Euphrates River sediments ranged from 0.025 at S9 to 0.095 at S8, with a mean value of 0.062. Because of the CF values for Fe in all sampling sites less than 1, Euphrates River Sediments face low contamination by Fe.

The I_{geo} values for Fe at all sampling sites were negative. According to Muller's classification, Euphrates sediments were unpolluted by Fe.

Mn concentration ranged between 136.05 and 312.11 mg/kg and mean value was 228.18 mg/kg. The mean value of Mn was less than world surface rock average and shale concentration as geochemical background level, **Table 5**. Mn mean value exceeded USEPA sediment quality guidelines. Except S8 and S9, others showed higher values during winter than spring, **Figure 3(h)**. The concentration of Mn at S4 was the highest with value of 307.9 mg/kg and the lowest concentration was at S9 with a value of 136.05 mg/kg, **Figure 4(h)**. Mn concentration was less than that reported in the local previous studies and the world rivers average, **Table 6**.

The enrichment factor (EF) values for Mn ranged from 2.56 at S8 and 7.09 at S4, **Table 8**. The EF values for Mn at majority of sampling sites (S1, S6, S7, S8, S10, S11, S12 and S14) were greater than 2 and less than 5. At

these sites, Euphrates River sediments are classified as moderate enrichment for Mn. Other sampling sites (S2, S3, S4, S5, S9, and S13), the EF values were more than 5 and less than 20 and Euphrates sediments are classified as significant enrichment for Mn.

The contamination factor (CF) values for Mn in Euphrates sediments varied from 0.181 at S9 to 0.416 at S5, **Table 9**. At all sampling sites, the CF values were less than 1. According to [31], Euphrates sediments at all sampling sites were low contaminated. The I_{geo} values for Mn at all sampling sites were negative. According to Muller's classification, Euphrates sediments are unpolluted by Mn.

Cr concentration varied between 36.45 and 120.11 mg/kg. The mean value was 58.4 mg/kg. It was less than world surface rock average and mean shale concentration as geochemical background level, **Table 5**. In comparison, it was found that Cr mean value exceeded WHO, USEPA and CCME Sediment guidelines. With except of S1, S4, S12 and S14, highest concentration of Cr was observed in spring than winter, **Figure 3(i)**. The highest concentration of Cr was observed at S14 (120.11 mg/kg). while the lowest concentration was 36.45 mg/kg at S9, **Figure 4(i)**. The high values of Cr was at township area. Cr concentration mean was less than that estimated by [29] for Euphrates River and the world rivers average [23].

The EF values for Cr in Euphrates sediments ranged from 6.04 at S8 to 21.28 at S14. All sampling sites have EF more than 5 and less than 20, except S14 has more than 20, **Table 8**. Euphrates sediments at all sampling sites are classified as significant to very high enrichment for Cr.

The CF values for Cr in Euphrates sediments varied from 9.87 at S9 to 22.21 At S14 with mean value of 16.36, **Table 9**. At all sampling sites, the CF values were greater than 6, suggestion that sediments were very high contamination.

The I_{geo} values for Cr at all sampling sites were negative except S14 was positive. According to Muller's classification, Euphrates sediments were unpolluted by Cr at all sites except at S14 was from unpolluted to moderate polluted.

The overall total geo-accumulation index (Itot) of the entire study area for different metals were found to be negative, **Table 10**. This suggests that concentration mean of most heavy metals in Euphrates sediments are lower than world surface rock average.

To effectively compare whether the sampling sites suffer contamination or not, the pollution load index (PLI), was used. PLI values of the analyzed samples ranged from 0.45 to 1.15 with a mean value of 0.69, **Figure 8**, **Table 11**. At all sampling sites, the PLI values were less than 1 except S14 was greater than 1. Accord-

ing to [25], all sampling sites suggest perfection (or no overall pollution), whereas S14 shows signs of pollution or deterioration of site quality. Relatively high PLI value at S14 (Ramadi city) suggests input from anthropogenic sources.

4. Conclusions

To investigate the status of metal contamination in Euphrates River sediments, Pb, Cd, Zn, Cu, Ni, Co, Fe, Mn and Cr concentrations were estimated in Fourteen sampling sites. The order of the mean concentrations of tested heavy metals: Fe > Mn > Ni > Cr > Zn > Co> Pb > Cu > Cd. The correlation analysis of mean concentrations showed good to strong positive correlations among Pb, Cd, Zn, Ni, Co, Fe, Mn and Cr, suggesting that these metals have common sources.

International sediment quality guidelines (WHO, USEPA and CCME), enrichment factor (EF), contamination factor (CF), geo-accumulation index (I_{geo}) and pollution load index (PLI) were applied for assessment of contamination. According to sediment quality guidelines, Euphrates sediments were polluted by Cd, Cu, Ni, Fe, Mn and Cr. The EF values suggest that Euphrates sediments were very high enriched for Pb, extremely high for Cd, moderately for Zn, significantly for Cu, significantly to very high for Ni, very high to extremely high for Co, moderately to significantly for Mn and significantly to very high for Cr. According to CF, Cd and Cr are responsible for very high contamination. The I_{geo} values showed that Euphrates sediments quality was moderately to strongly polluted for CD. According to PLI, all sites suggest perfection or no overall pollution of site quality. In general, I_{tot} indices for most heavy metals were negative; this implies that mean concentration of heavy metals Euphrates sediments are lower than world surface rock average. Considering all assessing criteria, Cd is responsible for significant amount of heavy metal contamination, while Co and Cr are responsible for moderate to high contamination. S14 (Ramadi city) contains highest amount of heavy metals contamination and S9 (Hajlan) contains lowest amount of heavy metal contamination.

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