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Assessment of Heavy Metal Pollution in Clay Fraction of the Euphrates River Sediments, AlQaim, Haditha Area, Western Desert Iraq

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Abstract

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Clay fractions (<2 μ m) from ten stream sediments were collected from the Euphrates River between AlQaim-Haditha area in the western desert of Iraq. The clay fractions were analyzed for Cd, Co, Cr, Cu, Ni, Pb, Sr, and Zn using an Atomic Absorption Spectrophotometer. The aim of this research is to study the extent to which the industrial waste liquids from chemical complex of phosphates pollute stream sediments of Euphrates River. The total metal concentrations in the clay fraction are placed in the following descending order: Sr> Zn> Cr> Ni> Co> Pb> Cu> Cd. Contamination factor pollution load index, geo-accumulation index, the metal contamination index, and potential ecological risk index were calculated to evaluate the environmental impacts of these heavy metals. The study area was found to be highly contaminated with Cd and Ni, moderately contaminated with Co, Pb and Sr, and uncontaminated with Cr, Cu and Zn. 100% of Cd and 93% of Sr were concentrated in the extracted part of the clay fraction, suggesting that Cd is totally derived from the industrial and human activities in the studied area, and Sr which can be attributed to the carbonates of Euphrates Formation as its source which dominate the geology of the area.

Keywords: Euphrates River; Clay fraction; Assessment; Heavy metals; Pollution

1. Introduction

With population growth, rapid industrial development, and a lack of pollution control measures, soil trace metal contamination is becoming a global problem at both the private and governmental levels, particularly because soils are an important component of both rural and urban environments (USDA, 2001; Rahman et al., 2012; Tang et al., 2014). Heavy metal accumulation in river sediments exposed to mining and industrial wastes is a regular occurrence in most developing countries (Islam et al., 2015). Heavy metals in the environment are sometimes carried and sourced by sediments (Haiyan et al., 2013). Heavy metals in river sediments enter through different pathways, either from point or non-point sources (Shazili et al., 2006). Grain size distribution plays an important role regarding the content of heavy metals in sediments. Many investigations indicated that when sediments grain size decreases, metal content increases more than those formed of coarser ones (Svetlana et al., 2012). This was attributed to the fact that smaller grains, such as clay fraction sediments, have a larger surface area, which allows heavy metals to be retained in high concentrations (Wang et al., 2006).

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The background level is a measure used to differentiate between the concentration with an anthropogenic influence and the concentrations of the natural occurrence in a given environmental sample (Matschullat et al., 2000; García Sánchez et al., 2010). Heavy metal concentrations in the natural soil background are determined by geological substrates in the Earth's crust and soil formation processes (Alloway, 1990; Kabata - Pendias and Pendias, 2001). Rocks have a large influence on the heavy metal content of soils, with concentrations sometimes exceeding critical values (Salonen and Korkka-Niemi, 2007). The phosphate industry is the major cause of pollution in the area because most of the waste is directly discharged into the river with preliminary treatment. Iraq's major phosphate factory, which is located 20km in the western city of AlQaim, was once used to produce fertilizer for agricultural purposes. The waste is liquid or solid and its acidic or basic throw-out from different units. The units that produce the waste material from the factory are fertilizer phosphate unit, phosphoric acid unit and fluoride salt unit. The study area is located between $34^{\circ}22'12.33''$ – $34^{\circ}08'3.04''$ N and $41^{\circ}05'46.44''$ – $42^{\circ}22'42.19''$ E including the Euphrates River from AlQaim on the Iraqi Syrian borders to Haditha city for a length of about 160 km (Fig. 1).

Fig. 1. Location map of the Euphrates River in the study area showing the location of samples and the relevant phosphate chemical complex

Haditha reservoir is the largest dam along the Iraqi stretch of the Euphrates River with a maximum capacity of 8.2 km³. The main fluvial units on the Euphrates River in Iraq are terraces and flood plains, which are geomorphological units and forms of the river's course. The Euphrates River defines the boundary between two tectonic zones, Al-Jazira and Western Desert zones, as it enters Iraqi territory from Syria (Fig. 1). The river flows parallel to Anah anticline in W–E trend which is the only surface anticline along the course of the river within the Iraqi territory and continues until Haditha town. Although the major part of the Euphrates River's basin is located within the Stable Shelf, but still a lot of indications exist in the basin witnessing Neotectonic activities (Sissakian et al., 2014). According to Sissakian and Al-Jiburi (2007), the exposed formations in the study area are: (1) Anah (Oligocene) which consists of very hard limestone and corals with a thickness of about 40 m; (2) Euphrates Formation (Lower Miocene) which consists of highly fossiliferous limestone, dolostone, marl, with a thickness of about 60-130 m in AlQaim city; (3) Fatha Formation (Middle Miocene) which consists of cyclic deposits of green marl, reddish brown claystone, limestone and gypsum; (4) Nfayil Formation (Middle Miocene) which consists of an alternation of green marl and limestone; and (5) Zahra Formation (Pliocene–Pleistocene) and Quaternary sediments (Pleistocene) which consists of sand, gravel, fine gypsum, and silt with a thickness of about 12-35 m. Previous studies on the area include that of Ali (1972) who determined heavy mineral provinces of recent sediments in the Euphrates and Tigris Basin; Al Jalil (2000) studied the effect of industrial water leakage from the chemical complex of phosphates in Al-Qaim on ground and surface water pollution. Al-Bassam and Al-Mukhtar (2007) who studied the heavy minerals in the 63 μm fractions of the Euphrates River sediments that showed enrichment of some heavy metals in the river sediments. Al-Paruany et al., (2017) they studied the distribution of environmental isotopes ($\delta^{18}\text{O}$, $\delta^2\text{H}$ and ^3H) and hydrochemistry at eight stations in the Euphrates river between Qaim–Falluja. Hussain et al., (2020) twenty-five core samples were selected from eight river bed sediment sites to study the heavy metal contamination of the Euphrates and Shatt al-Arab. The Ta, W, Ni, and Mo were clearly the most contaminated heavy metals in the current investigation. The main aims of this study are to assess of heavy metal pollution in clay fractions and to evaluate the effect of waste material from phosphate chemical complex on the pollution of Euphrates River sediments in the studied area (Fig. 1).

2. Materials and Methods

2.1. Samples Collection

Ten surface clay samples were collected for the current study along the Euphrates River from the bank of the river between AlQaim on the Iraqi-Syrian border and Haditha towns (Fig. 1). These samples consist of sand, silt and clay. The selected samples were placed in a clean cloth bag and kept in a polyethylene bag. The samples were fully air dried at room temperature and sieved using 80 mesh sieves. The finer fraction was used to separate the clay fraction ($< 2 \mu\text{m}$) applying Pipette analysis based on Folk (1974). Fifty grams of each sample were placed into a 500 ml glass cylinder and filled to the mark by distilled water and left one day for the large particles to settle down. The suspended part was decanted into a clean tube for the separation of the $< 2 \mu\text{m}$ clay fraction size without adding any chemicals. The separated clay fraction was placed in a polyethylene bag for chemical analysis. The clay samples were analyzed for Cd, Pb, Cu, Ni, Co, Cr, Zn and Sr using PYE Unicam SP9 Atomic Absorption Spectrophotometer (AAS) in chemical laboratory at Babylon University. The analysis of these heavy metals was taken place in two stages:

2.1.1. Extraction of heavy metals by cold acid

Include the heavy metals that present in the clay fraction from solution by adsorption and organic complex, that come from the water pollution. This method is available, rapid and not expensive. The procedure of sample preparation is simple, and the analysis consists of only three steps, which can be performed simultaneously: A prepared clay samples (1.0 g) are placed in a plastic tube (50ml), and added (20) ml of cold (0.5) N hydrochloric acid (Chester and Voutsinou, 1981). The tube closed and shacked in shaker for (16) hours. Finally, put it in a centrifuge (3000) RPM for 20 min to separate the acid from heavy metals, the solution transferred to plastic tubes (20) ml closed and kept. The heavy metals content from extracted are measured with an Atomic Absorption Spectrophotometer.

2.1.2. Residual heavy metals

The procedure of residual extraction includes heavy metals mostly found within the structure of minerals in a silicate matrix of sediments. This extraction is determined by chemical digestion for residual clay fraction after cold extraction. The clay fraction is rinsed with 40 ml of deionized water (DIW) to remove the hydrochloric acid and ionic exchange followed by shaking the tube. The 3000-rpm centrifuge was operated for 30 minutes to separate the water and transfer the deposit to a teflon (P.T.F.E) tube. The deposit was evaporated at 80°C to near dryness; followed by adding 6 ml of HNO₃ + HCl (1:1) acid mixture to be evaporated again 80°C to near dryness. An acid mixture of HF+Br l (1:1) is added to the sample and evaporated to near dryness again, followed by adding 1 ml of hydrochloric acid for 10 minutes. The digestion was diluted by 20 ml of deionized water and separated again by centrifuge and finally transferred to a plastic bottle ready to be measured by Atomic Absorption Spectrophotometer.

2.2. Assessment of Heavy Metals

The state of heavy metal contamination in the clay fractions of the studied area was evaluated using different quantitative contamination indices. The geochemistry of sediments is an effective indicator to deduce the anthropogenic activity in stream sediments. Among various environmental indices for assessing the degree of anthropogenic induced impact are the contamination factor (CF), pollution load index (PLI), geo-accumulation index (I_{geo}), the metal contamination index (MCI), potential ecological risk index (RI) (Rahman et al., 2012; Jiang, 2013; Adepoju and Adekoya, 2014; Singh et al., 2017; Duncan and Nyarko, 2018; Khudhur et al., 2018; Wojciechowska et al., 2019).

2.2.1. Contamination Factor (CF)

CF is used to express the level of metal contamination in sediment, which is calculated as:

$$CF = C_m \text{ Sample} / C_m \text{ Background} \quad (1)$$

Where C_m Sample is the amount of a given metal in river sediment and C_m Background is the value of metal which is equivalent to Upper Continental Crust (UCC) in the studied sediments (Taylor and McLennan, 1985; McLennan, 2001; Rudnick and Gao, 2003; Avumadi et. al., 2019) which was widely used by Harikumar et al., 2009).

2.2.2. Pollution Load Index (PLI)

PLI for a specific site was calculated using the approach suggested by Tomlinson et al. (1980). The PLI for various sampling areas were determined as the geometric average for all assessed CF of a sampling site (Afrifa et al., 2013) (Table 2). This parameter is expressed as:

$$PLI = (CF_1 \times CF_2 \times CF_3 \times \dots \times CF_n)^{1/n} \quad (2)$$

Where n is the number of metals.

2.2.3. Geo-Accumulation Index

The I_{geo} was calculated using the method of Muller (1979). Geo-accumulation index is expressed as follows:

$$I_{geo} = \log_2 [C_m / (1.5B_m)] \quad (3)$$

Where C_m is the measured concentration of the metal examined in the sample, and B_m is the background level of the metal. The 1.5 factor was used to correct possible variations in the background values of a particular metal in the environment.

2.2.4. The Element Contamination Index and the Metal Contamination Index

The ECI and the overall metal contamination index (MCI) are expressions of single metal contamination within a sample or total metal contamination for a sample in comparison to the corresponding metal's background values (Singh et al., 2015). They are expressed as:

$$ECI = (C_m - B_m) / B_m \quad (4)$$

$$MCI = \sum (C_m - B_m) / B_m^i \quad (5)$$

According to Aikpokpodion et al. (2010), MCI was designed to describe general trace elements contamination.

2.2.5. Potential Ecological Risk Index

The E_r evaluates the toxicity of trace elements in sediments and has been extensively applied to assess the comprehensive pollution status in the sediments and environmental effects (Gholizadeh et al., 2019, Liu et al., 2019). Sediments contaminated by heavy metals can cause serious ecological risks and negatively impact human health due to various forms of interaction where highly toxic heavy metals can enter the food chain. To calculate the E_r for individual metals, we used the following equation:

$$E_r = T_r * CF \quad (6)$$

where E_r is the potential ecological risk factor/index, T_r represent the toxicity coefficient of each metal whose standard values are: Hg= 40, Cd= 30, As= 10, Co=5, Cu=5, Ni=5, Pb=5, Cr=2, and Zn=1 (Hakanson, 1980; Xu et al., 2008). CF represents the contamination factor ($CF = C/B$), where C_m is the measured concentration of the pollutant, and B_m is the level of geological background. To calculate the potential response rate to the toxicity of all the studied heavy metals (RI), we used the following equation:

$$RI = \sum_{i=1}^m E_r^i \quad (7)$$

3. Results

Results of heavy metals analysis in clay fraction samples of Euphrates stream sediments are listed in Table 1 and Fig. 2. The results of the Cd content showed that it ranged from 0.27-3.31ppm with an average value of 1.09ppm. The highest concentration of Cd in Alshallal reached 3.31ppm and Rumanah 1.67ppm. Alshallal area is considered as the area where phosphate chemical complex waste water is discharged in the Euphrates River. The Ni values varied between 115-383 ppm with an average value of

180 ppm. The highest concentration of Ni in clay fractions at Alhasa is 383 ppm while in Rawa is 212 ppm. Strontium ranged from 88 to 484 ppm with an average of 139 ppm, and the highest concentration of Sr at Rawa is 484 ppm and Alhasa company is 389 ppm as shown in Fig. 2. Zinc value varied between 51 to 72 ppm with an average reached to 62 ppm.

The highest Zn concentration in the clay fractions has been found at Rawa and Alnahiya reached 72 ppm. Lead concentration ranged between 24 to 66 ppm with an average value reached to 35 ppm. The highest content (66) ppm of Pb was found at Rawa. Copper concentrations ranged from 28 to 47 ppm with an average of 37 ppm. Cobalt value varied between 22 to 31 ppm with an average of 26 ppm. The chemical analyses did not show a significant variation in the cobalt concentration content, except for a relatively slight increase in the Alnahiya, Alhasa and Rawa. The result of Cr analysis in clay fractions ranged from 28 to 53 ppm with an average of 39 ppm. In general, it has been observed that there is a relative increase in the content of the cadmium, copper, and chromium in the sites located in the downstream, below Alshallal area and the disposal of liquid industrial wastes from the phosphate chemical complex, relative to its concentration when entering the Euphrates River, the Iraqi-Syrian border at Rummana. The CF value for Cd was ranged (3 - 36.78) while Ni was (5.75-19.15) especially in the Alshallal which was contaminated by Cd and Alhasa accompanied by Ni; other metals range from Co (2.2-3.1), Pb (1.2-3.3), Cu (1.12- 1.88), Cr (0.8-1.51), Zn (0.72-1.01) and Sr (0.25-1.38) (Fig. 3).

The PLI value in the studied clay samples varied from (1.51 to 2.50) with an average of (2.00) (Table 2). The highest PLI value in the studied clay has been found at Rawa (2.50) and Alshallal (2.38). The study area can be divided into three groups according to the level of PLI values for the eight elements calculated by Tomlinson et al. (1980). The first group includes Maaideg, Alobeidi, Safra, and Rumanah where PLI values range from (93.32 to 14.6). The second group includes Alnahiya, Right Albeida (R. Albeida), Left Albeida (L. Albeida), and Alhasa where PLI values varied from (36.6 to 63.18), and the third group includes Rawa (189.8) and Alshallal (130.4) (Fig. 4). The average I_{geo} value in clay fractions of heavy metals varied from $I_{geo} \leq 0$ to 2.68. The highest I_{geo} average value of trace metals in the studied area has been found in Cd I_{geo} 2.68 and Ni (I_{geo} 2.49) (Table 3).

The results shown that the I_{geo} of Zn, Cu, Sr, and Cr within $I_{geo} \leq 0$, while its lead and cobalt values varied from $0 < I_{geo} < 1$. The study showed that the I_{geo} value of nickel is relatively homogeneous within the different locations, while a relative decrease was observed in the I_{geo} values of lead in the locations of the Down Stream (Fig. 5). The current study compared the results of the clays analyzes of heavy metals with their average in Upper Continental Crust (UCC) to assess contamination levels of the Euphrates River areas by used Element Contamination (ECI) and the Metal Contamination Index (MCI). The highest Cd-ECI value in the studied clay samples has been found at Alshallal (35.78) and lowest at Alhasa (2.0) with an average of (10.39), while the Ni-ECI value reach to 18.15 in Alhasa and to 4.75 in Rumanah. The results also showed that the values of ECI for the other elements varied from negative values and less than < 5 (Table 4). As for the MCI values varied from 11.06 to 23.52, except for Alshallal where its values increased to reach 44.32 (Fig. 6).

The assessment of heavy metals showed that the average potential ecological risk indices of Zn (0.9), Pb (8.8), Cu (7.4), Co (13.1), and Cr (2.2) in all locations of the study area were lower than $Er < 40$ (Table 5). Cadmium and nickel in the present study considered the main elements causing ecological hazards were Cd ($Er = 365$) and Ni ($Er = 45.0$). For the Cd element, there were Alhasa (90) and Rawa (147) have $80 \leq Er < 160$. As that L. Albeida (257), Alnahiya (283) and Maaideg (160) have $160 \leq Er < 320$, while Rumanah (557), Alshallal (1103), Alobide (323), Albeida R. (383) and Safra (343) have $320 \leq Er$. As for the element nickel, Er in the Rumanah (28.8), Alshallal (34.8), Alobeidi (30.5), Safra (33.5) and Maaideg (32.5) with a content of less than $Er < 40$ (Table 6).

The study area can be divided into three regions according to its content of Potential toxicity response indices for heavy metals (RI) includes Rumanah (613) and Alshallal (1171) with a content of more than $600 \leq RI$, and the second group includes Alobide (381), Albeida R. (341). Albeida L. (460),

Safra (406) and Alnahiya (365) with a content between $300 \leq RI < 600$. The third group includes Alhasa (220), Rawa (244) and Maaideg (222) with a content between $150 \leq RI < 300$ (Fig. 7).

Table 1. Concentrations of specific heavy metals in ppm in the extraction and residual clay fractions of the Euphrates River sediments

Stations	Extraction clay fraction								Residual clay fraction							
	Cd	Zn	Ni	Pb	Cu	Co	Sr	Cr	Cd	Zn	Ni	Pb	Cu	Co	Sr	Cr
Rumanah	1.67	16	29	12	6	7	126	2.4	<0.01	41	86	18	22	16	5	31
Alshallal	3.31	23	41	14	17	7	158	4.12	<0.01	43	98	24	24	18	19	35
Alobeidi	0.97	17	31	8	9	5	104	1	<0.01	42	91	16	25	17	5	35
L. Albeida	0.77	18	51	12	13	7	158	2.56	<0.01	46	148	19	34	20	5	41
R. Albeida	1.15	23	51	17	11	9	144	3.1	<0.01	44	131	16	22	16	5	40
Safra	1.03	16	31	8	9	7	94	1.78	<0.01	42	103	22	23	17	14	35
Alnahiya	0.85	25	53	20	11	12	122	1.66	<0.01	47	131	21	24	19	5	36
Alhasa	0.27	14	80	8	13	7	348	3.33	<0.01	41	303	19	30	22	41	50
Rawa	0.44	33	69	48	15	12	452	0.2	<0.01	39	143	18	30	18	32	41
Maaideg	0.48	13	29	12	9	9	83	0.93	<0.01	38	101	18	25	17	5	27
Average	1	20	47	20	11	8	179	2	-	42	134	19	26	18	14	37

B.L. = the data below detected limit < 0.01ppm; L.= Left, R.= Right source: Al-Jaleel (2000)

Fig. 2. Average concentrations of heavy metals in extraction, residual, and accumulation of clay fractions with the standards in the study area

Table 2. CF values and PLI value of heavy metals in the study area and level of contamination (Hakanson, 1980) and pollution (Tomlinson et al., 1980)

Contamination factors of heavy metal (C F)									
stations	Cd	Zn	Ni	Pb	Cu	Co	Sr	Cr	PLI
Rumanah	18.56	0.8	5.75	1.5	1.12	2.3	0.37	0.94	1.81
Alshallal	36.78	0.93	6.95	1.9	1.64	2.5	0.51	1.11	2.38
Alobeidi	10.78	0.83	6.1	1.2	1.36	2.2	0.31	1.03	1.68
L. Albeida	8.56	0.9	9.95	1.55	1.88	2.7	0.47	1.26	2.08
R. Albeida	12.78	0.94	9.1	1.65	1.32	2.5	0.43	1.23	2.05
Safra	11.44	0.82	6.7	1.5	1.28	2.4	0.31	1.06	1.76
Alnahiya	9.44	1.01	9.2	2.05	1.4	3.1	0.36	1.09	2.05
Alhassa	3	0.77	19.15	1.35	1.72	2.9	1.11	1.51	2.18
Rawa	4.89	1.01	10.6	3.3	1.8	3	1.38	1.17	2.50
Maaidged	5.33	0.72	6.5	1.5	1.36	2.6	0.25	0.8	1.51

CF<1 (Low contamination); $1 \leq \text{CF} < 3$ (Moderate contamination); $3 \leq \text{CF} < 6$ (Considerable contamination); and $\text{CF} > 6$ (Very high contamination). $\text{PLI} < 1$ (Perfection); = 1 (only baseline levels of pollutants are presented); > 1 (Deterioration).

Fig. 3. CF values of heavy metals in the study area

Fig. 4. PLI values of heavy metals in the study area

Table 3. I_{geo} values of heavy metals in the study area according to Muller's classification (1979)

Studied station	Cd	Zn	Ni	Pb	Cu	Co	Sr	Cr
Rumanah	3.63	-0.90	1.94	0.00	-0.42	0.62	-2.00	-0.67
Alshallal	4.62	-0.69	2.21	0.34	0.13	0.74	-1.57	-0.43
Alobeidi	2.85	-0.85	2.02	-0.32	-0.14	0.55	-2.27	-0.54
L. Albeida	2.51	-0.73	2.73	0.05	0.33	0.85	-1.69	-0.25
R. Albeida	3.09	-0.67	2.60	0.14	-0.18	0.74	-1.82	-0.29
Safra	2.93	-0.88	2.16	0.00	-0.23	0.68	-2.28	-0.50
Alnahiya	2.65	-0.56	2.62	0.45	-0.10	1.05	-2.05	-0.47
Alhassa	1.00	-0.95	3.67	-0.15	0.20	0.95	-0.43	0.01
Rawa	1.70	-0.56	2.82	1.14	0.26	1.00	-0.12	-0.36
Maaidged	1.83	-1.06	2.12	0.00	-0.14	0.79	-2.58	-0.91

$I_{geo} \leq 0$ (Unpolluted); 0-1 (Unpolluted to moderately polluted); 1-2 (Moderately polluted); 2-3 (Moderately to strongly polluted); 3-4 (Strongly polluted); 4-5 (Strongly to extensive polluted); and $I_{geo} > 6$ (Extremely polluted).

Fig. 5. I_{geo} values of heavy metals in the study area

Table 4. ECI and MCI values of heavy metals in the study area and contamination level (Aikpokpodion et al., 2010)

Station	Element Contamination Index (ECI)								MCI
	Cd	Zn	Ni	Pb	Cu	Co	Sr	Cr	
Rumanah	17.56	-0.2	4.75	0.5	0.12	1.3	-0.63	-0.06	23.35
Alshallal	35.78	-0.07	5.95	0.9	0.64	1.5	-0.49	0.11	44.32
Alobeidi	9.78	-0.17	5.1	0.2	0.36	1.2	-0.69	0.03	15.81
L. Albeida	7.56	-0.1	8.95	0.55	0.88	1.7	-0.53	0.26	19.26
R. Albeida	11.78	-0.06	8.1	0.65	0.32	1.5	-0.57	0.23	21.95
Safra	10.44	-0.18	5.7	0.5	0.28	1.4	-0.69	0.06	17.51
Alnahiya	8.44	0.01	8.2	1.05	0.4	2.1	-0.64	0.09	19.66
Alhassa	2	-0.23	18.15	0.35	0.72	1.9	0.11	0.51	23.52
Rawa	3.89	0.01	9.6	2.3	0.8	2	0.38	0.17	19.16
Maaidged	4.33	-0.28	5.5	0.5	0.36	1.6	-0.75	-0.2	11.06
Average	10.39	-0.19	7.5	0.7	0.44	1.55	-0.56	0.07	21.56

MCI < 5 (Very low contamination); 5-10 (Low contamination); 10-25 Medium contamination; 25-50 (High contamination); 50-100 (Very high contamination); and MCI > 100 (Extremely high contamination)

Fig. 6. ECI values and MCI level of heavy metals in the study area

Table 5. Er and RI values of heavy metals in the study area

Potential ecological risk indices for single heavy metal (Er)								
stations	Cd	Zn	Ni	Pb	Cu	Co	Cr	RI
Rumanah	556.7	0.8	28.8	7.5	5.6	11.5	1.9	612.8
Alshallal	1103.3	0.9	34.8	9.5	8.2	12.5	2.2	1171.4
Alobeidi	323.3	0.8	30.5	6	6.8	11	2.1	380.5
L. Albeida	256.7	0.9	49.8	7.8	9.4	13.5	2.5	340.6
R. Albeida	383.3	0.9	45.5	8.3	6.6	12.5	2.5	459.6
Safra	343.3	0.8	33.5	7.5	6.4	12	2.1	405.6
Alnahiya	283.3	1	46	10.3	7	15.5	2.2	365.3
Alhassa	90	0.8	95.8	6.8	8.6	14.5	3	219.5
Rawa	146.7	1	53	16.5	9	15	2.3	243.5
Maaidged	160	0.7	32.5	7.5	6.8	13	1.6	222.1
Average	364.66	0.86	45.02	8.77	7.44	13.1	2.24	442.09

Table 6. Categories of Er and RI (Hakanson 1980; Zhu et al., 2008)

Er	Ecological Risk Level of Single Factor Pollution	RI value	General Level of Potential Ecological Risk
$Er < 40$	low risk	$RI < 150$	low ecological risk
$40 \leq Er < 80$	moderate risk	$150 \leq RI < 300$	moderate ecological risk
$80 \leq Er < 160$	considerable risk	$300 \leq RI < 600$	considerable ecological risk
$160 \leq Er < 320$	high risk	$RI > 600$	very high ecological risk
$Er > 320$	very high risk

Fig. 7. Er values and RI level of heavy metals in the study area

4. Discussion

4.1. Assessment of Heavy Metals Contamination Indices

Heavy metals content varies in the environment depending on the geological nature of river crossing areas as well as human activities such as industrial plants, pesticides, agricultural fertilizers, fossil fuel, land construction activities and soil erosion caused by rainfall (Xiang et al., 2002; Chen et al., 2004; Higgins et al., 2007). The accumulations of metal concentrations in the clay fraction are placed in the following descending order: $Sr > Zn > Cr > Ni > Co > Pb > Cu > Cd$. The results of Cd analysis in the present study represent the influence of the waste water disposed from the phosphate chemical complex. Generally, Cd and other metals occur in waste water at low concentrations until below detection limit of analytical instruments (Al-Jaleel, 2000). These metals tend to accumulate in the clay fraction because it contains high clay minerals that have high adsorption potential in the sedimentation environment. The

highest concentration of Cd in Alshallal and Rumanah which is attributed to the urban influence of the city of AlQaim. Drever (1997) showed that Cd has the ability to be adsorbed at the surfaces of clay minerals. Fig. 2 shows that the highest concentration of zinc in Rawa and Alnahiya reached 72 ppm; this was due to human activities and waste water from the phosphate chemical complex (Yan et al., 2018). Also, Zn is found in minerals like ilmenite and magnetite which are present mainly in the sediments of the Euphrates River; this Zn can be released to the environment during weathering processes and then deposited in light basic conditions (Benni, 2014; González-Costa et al., 2017). The difference in distribution of Zn in clay fraction may be due to the effect of organic matter, iron and manganese oxides in the river environment because of high adsorption on clay minerals and organic matter (Steenfelt, 1993; Uddin, 2017). The predominance of montmorillonite over the other clay minerals may be due to the increasing rate of Ni in these areas (Forstner and Wittman, 1981; Mu'azu et al., 2018). The burning of fuel and the emission of water pumps used for irrigation also pollute the sediments of the Euphrates River with Pb (Chester and Voutsinos, 1981; Sekabira et al., 2010). Therefore, their weathering by river can be a source of Pb in Euphrates River.

The presence of Cu explains the effect of waste water from the phosphate chemical complex at Alshallal in addition to human activity. Co is transported to the sediments after degradation of its bearing minerals, especially pyroxene, and it tends to be adsorbed on clay minerals, mineral oxides and organic matter (Steenfelt, 1993; Baghernejad et al., 2014; Maciag, 2019). The Co content indicates the effect of the dense population and dumping of heavy waste, manufacturers and waste water that flow directly to the river and pollutes the sediment of the Euphrates River. The increase in Sr (484 ppm) content in Rawa is due to the Sr-rich rocks such as limestone and gypsum which are dominant along the Euphrates River in the study area (Ali and Wagreich, 2017). The waste water from the phosphate chemical complex contributes to the increase of the Sr content in the sediment of the Euphrates River, where the concentration in the clay extracts reaches 185 ppm at Al-Shallal area. The waste water from the agriculture land which directly drains to the river also increases the Sr content in sediments at Albeida which reached 158 and 144 ppm on both sides of the river. Sr have a tendency for ion exchange with the clay rich in calcium because of their similar property (Wissocq et al., 2017). The increasing phosphorous content in the waste water from the phosphate chemical complex can also be considered the determining factor of the increased Cr content in the clay fraction. Dissolved phosphorous in water is a catalyst for the adoption of Cr and its concentration in sediments (Ramessur and Ramjeawon, 2002; France et al., 2013).

The results of the chemical analyses of the clay models showed that the content of the elements (Zn, Ni, Pb, Cu, Co and Cr) included in the current study in the residual fractions is relatively higher than in the extracted part, except for the cadmium, which reached 100% in the extracted part, and conversely the concentration of the strontium reached to 93% in the residual fractions. The study showed that the concentration of the nickel, copper, cobalt, and zinc in the acid extracted fractions of the clay minerals is relatively homogeneous, and ranges between (26-32) %, while its percentage of lead reached 46%, and in chromium, it reached 5.4% (Table 1).

To assess the contamination levels of the Euphrates River, we compared our observations of heavy metal concentrations in clay fractions with published values for Upper Continental Crust (UCC). Pollution indices can be a helpful tool for assessing sediment contamination and have been extensively used by numerous researchers to gauge sediment pollution (e.g., Jing-Jun et al., 2013; Shaari et al., 2015; Yalcin et al., 2016). The current study showed that heavy metal pollution and their descriptive statistical results can be assessed with respect to UCC. CF values for Cd and Ni in clay fractions represent considerable to very high contaminated ($CF > 6$), especially in Alshallal and Rummanah. Anthropogenic input, such as leaded fuel from automobiles and car batteries, is assumed to be the main source of these elements. The first source of Cd is the Phosphate chemical complex and added fertilizers to the agricultural soil also supplies a considerable amount of Cd; the Iraqi fertilizers contain Cd as TSP

(21 ppm), MAP (27 ppm), NP (11 ppm), and NPK (8 ppm) (Al-Qaraqhuli, 2005). Co, Pb, Cu and Cr were moderate contaminated ($1 \leq CF < 3$; Zn and Sr in low contaminated ($CF < 1$) (Table 7). The phosphorite deposit in the study area contains varying amounts of Cd, some of which is transferred to fertilizer products during the manufacturing process (Alloway and Steinnes, 1999; Grant and Sheppard, 2008; Terry, 2014). The accumulation of Cd in the aquatic environment can be potentially harmful due to biological activities in sediment and health of aquatic environments (Rzetala, 2016). The high levels of Cd are due to a number of sources, including municipal runoff, atmospheric deposition, and residential and industrial effluents. (Khan, 2017).

The clay fractions of Alhasa are also very highly enriched in Ni such an average comes from significant human influence (Liu et al., 2005; Zhang et al., 2007). Co, Pb, Cu and Cr showed moderate contamination especially at Alnahiya and Rawa which have an average value of 2.62, 1.75, 1.49 and 1.12, respectively. The residual Zn (0.87) and Sr (0.55) with CF averages have low contamination effect which indicates that there was no human influence on the clay fractions by these metals. The PLI is a quick tool for comparison of pollution status in various places. The highest value of PLI has 190 at sampling sites to Rawa and Alshallal, indicating the most contaminated sites (Table 11). The sites with PLI values greater >3 are polluted sites and suggest input of an anthropogenic source of pollution due to increased human activities (Mmolawa et al., 2011). However, the lowest PLI value is observed at sampling site is 3.32 indicating decreasing pollution load index trend across the Euphrates River; this represents the dilution and dispersion of metals and random fluctuation from source areas (Chakravarty and Patigiri, 2009).

According to Muller's classification, it is evident that the I_{geo} values for Sr (-1.68) and Zn (-0.79) falls in class (0) ($I_{geo} \leq 0$) in all sampling locations, indicating that they are unpolluted by this metal in the clay fractions of Euphrates River; meanwhile Cd (2.68) and Ni(2.49) fall in class 4 ($I_{geo}=3-4$), suggesting moderate to strong pollution. The other metals fall in class 1 ($I_{geo}=0-1$) with unpolluted to moderately polluted effects are Co (0.8), Pb (0.16) and Cu (-0.03) (Table 8). This demonstrates that the I_{geo} values seem to be influenced by the lithology of terrain besides possible anthropogenic contribution of Cd (industrial), Cu (irrigation water and phosphate fertilizer plant), and Co, Cu and Cr (Sewage sludge mainly from municipal wastes) (Kabata and Mukherjee, 2007; Dou et al., 2013; Jing, 2014; Issa and Qanbar, 2016). Pb is used as a tracer of motor vehicles, and the combustion of leaded gasoline in cars and trucks can be considered a Pb pollution source due to atmospheric deposition (Rashed, 2001). The increased CF, PLI and I_{geo} were attributed to industrial and vehicle emissions and inflows (Sekabira et al., 2010). The MCI with average of 26.95, suggested a Medium to very high contamination by heavy metals in the ecological system such as plants, soil invertebrates and/or mammalian wildlife (Bortey-Sam et al. 2015); this is especially the case in Alshalal (Table 8).

The result of Er show low to moderate risk by Ni (45) and considerable to very high risk from Cd (365), especially in Alshalal and Alnaya areas by Cd and Ni, respectively. The RI range of 219-1171 and average of 442 suggests a moderate to very high ecological risk of heavy metals by Cd and Ni in the ecological system such as industrial, plants, soil invertebrates and/or mammalian wildlife (Bortey-Sam et al., 2015), especially in Al-Shallal area. The results also showed that the existence of a gradient of decreasing RI content from entering the Euphrates River to the Iraqi-Syrian border and into the Maaaidged (Table 9).

Table 7. Range and average of CF and PLI values and grade for elements in the clay fraction of the Euphrates River sediments.

CF and PLI value of River Clay Fractions			
Heavy metals	Range	Average	CF and PLI Grade
Cd	3.00 - 36.78	12.16	Considerable to very high contamination
Zn	0.72 - 1.01	0.87	Low contamination
Ni	5.75 - 19.15	9	Considerable to very high contamination
Pb	1.20 - 3.30	1.75	Moderate contamination
Cu	1.12 - 1.88	1.49	Moderate contamination
Co	2.20 - 3.1	2.62	Moderate contamination
Sr	0.25 - 1.38	0.55	Low contamination
Cr	0.80 - 1.51	1.12	Low to moderate contamination
PLI	3.32 – 190	54.24	Deterioration

Table 8. Range, average and grades of I_{geo} and MCI values for elements in the sediments of Euphrates River.

I_{geo} and MCI values of River Clay Fractions			
Heavy metals	Range	Average	I_{geo} Grade
Cd	1.00 - 4.62	2.68	Moderately to strongly polluted
Zn	(-1.06) - (-0.56)	-0.79	Unpolluted
Ni	1.94 - 3.67	2.49	Moderately to strongly polluted
Pb	(-0.32) - 1.14	0.16	unpolluted to moderately polluted
Cu	(-0.42) - 0.33	-0.03	unpolluted to moderately polluted
Co	0.55 - 1.05	0.8	unpolluted to moderately polluted
Sr	(-2.58) - (-0.12)	-1.68	Unpolluted
Cr	(-0.91) - 0.01	-0.44	unpolluted to moderately polluted
MCI	11.06 - 44.32	21.56	Medium to very high contamination

Table 9. Range and average of Potential Ecological Risk Indices (Er) and Potential Toxicity Response Indices (RI) of heavy metals

Er value of River Clay Fractions			
Heavy metals	Range	Average	Er Level
Cd	90.0 – 557.0	365	Considerable to very high risk
Zn	0.7 - 1.0	0.9	low risk
Ni	28.8 - 95.8	45	low to moderate risk
Pb	6.0 - 16.5	8.8	Low risk
Cu	5.6 - 9.4	7.4	Low risk
Co	11.0 – 15.0	13.1	Low risk
Cr)	1.6 - 3.0	2.2	Low risk
RI	219 - 1171	442	moderate to very high ecological risk

5. Conclusions

Geo-accumulation index, Contamination Factor, Pollution load index and Potential Ecological Risk Index were calculated to evaluate the environmental impacts of key pollutant heavy metals in the clay fraction of the Euphrates River. The study area was found to be highly contaminated with Cd and Ni, moderately contaminated with Co, Pb and Sr, and uncontaminated with Cr, Cu and Zn. 100% of Cd was found in the extracted part of the clay fraction, thus it may be deduced that Cd in these clay fractions is derived from industrial activities of the phosphate chemical complex and the human activities in the studied area. In spite of the very low concentrations of heavy metals in the waste water from the phosphate complex at present, their concentration may cumulatively increase in the Euphrates sediments, such an increase was observed in the content of Cr, Zn, Cu and Cd metals in the clay fractions downstream from AlQaim which may be due to pollution by the waste water from phosphate company complex at that locality.

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