DOI: 10.4408/IJEGE.2021-02.O-01

GEOCHEMICAL ASSESSMENT OF HEAVY ELEMENTS IN SEDIMENTS OF MAIN WADIS OF WESTERN PART OF MOSUL CITY, IRAQ

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EXTENDED ABSTRACT

È noto come i sedimenti rappresentino una trappola permanente o temporanea per diversi tipi di contaminanti, quindi valutare la qualità del sedimento risulta un indicatore ambientale essenziale della contaminazione delle acque. È stato quindi effettuato uno studio geochimico sui sedimenti di quattro uadi principali (Ugab, Al-Yarmoukm, Al-Einb e Al-Mamoun) nella parte occidentale della città di Mosul, in Iraq.

La città di Mosul è circondata dal lato occidentale della parte destra da aree morfologicamente rilevate rappresentate dalle anticlinali di Atshan, Sheikh Ibrahim, Adayah e Allan, questa configurazione topografica impone agli uadi di attraversare la città in direzione del fiume Tigri. Questi uadi contengono sedimenti provenienti dalle rocce affioranti della Formazione Fat'ha costituita da rocce calcaree, gesso e marna oltre che da depositi e terreni quaternari. Questi uadi attraversano aree residenziali ad alta densità di popolazione e caratterizzate da diverse attività (domestiche, industriali, commerciali e agricole), e vengono utilizzati come discariche per rifiuti solidi e acque reflue.

Le sorgenti di metalli pesanti sono legate ad attività domestiche, agricole e industriali. Si osserva infatti che le concentrazioni di piombo, cromo, zinco e rame sono cresciute negli uadi Ugab e Al-Yarmouk a causa della presenza di siti industriali quali officine idrauliche e tintorie, siti di forgiatura, produzioni alimentari e fabbriche di detersivi, oltre alla presenza di rottami di veicoli e rifiuti di ferro. Mentre negli uadi Al-Mamoun e Al-Ein le concentrazioni di elementi pesanti diminuiscono in quanto questi uadi attraversano regioni residenziali e agricole.

Venticinque campioni sono stati analizzati chimicamente con la tecnica della fluorescenza a raggi X per determinare gli ossidi maggiori e minori e i metalli pesanti nel German-Iraqi Laboratory dell'Università di Baghdad. La materia organica e la perdita per ignizione sono state misurate nel laboratorio geochimico del dipartimento di geologia dell'Università di Mosul. I principali ossidi misurati sono: % in peso di SiO_2 (25,22-37,22), % in peso di CaO (20,32-33,59), % in peso di Al_2O_3 (5,50-8,31), % in peso di Fe_2O_3 (3,86-6,10), MgO (2,15-4,30) e CO_2 (7,42-16,79), gli ossidi minori misurati sono; % in peso di TiO_2 (0,52-0,78), % in peso di Na_2O (0,37-1,08), % in peso di K_2O (0,88-1,16), % in peso di P_2O_5 (0,12-0,63), % in peso di SO_3 (0,23-1,39) e % in peso di Cl (0,01- 0,05), la materia organica (OM) era in % in peso (4,47-17,72) Gli elementi pesanti sono; Cr (170-399) ppm, Ni (91-157) ppm, Cu (27-151) ppm, Zn (83-735) ppm, Pb (12-536) ppm e As (4-10) ppm.

Le concentrazioni di Cr, Cu, Zn, Pb che si associano alla materia organica risultano basse all'inizio degli uadi e aumentano verso valle alla fine di ogni uadi. Le concentrazioni più elevate sono presenti nelle aree industriali soprattutto negli uadi Ugab e Al-Yarmouk. La più alta concentrazione di Ni associata ai minerali argillosi è misurata all'inizio degli uadi, e diminuisce leggermente procedendo verso valle a causa del processo di lisciviazione dei sedimenti da parte degli agenti atmosferici, oltre che a causa del passaggio ai sedimenti quaternari e ai depositi di pianura alluvionale del fiume Tigri alla fine degli uadi, come mostrato dallo uadi Ugab.

L'analisi fattoriale seleziona tre componenti principali che rappresentano 78,45 % della varianza totale, sono rispettivamente (43,84, 27,39, 7,23 %) per il primo, secondo e terzo fattore, che riflettono il controllo della distribuzione degli elementi nei gruppi minerali dei sedimenti; il gruppo della materia organica e dei minerali secondari, il gruppo dei minerali argillosi e il gruppo degli ossidi di ferro; oltre al gruppo del carbonato. I fattori hanno indicato che lo uadi Ugab risulta essere il più colpito dall'inquinamento, seguito dallo uadi Al-Yarmouk a causa della vicinanza delle fonti di inquinamento. Piombo e cromo costituiscono gli elementi più inquinanti (fortemente contaminati), mentre l'I_{geo} indica che gli uadi Al-Mamoun e Al-Ein sono moderatamente contaminati.

L'indice di geoaccumulo (I_{geo}) indica che in due aree industriali negli uadi Ugab e Al-Yarmouk c'erano le più alte concentrazioni di elementi inquinati rispetto al resto degli uadi, e quindi questi siti apparentemente mostravano livelli di inquinamento elevati rispetto ad altri siti che sembravano essere moderatamente inquinati.

In generale si nota un aumento delle concentrazioni di elementi pesanti lungo il corso degli uadi a causa dell'erosione, trasporto e movimento dell'acqua durante l'anno, soprattutto durante il periodo delle precipitazioni. Tenendo conto delle alte concentrazioni rilevate lungo il corso degli uadi dovute alla presenza di siti inquinati, come nello uadi Al-Ein, nessun cambiamento è stato osservato nel grado di arricchimento del nichel in tutte le valli a causa del suo assorbimento nei minerali argillosi. I valori più alti del fattore di arricchimento (EF) hanno restituito che gli elementi pesanti sono ordinati come piombo > zinco > cromo > rame > nichel > arsenico.

ABSTRACT

To assess the quality of sediment as it is an essential environmental indicator of water contamination due to sediments represent a permanent or temporary trap for various pollutants, a geochemical study was performed for sediments of four main wadis (Ugab, Al-Yarmouk, Al-Ein, and Al-Mamoun) in the western part of Mosul city, Iraq.

Mosul city is surrounded from the western side of the right part by high areas represented by Atshan, Sheikh Ibrahim, Adayah, and Allan anticlines, this topographic situation imposes the wadis to pass the city towards the Tigris River. These wadis contain sediments derived from the exposed rocks of Fat'ha Formation which consist of limestone, gypsum, and marl rocks in addition to the Quaternary deposits and soils. These wadis pass from residential areas with high population density and diverse activities (domestic, industrial, commercial, and agricultural), so these wadis are used as dumping sites for solid waste and wastewater.

Twenty-five samples were analyzed chemically by X-ray fluorescence technique to determine the major and minor oxides, heavy elements in the German-Iraqi laboratory at the University of Baghdad. The organic matter and loss on ignition were performed in the geochemical laboratory at the department of geology in Mosul University. The major oxides were; SiO_2 (25.22-37.22) wt%, CaO (20.32-33.59) wt%, Al_2O_3 (5.50-8.31) wt%, Fe_2O_3 (3.86-6.10) wt%, MgO (2.15-4.30) wt%, and CO_2 (7.42-16.79) wt%, minor oxides were; TiO_2 (0.52-0.78) wt%, Na_2O (0.37-1.08) wt%, K_2O (0.88-1.16) wt%, P_2O_5 (0.12-0.63) wt%, SO_3 (0.23-1.39) wt%, and Cl (0.01-0.05) wt%, Organic matter (OM) was (4.47-17.72) wt%. Heavy elements were; Cr (170-399) ppm, Ni (91-157) ppm, Cu (27-151) ppm, Zn (83-735) ppm, Pb (12-536) ppm, and As (4-10) ppm.

The factor analysis sorts three main components representing 78,45 of total variance were (43,84, 27,39, 7,23) for the first, second and third factors, respectively, that reflect the controlling of elements distribution in the mineral groups of the sediments; the group of organic matter and secondary minerals, the clay minerals group, and the iron oxides group. In addition to the carbonate group. The geoaccumulation index (I_{geo}) indicates that in two industrial areas in Ugab wadi and Al-Yarmouk wadi there were highest concentrations of polluted elements in relation to the rest of wadis, and therefore these sites seemingly had high levels of pollution compared to other sites that appeared to have been moderately polluted. The maximum enrichment factor (EF) values were ordered as lead> zinc> chromium> copper> nickel> arsenic.

***Keywords**: geochemical assessment, heavy metals, pollution, wadi's sediments, Mosul, Iraq*

INTRODUCTION

The problem of pollution has become a clear phenomenon in urban societies, which is increasing significantly, as the concentrations of elements in sediments, water, and air are increasing, as a result of accidental or deliberate influences through subtractions resulting from various human activities (Ali *et alii*, 2019; Ahmadpour, 2012). The surface sediments of rivers and wadis are exposed to various types of pollution, including pollution with heavy metals, due to their ease of transmission from different sources (Wuana & Okieimen, 2011). Heavy elements appear in aquatic systems naturally as a result of successive erosion processes of the bearing mineral in the rocks, and through human resources including civil, industrial, and agricultural (Çevik *et alii*, 2009), animal husbandry (livestock, sheep and poultry), land runoff, water and sewage sludge (Wuana & Okieimen, 2011).

Sediment quality is an important environmental indicator of water pollution (Chabukdhara & Nema, 2012) as sediment is a permanent or temporary sink for various pollutants, including elements discharged into the environment (Elkady *et alii*, 2015).

Heavy elements cannot degrade chemically or biologically, unlike organic matter, which can be oxidized by bacterial activity, and thus accumulate in the soil for a long time (Lukman *et alii*, 2013). Heavy metal pollution poses a threat to human life and the ecosystem, by the intake of these elements through the food chain (Fu *et alii*., 2014; Huang *et alii*., 2020), and the exploitation of polluted groundwater for drinking purposes. The concentrations of heavy metals above their natural levels affect the microbiological balance in the soil and reduces its fertility (Barbieri, 2016) and thus leads to a decrease in land use for agricultural production (Akcay *et alii*, 2003; Jia *et alii*, 2020).

The sources of river sediments are different and varied, and therefore they are heterogeneous aggregates of multiple phases such as organic matter, clay minerals, oxides, sulfides, and carbonates, which are carriers of pollutants mainly through cation exchange, geochemical behavior, and adsorption (Zhang *et alii*, 2014).

The direct estimation of heavy metal concentrations in sediments is an ineffective method for assessing pollution because heavy elements, from both natural and human sources, accumulate similarly in sediments. The geochemical interpretation methods and various statistical methods such as factor analysis and principal components analysis are used in processing and interpretation of the data obtained from geochemical analysis with its different techniques (Idris, 2008; Liu *et alii*, 2016)

STUDY AREA

Mosul city is located between longitudes 43◦ 01′ - 43◦ 20′ and latitudes 36◦ 15′ - 36◦ 27′ (Fig. 1). It is considered the second largest Iraqi city in terms of population, as its population until March 2021 reached (1,667,731) people according to (World Population, 2021). The Tigris River passes through the city, dividing it into

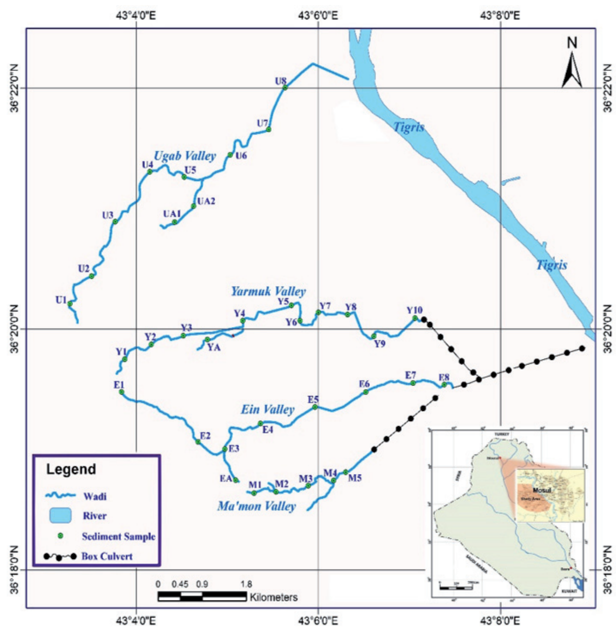

Fig. 1 - Map showing the right bank of Mosul city, Iraq, and the samples location of study area

two parts located on its sides. The city is an important commercial and industrial center, with two industrial areas distributed on both sides of the city. It is one of the first Iraqi agriculturally productive cities, in addition to the presence of a large livestock wealth about 12% of the national share, (Agrarian Statistical Atlas, 2008), the city's climate is characterized as semi-arid, and the annual rainfall is about 356 mm (Awchi & Jasim, 2017).

The study area represents the west part of the city (Fig. 1). The topography of the area imposes the formation of wadis to drain rainfall downstream to the Tigris River. Four main wadis appear in the study area, which are from the north, Ugab wadi, Al-Yarmouk wadi, Al-Ein wadi, and Al-Mamoun wadi, due to the increase in the population and urban expansion in the city and the weakness of the drainage network system. These wadis have become an alternative and a natural drainage network for water paths. Al-Yarmouk wadi, Al-Ein wadi, and Al-Mamoun wadi are connected to a box culvert system to eventually drain into the Tigris River, while Ugab wadi is the only one that flows directly into the river. These wadis are used as dumping sites for solid waste and waste water. Different types of plants grow in the wadis and their banks, reeds represent the most widespread of these plants.

GEOLOGICAL SITUATION

Mosul is located on the Arab plate and the edge of the unstable fault- thrust belt within the foothills zone (Jassim & Goff, 2013). The city is surrounded from the right side by several anticlines represented by the folds of Atshan, Sheikh Ibrahim, Adayah, and Allan, while the northern and southern parts form wavy areas with low terrain interspersed with flat and long wadis heading towards the Tigris River. The study area can be considered a topographic depression, the elevation of the lowest point is 215 m above sea level located on the flood plain of the Tigris River, while the highest point reaches 330 m above sea level on the western side (Zuhair D. Al-Shaikh, 2005). The geological formations of the study area are revealed from the oldest; Fat'ha Formation (Middle Miocene) consisting of alternating of green marl, nodular gypsum, and layers of limestone in the form of successive cycles, followed by the Injanah Formation (Upper Miocene) consisting of alternating of mud, sandy, and alluvial rocks, and Quaternary deposits, generally consist of conglomerates, sediments of gravel, sand, and clay that have eroded from formations scattered along the wadis (Al- Nuaimi, 2013).

This study aims to assess contamination of heavy metals in the wadis' sediments on the west part of Mosul city using a geochemical study to evaluate the impact on the sediments in the wadis of the various sources of waste.

SAMPLING AND METHODOLOGY

Twenty-five selected samples of surface sediments were collected along the wadis in the study area using a shovel at a depth of (0-25) cm (Fig. 2), and their locations were determined by GPS application, between (July 2020 - September 2020).

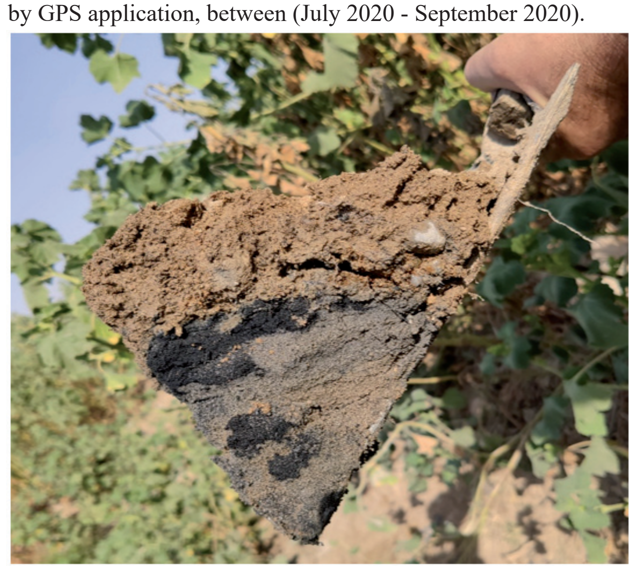

Fig. 2 - Photo shows sediment sample at depth about 20 cm

The samples were kept in plastic bags, and dried by oven at a temperature of 40 °C. The plants, roots, pieces of glass, plastic pieces, and other impurities were removed. The samples were homogenized well and crushed by a HERZOG pulverizing mill. The crushed samples were sent for chemical analysis of the major oxides and heavy elements in the German-Iraqi laboratory at the University of Baghdad / Iraq by X-Ray fluorescence Spectrometer device model (Spectro Xepos). Corundum metal was used as standard material (Feret *et alii*, 2000). The samples were dried in an oven at 105 °C to calculate the moisture content. The organic matter content was measured after burning at 550 °C (Dean, 1974; Heiri *et alii*, 2001). Total loss on ignition (LOI) was measured by Muffle furnace at a temperature of 1000-1100 °C. CO_2 was measured using acidification by N 0.1 HCl (Carver, 1971). TOM, LOI, and the amount of CO_2 were performed in the Geochemistry Laboratory of the Department of Geology at the University of Mosul / Iraq.

Microsoft Excel 2019 was used to perform the correlation coefficient among the main oxides, organic matter, carbon dioxide, and heavy elements. The significant levels were ±0.4 at p-value 0.05 for 25 samples. The Statistical Program Package for the Social Sciences (IBM SPSS Statistics V26.0) (SPSS Inc., Chicago, IL, USA) to perform factor analysis test and principal components analysis.

Due to the similarity in the sediment sources derived from the Fat'ha Formation rocks and the Quaternary deposits, as well as the same weathering conditions that transported the sediments through the wadis, spatial distribution maps for sediment samples were performed using ArcMap V10.8 as well as the location map of the study area.

Geoaccumulation index

The geoaccumulation index (Igeo) was used to determine the heavy metals contamination in sediment. It is a quantitative method to measure metals pollution in water sediments and solid wastes, using the equation (1) (Müller, 1979; Förstner & Müller, 1981). The geochemical background concentration value of the heavy metal is based on average shale (Turekian & Wedephol, 1961).

$$I_{geo} = Log_2 (C_n/_{1.5}*Cb_n) \quad (1)$$

where:

C_n = The concentration of heavy metal (n) in the sediment samples (ppm).

Cb_n = The geochemical background concentra-tion value of heavy metal (n) (ppm).

1.5 = correction factor used for lithologic variations of trace elements.

I_{geo} index was classified into seven classes as shown in Tab. 1 (Förstner & Müller, 1981).

I_{geo} value	I_{geo} class	Sediment quality designation
> 5	6	extremely contaminated
4-5	5	strongly to extremely contaminated
3-4	4	strongly contaminated
2-3	3	moderately to strongly contaminated
1-2	2	moderately contaminated
0-1	1	uncontaminated to moderately contaminated
< 0	0	Uncontaminated

Tab. 1 - Classification of geoaccumulation index (I_{geo}) (Förstner & Müller, 1981)

Enrichment factor

The enrichment factor (EF) is used to assess the contamination degree of heavy elements driven by natural processes and/or anthropogenic activities in sediments (Kumar *et alii*, 2017; Wang *et alii*, 2020). The enrichment factor is calculated by the equation (2):

$$EF = (C_n/Al)\ sample\ /(C_n/Al)\ background \quad (2)$$

where:

(C_n/Al) sample = The ratio of heavy metal (n) and Al concentration in the sediment samples.

$(C_{n/}Al)$ background = The ratio of heavy metal (n) and Al concentration in the background based on Average shale (Turekian *et alii*, 1961).

The EF index was classified into five categories from EF< 2 to EF> 40, (Deficiency to minimal enrichment) to (Extremely high enrichment) respectively, as in Tab. 2, (Barbieri, 2016).

EF value	Soil contamination description
EF < 2	Deficiency to minimal enrichment
EF 2-5	Moderate enrichment
EF 5-20	Significant enrichment
EF 20-40	Very high enrichment
EF > 40	Extremely high enrichment

Tab. 2 - The enrichment factor categories (Barbieri, 2016)

This entails normalizing metal data based on the contents of a conservative element such as Al, Fe, Rb, Li, Sc, and organic carbon, etc., which represents one or more of the major element carriers of sediments, such as (clay minerals, manganese, and iron oxides, and organic matter, etc.) (Ho *et alii*, 2012). In this study, as one of the main components of the studied sediments is clay minerals as well as organic matter, Aluminum (Al) was used as a reference value for normalization.

Sediment quality guidelines

Sediment quality guidelines (SQGs) set of criteria, factors, and approaches to account for the various conditions under which sediment contamination occurs (Kwok *et alii*, 2013). The effects range low/median (ERL/ERM) is one of the commonly used guideline. The low-range values of (ERL) represent level that are unlikely to adversely influence sediment-dwelling organisms. The upper range value of (ERM) represent concentration that is expected to cause adverse effects (Hahladakis *et alii*, 2013).

Tab. 3 shows the limits of (SQGs).

U.S. Environmental Protection Agency's (USEPA) toxicity reference values (TRV) was also used to determine the quality of sediments (USEPA, 1999).

SQG	Cr	Ni	Cu	Zn	Pb	As
ERL	80	30	70	120	35	33
ERM	145	50	390	270	110	85
TRV	26	16	16	110	31	6

Tab. 3 - The limits of (SQGs) for heavy elements in (ppm)
ERL: Effect range low
ERM: Effect range median. (Long & Morgan, 1991)
TRV: Toxicity reference value (USEPA, 1999)

RESULTS AND DISCUSSION

Tab. 4 shows concentrations of major and minor oxides, chlorine, carbon dioxide, organic matter in sediments, and upper crust concentration values (UCC) according to Rudnick & Gao, 2013.

The values of silica range for Ugab wadi, Al-Yarmouk wadi, Al-Ein wadi, and Al-Mamoun wadi, (30.12-35.42%, average 32.40%), (31.58-35.70%, average 34.14%), (25.22-37.92%, average 31.02%), (26.54-35.35%, average 30.96%) respectively.

The difference in concentration rates with the reference value above in silica, aluminum oxides, calcium, sodium and phosphorus. The general similarity in the concentration rates of silica and calcium oxide indicates the nature of the source rocks and their exposure to the same conditions of erosion and transport along the studied wadis (Hussein & Al-Owaidi, 2021). Aluminum oxide concentrations are less than their value in UCC, they were in Ugab wadi, Al-Yarmouk wadi, Al Ein wadi, and Al-Mamoun wadi, (5.64-8.11%, average 6.76), (5.57-8.26%, Average 6.68%), (5.50-8.31%, Average 6.76%), (6.36-8%) .63%, Average 7.23%), respectively. Tab. 5 shows a strong positive relationship between aluminum oxide, titanium oxide, magnesium oxide, and potassium oxide

Sample	SiO_2	TiO_2	Al_2O_3	Fe_2O_3	MgO	CaO	Na_2O	K_2O	P_2O_5	SO_3	Cl	CO_2	OM
U1	33.57	0.74	8.11	5.07	3.31	27.53	0.54	1.03	0.13	0.25	0.03	11.42	4.47
U2	31.33	0.65	6.94	4.29	2.90	27.14	0.62	0.98	0.19	0.43	0.03	13.44	6.27
U3	32.73	0.78	7.42	4.89	3.05	25.27	0.70	1.16	0.28	0.43	0.04	12.63	8.50
U5	30.64	0.61	5.64	6.10	2.15	31.18	0.76	0.95	0.17	0.41	0.03	14.38	5.42
U6	33.01	0.63	6.49	4.52	2.71	22.70	0.86	1.08	0.38	0.95	0.05	11.38	10.49
U8	30.12	0.67	6.82	4.71	2.92	26.88	0.79	1.07	0.32	1.13	0.03	14.32	6.83
UA2	35.42	0.63	5.91	4.63	2.26	23.32	1.08	0.95	0.63	1.19	0.05	12.58	9.22
Y1	35.26	0.76	8.26	5.19	4.30	25.00	0.46	1.11	0.14	0.23	0.02	9.94	5.72
Y3	32.00	0.62	6.59	4.03	2.87	28.00	0.79	0.98	0.28	0.93	0.03	12.91	7.22
Y4	35.70	0.69	7.24	4.57	3.22	24.22	0.80	1.13	0.20	1.19	0.04	13.26	5.74
Y5	31.58	0.56	5.57	4.71	2.49	29.11	0.85	0.96	0.33	0.56	0.04	16.22	6.26
Y7	33.81	0.64	6.56	4.51	2.84	20.90	0.91	0.98	0.41	0.82	0.05	13.34	10.34
Y9	35.22	0.68	6.66	4.83	2.83	22.56	1.03	1.05	0.48	1.13	0.04	10.12	9.57
Y10	31.60	0.66	6.28	4.97	2.76	21.17	1.26	1.00	0.54	2.42	0.06	8.67	17.72
E1	31.05	0.73	7.65	4.70	3.08	29.41	0.49	1.05	0.12	0.61	0.01	13.03	5.19
E3	25.22	0.54	5.80	3.86	2.49	33.59	0.59	0.88	0.14	0.69	0.02	16.79	6.21
E5	37.92	0.67	6.38	4.38	2.62	20.32	1.03	1.05	0.37	1.39	0.03	8.89	10.53
E7	27.05	0.52	5.50	3.89	2.32	32.11	0.69	0.96	0.25	0.71	0.02	15.68	6.49
E8	31.00	0.64	6.95	4.76	3.01	25.16	0.77	1.14	0.26	1.32	0.03	7.42	9.27
EA	33.88	0.73	8.31	5.07	3.32	25.96	0.37	0.99	0.16	0.25	0.01	8.75	6.82
M1	35.35	0.79	8.63	5.29	3.50	24.82	0.49	1.17	0.13	0.19	0.03	10.07	5.86
M2	31.66	0.70	7.31	4.91	2.99	28.50	0.62	1.07	0.37	0.47	0.03	13.35	6.90
M3	29.90	0.66	6.93	4.68	2.82	27.35	0.69	1.00	0.23	0.56	0.03	12.31	8.72
M4	31.34	0.65	6.90	4.42	2.80	29.07	0.64	1.01	0.22	0.38	0.03	14.33	6.02
M5	26.54	0.61	6.36	4.59	2.61	31.23	0.67	0.92	0.16	0.25	0.03	16.16	4.37
Min.	25.22	0.52	5.50	3.86	2.15	20.32	0.37	0.88	0.12	0.23	0.01	7.42	4.47
Max.	37.92	0.78	8.31	6.10	4.30	33.59	1.26	1.16	0.63	2.42	0.06	16.79	17.72
Mean	32.60	0.66	6.73	4.67	2.85	26.18	0.76	1.02	0.29	0.79	0.03	12.26	7.91
UCC	66.62	0.64	15.4	5 04	2.48	3.59	3.27	2.8	0.15	-	-	-	-

Tab. 4 - Concentrations of major and minor oxides; upper continental crust (UCC) according (Rudnick, 2013) in (wt%)

	SiO_2	TiO_2	Al_2O_3	Fe_2O_3	MgO	CaO	Na_2O	K_2O	P_2O_5
SiO_2	1.00*								
TiO_2	0.56*	1.00*							
Al_2O_3	0.36	0.91*	1.00*						
Fe_2O_3	0.31	0.53*	0.38	1.00*					
MgO	0.33	0.77*	0.90*	0.27	1.00*				
CaO	-0.86*	-0.41*	-0.23	-0.10	-0.22	1.00*			
Na_2O	0.33	-0.40*	-0.66*	-0.20	-0.62*	-0.51*	1.00*		
K_2O	0.48*	0.75*	0.66*	0.32	0.65*	-0.47*	-0.16	1.00*	
P_2O_5	0.40*	-0.24	-0.48*	-0.16	-0.48*	-0.56*	0.86*	-0.13	1.00*
SO_3	0.29	-0.31	-0.45*	-0.37	-0.38	-0.50*	0.80*	0.06	0.66*
Cl	0.41*	-0.15	-0.39	0.01	-0.42*	-0.57*	0.81*	0.01	0.79*
CO_2	-0.70*	-0.55*	-0.48*	-0.30	-0.39	0.71*	-0.09	-0.51*	-0.22
OM	0.41*	-0.11	-0.31	-0.15	-0.34	-0.61*	0.69*	-0.02	0.80*
Cr	0.48*	-0.03	-0.26	-0.07	-0.14	-0.57*	0.64*	0.18	0.46*
Ni	0.05	0.74*	0.88*	0.42*	0.85*	0.01	-0.77*	0.59*	-0.62*
Cu	0.45*	-0.18	-0.50*	0.11	-0.51*	-0.60*	0.83*	-0.02	0.77*
Zn	0.44*	-0.27	-0.52*	-0.12	-0.51*	-0.65*	0.90*	-0.14	0.94*
As	0.19	0.28	0.20	0.43*	0.25	-0.20	0.15	0.38	0.12
Pb	0.36	-0.14	-0.31	0.08	-0.31	-0.42*	0.59*	-0.12	0.67*

SO_3	Cl	CO_2	OM	Cr	Ni	Cu	Zn	As	Pb
1.00*									
0.47*	1.00*								
-0.28	-0.11	1.00*							
0.61*	0.64*	-0.51*	1.00*						
0.62*	0.29	-0.23	0.37	1.00*					
-0.55*	-0.53*	-0.33	-0.41*	-0.39	1.00*				
0.62*	0.69*	-0.28	0.70*	0.70*	-0.57*	1.00*			
0.71*	0.77*	-0.31	0.83*	0.57*	-0.64*	0.89*	1.00*		
0.14	0.23	-0.23	0.01	0.11	0.21	0.08	0.11	1.00*	
0.38	0.50*	-0.25	0.50*	0.40*	-0.41*	0.61*	0.69*	0.36	1.00*

Tab. 5 - Correlation coefficient matrix (Significant Correlation at $p < 0.05$)*

(correlation coefficient) = (0.905, 0.897, 0.659, 0.880) respectively, that may reflect the clay minerals phases resulting from weathering of parent rocks of Fat'ha Formation. High concentration of magnesium and the low concentration of potassium may reflect the represent of (Mg-chlorite) and/or palygorskite. High concentration of calcium oxide (20.32-33.59%, Average 26.18%), carbon dioxide and low concentration of magnesium oxide (2.15-4.30%, average 2.85%) In sediments, reflect the calcite phase derived from limestone rocks of Fat'ha Formation after exposure to weathering and transportation during periods of precipitation in the form of fine grains along the wadi floor.

Heavy elements and sediment quality guides

Table 6 shows the range and average concentrations of chromium (167.56-399.03, avg. 231.42), nickel (91.39-156.53, avg. 116.95), copper (27.32-150.91, avg. 74.25), zinc (82.51-841.96, avg. 319.31), lead (11.88-536.01, avg. 110.86) and arsenic (4.09-10.38, avg. 6.59) in ppm, as well as the refences concentration values of heavy elements in upper continental crust (UCC) according (Taylor & Mclennan, 1995), ERL, ERM and TRV. In general, the concentrations of (Cr, Ni, Cu, Zn, Pb, and As) were higher than UCC. Cr, Cu and Zn in all wadis are higher than ERL values and lower than ERM values, which represent probable effects range that may sometimes have a negative biological effect on organisms in the sediment (Long *et alii*, 1995). Ni concentrations in all wadis are higher than ERM values, which represent the range of potential effects that occur frequently. Pb vary from lower than ERL at the upstream of each wadi, that falls within the range of lower effects that effects rarely appear, the Pb concentrations are increasing along each wadi to become higher than ERL values and below ERM values. However, some Pb concentrations are higher than ERM values in Al-Yarmouk wadi, Ugab wadi, and Al-Ein wadi due to

Sample	Cr	Ni	Cu	Zn	Pb	As
U1	185.42	135.31	37.71	101.79	14.95	7.80
U2	217.78	106.55	54.16	246.32	34.63	5.60
U3	230.37	125.34	94.03	292.84	79.00	6.44
U5	239.20	102.63	129.82	283.36	97.75	7.04
U6	261.57	119.36	138.84	498.83	273.30	6.29
U8	289.90	117.56	76.37	314.93	90.42	8.26
UA2	227.43	92.80	130.22	734.63	258.72	6.36
Y1	239.34	156.53	36.03	116.98	21.26	7.27
Y3	228.87	101.60	50.09	247.05	44.37	6.36
Y4	238.17	116.22	56.96	197.07	38.43	6.82
Y5	239.40	91.39	67.58	343.94	318.69	6.74
Y7	258.22	101.53	116.00	602.55	106.48	5.91
Y9	323.97	106.48	127.42	631.31	536.01	10.38
Y10	229.69	110.96	124.54	841.96	190.77	9.62
E1	210.94	128.71	27.32	82.51	11.88	6.06
E3	184.33	108.52	27.72	140.35	17.36	5.53
E5	399.03	98.46	150.91	558.85	107.59	4.09
E7	230.44	101.29	68.62	286.81	58.30	4.70
E8	206.36	127.06	71.02	380.33	66.84	7.88
EA	169.96	137.36	41.86	178.44	232.36	4.70
M1	192.67	147.10	34.03	94.24	13.55	7.80
M2	215.94	125.65	61.91	253.15	54.77	6.13
M3	193.70	130.13	61.11	274.12	53.56	6.74
M4	205.26	114.81	42.58	183.74	34.25	4.62
M5	167.56	120.38	29.32	96.65	16.34	5.68
Min.	167.56	91.39	27.32	82.51	11.88	4.09
Max.	399.03	156.53	150.91	841.96	536.01	10.38
Aver.	231.42	116.95	74.25	319.31	110.86	6.59
UCC	35.00	20.00	25.00	71.00	20.00	1.50
ERL	81.00	20.90	34.00	150.00	46.70	8.20
ERM	370.00	51.60	270.00	410.00	218.00	70.00
TRV	26.00	16.00	16.00	110.00	31.00	6.00

Tab. 6 - Concentrations of heavy elements (in ppm) industrial activities and wastes as well as car scrapyards. Concentrations of As are mostly lower than ERL values; therefor, they do not have a detrimental impact on the organisms in the sediments.

Compared to (TRV), it appears that concentrations of Cr, Ni, Cu, Zn and Pb in all wadis are higher than TRV values. While the concentrations of As in the Ugab wadi and Al-Yarmouk wadi are higher than reference values. On the other hand, they are lower than the reference values and sometimes fall on the threshold of those values in Al-Ein wadi and Al-Mamoun wadi due to same reason above.

Factor analysis (principal components analysis; PCA)

In order to understand the relationship between the main sediment components and the heavy elements associated with them, the factor analysis was performed using the extraction method: analysis of the main components, varimax with Kaiser normalization, applied to the concentrations of major and minor oxides, organic matter, carbon dioxide and heavy elements, Kaiser-Meyer-Olkin value (KMO) which adopts eigenvalues greater than 1, was 0.592, after applying varimax rotation for an easier explanation (Anbuselvan *et alii*, 2018) three main factors representing 78,45 of total variance were (43,84, 27,39, 7,23) for the first, second and third factors, respectively, Tab. 7, Fig. 3.

Oxides, OM, CO_2 and elements	Component		
	PC1	PC2	PC3
SiO_2	0.561	***0.686***	0.129
TiO_2	-0.184	***0.887***	0.264
Al_2O_3	-0.445	***0.857***	0.121
Fe_2O_3	-0.127	0.319	***0.788***
MgO	-0.433	***0.822***	0.062
CaO	-0.732	-0.622	-0.011
Na_2O	***0.928***	-0.279	0.022
K_2O	0.008	***0.817***	0.142
P_2O_5	***0.907***	-0.147	0.064
SO_3	***0.795***	-0.039	-0.263
Cl	***0.779***	-0.126	0.258
OM %	***0.834***	0.062	-0.106
CO2%	-0.388	-0.754	-0.063
Cr	***0.687***	0.144	-0.116
Ni	-0.615	***0.694***	0.178
Cu	***0.895***	-0.087	0.144
Zn	***0.966***	-0.123	0.046
As	0.139	0.211	***0.747***
Pb	***0.669***	-0.120	0.417
Eigenvalue	8.329	5.203	1.373
Total variance (%)	43.838	27.385	7.225
Cumulative of variance (%)	**43.838**	**71.223**	**78.448**
PC values ≥ 0.6			

Tab. 7 - Factor analysis data

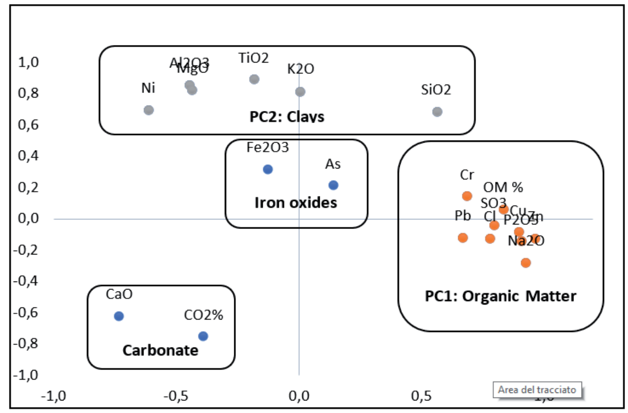

Fig. 3 - First principal component versus second principal component

The first main component

This component shows the association of organic matter with sodium, phosphorus, sulfur oxides, chlorine, chromium, copper, zinc and lead. The presence of phosphorus, copper, zinc and lead can be attributed to civil industrial activities, agricultural sources and their residues. Domestic sewage and industrial wastewater are nutrients of organic matter in the sediments (Michael-Kordatou *et alii*, 2015).

Table 5 shows strong correlations between organic matter and sodium oxide (r =0.693), chlorine (r =0.640), and sulphate (r =0.614). These mean the sulphate, sodium, and chlorine represent the secondary minerals of sulphate and halite which resulting from the erosion of the source rocks of Fat'ha Formation that consist of gypsum and halite. Furthermore, the relation between organic matter and phosphorus (r =0.804) may result from the fertilization of agricultural land in the form of orthophosphate, or as a result of the bio-processes of plants as organic phosphate compounds, or from the waste of detergent industries, and/or domestic washing products wastewater in the form of polyphosphate tripod compounds, (Kome *et alii*, 2019; Nash *et alii*, 2014).

Table 5 displays the values of the correlation coefficient between organic matter, copper, zinc and lead (r =0.702), (r =0.835) & (r =0.497) respectively, which most likely indicate that the source of these elements is an industrial source representing the plumbing and dyeing and batteries workshops, byproducts of food manufacturing and detergent industries. These elements are usually adsorbed on the organic matter, so it is noted that their concentrations are high in the sediments of wadis near the industrial sites.

This factor represents the main effect of organic matter and slightly effect of secondary minerals on the sediments of wadis, Tab. 7, Fig. 3.

The second main component:

This component shows the association of silica, titana, alumina, magnesia, and potassium oxide, as well as Ni. These oxides represent various clay mineral phases (Kome *et alii*,

	Cr	Ni	Cu	Zn	Pb	As
U1	0.46	0.41	-0.84	-0.49	-1.01	-1.32
U2	0.69	0.06	-0.32	0.79	0.21	-1.80
U3	0.77	0.30	0.48	1.04	1.40	-1.60
U5	0.83	0.01	0.94	0.99	1.70	-1.47
U6	0.95	0.23	1.04	1.81	3.19	-1.63
U8	1.10	0.20	0.18	1.14	1.59	-1.24
UA2	0.75	-0.14	0.95	2.37	3.11	-1.62
Min	**0.46**	**-0.14**	**-0.84**	**-0.49**	**-1.01**	**-1.80**
Max	**1.10**	**0.41**	**1.04**	**2.37**	**3.19**	**-1.24**
Y1	0.83	0.62	-0.91	-0.28	-0.50	-1.42
Y3	0.76	-0.01	-0.43	0.79	0.56	-1.62
Y4	0.82	0.19	-0.24	0.47	0.36	-1.52
Y5	0.83	-0.16	0.00	1.27	3.41	-1.53
Y7	0.94	-0.01	0.78	2.08	1.83	-1.72
Y9	1.26	0.06	0.92	2.15	4.16	-0.91
Y10	0.77	0.62	0.88	2.56	2.67	-1.02
Min	**0.76**	**-0.16**	**-0.91**	**-0.28**	**-0.50**	**-1.72**
Max	**1.26**	**0.19**	**0.92**	**2.56**	**4.16**	**-0.91**
E2	0.64	0.34	-1.30	-0.79	-1.34	-1.69
E3	0.45	0.09	-1.28	-0.02	-0.79	-1.82
E5	1.56	-0.05	1.16	1.97	1.84	-2.25
E7	0.77	-0.01	0.02	1.01	0.96	-2.05
E8	0.61	0.32	0.07	1.42	1.16	-1.31
EA	0.33	0.43	-0.69	0.32	2.95	-2.05
Min	**0.33**	**-0.05**	**-1.30**	**-0.79**	**-1.34**	**-2.25**
Max	**1.56**	**0.43**	**1.16**	**1.97**	**2.95**	**-1.31**
M1	0.51	0.53	-0.99	-0.60	-1.15	-1.32
M2	0.68	0.30	-0.12	0.83	0.87	-1.67
M3	0.52	0.35	-0.14	0.94	0.84	-1.53
M4	0.60	0.17	-0.66	0.37	0.19	-2.08
M5	0.31	0.24	-1.20	-0.56	-0.88	-1.78
Min	**0.31**	**0.17**	**-1.20**	**-0.60**	**-1.15**	**-2.08**
Max	**0.68**	**0.53**	**-0.12**	**0.94**	**0.87**	**-1.32**

Tab. 8 - Geoaccumulation index (I_{geo}) of heavy elements

	Cr	Ni	Cu	Zn	Pb	As
U1	3.93	3.50	1.46	1.98	1.74	1.12
U2	5.39	3.22	2.46	5.59	4.71	0.94
U3	5.33	3.54	3.99	6.21	10.05	1.01
U5	7.28	3.82	7.25	7.91	16.37	1.45
U6	6.93	3.86	6.74	12.11	39.80	1.13
U8	7.30	3.62	3.53	7.27	12.52	1.41
UA2	6.62	3.30	6.94	19.59	41.39	1.25
Y1	6.96	5.57	1.92	3.12	3.40	1.43
Y3	5.96	3.24	2.39	5.90	6.36	1.12
Y4	5.65	3.37	2.48	4.29	5.02	1.10
Y5	7.39	3.45	3.82	9.73	54.08	1.41
Y7	6.77	3.25	5.57	14.47	15.35	1.05
Y9	8.36	3.36	6.03	14.93	76.05	1.81
Y10	6.29	3.71	6.25	21.12	28.71	1.78
E1	4.74	3.53	1.12	1.70	1.47	0.92
E3	5.46	3.93	1.51	3.81	2.83	1.11
E5	10.75	3.24	7.45	13.80	15.94	0.75
E7	7.20	3.87	3.93	8.21	10.02	0.99
E8	5.10	3.84	3.22	8.61	9.08	1.32
EA	3.51	3.47	1.59	3.38	26.42	0.66
M1	3.83	3.58	1.24	1.72	1.48	1.05
M2	4.80	3.94	2.78	6.23	7.30	1.13
M3	4.53	3.97	1.45	2.39	2.43	1.04
M4	5.08	3.61	2.67	5.46	7.08	0.98
M5	5.11	3.49	1.94	4.19	4.69	0.78
Min.	**3.51**	**3.10**	**1.12**	**1.70**	**1.47**	**0.66**
Max.	**10.75**	**5.57**	**7.45**	**21.12**	**76.05**	**1.81**

Tab. 9 - Enrichment factor of heavy elements

2019), they may be chlorite and/or palygorskite minerals. This factor represents the weathering process on the source rocks (mainly marl) within Fat'ha Formation, Tab. 7, Fig. 3.

The third main component

Table 7 shows the association of iron oxides with arsenic as a main parameter of the third component. despite the weak relation between iron oxides and As (r =0.431) Tab. 5, arsenic usually adsorbed on the iron oxide phases, so it may be the way to remove it from water (Polowczyk *et alii*, 2018). Arsenic attributed to the natural sources such as weathering, bacterial activity, within organic complexes, or to human sources such as usage of agricultural pesticides (Hao *et alii*, 2018). This factor reflects of the effect of industrial wastes that related to dyeing and the manufacturing of iron plates and bars workshops, Fig. 3.

Figure 3 shows the carbonates component represented by calcium oxide and carbon dioxide derived from the erosion of limestones within the Fat'ha Formation rocks.

Spatial distribution of heavy metals:

The Fig. 4 and 5 show that the concentrations of Cr, Cu, Zn, Pb which associated with organic matter as mentioned earlier are low at the beginning of the wadis and increases towards downstream at the end of each wadi. The highest concentrations are present in the industrial areas of especially in Ugab wadi and Al-Yarmouk wadi. The highest concentration of Ni that associated with clay minerals is at the beginning of wadis, and gradually decreases slightly towards downstream due to the leaching process of the sediments by weathering, in addition to the change of sediments to the Quaternary sediments and the flood plain deposits of Tigris River at the end of wadi as shown in Ugab wadi.

Geoaccumulation Index: (I_{geo})

Table 8 indicates that the values of the geoaccumulation index of the heavy elements in the sediments of the studied area. It is

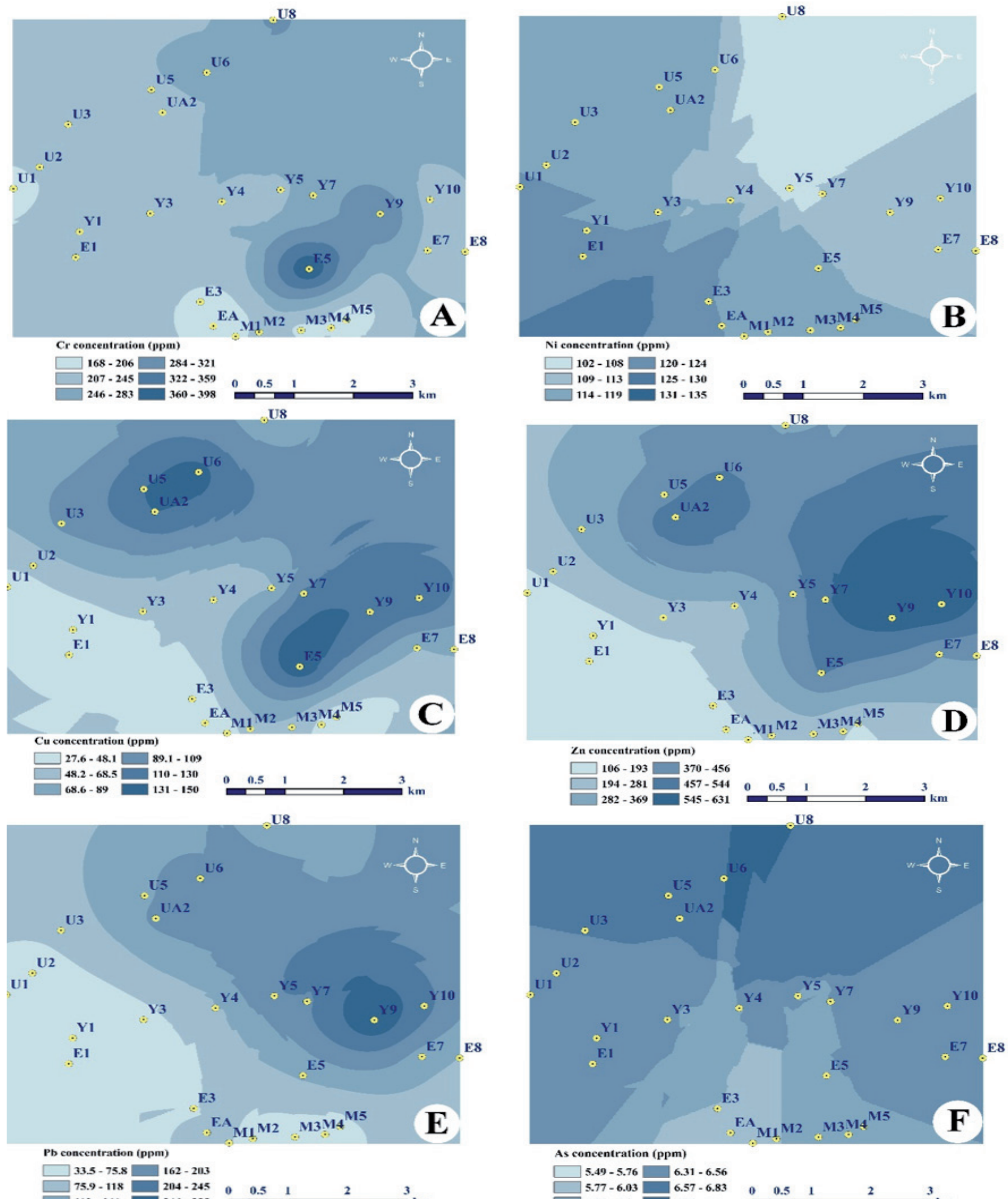

Fig. 4 - Spatial distribution of heavy elements; A: Cr, B: Ni, C: Cu, D: Zn, E: Pb, and F: As in the sediment samples in the study area

noted that the values of this index for the first samples in each wadi fall into the two categories (uncontaminated) and (uncontaminated-moderately contaminated). These samples represent the sites of the beginning of the wadis that were not exposed to the effects of pollution significantly because they are relatively far from the sites of pollution as industrial and agricultural areas. (Fig. 5).

Table 8 shows values of (I_{geo}) for Cr and Ni (0.31-1.56), (-0.16-0.53), respectively, which fall into the category (uncontaminated-moderately to contamin-ated) for all wadis.

Cu (I_{geo}) ranging (-1.30-1.16) in Ugab, Al-Yarmouk and Al-Ein wadis, fall in (uncontaminated-moderately contamin-ated) category, while ranging (-1.20—0.12) in Al-Mamoun wadi which mean (uncontaminated).

Zn (I_{geo}) ranging (-0.60-2.56) in all wadis, fall in the category (moderately-strongly contaminated). In general, these values increase along the wadis, due to passing through residential,

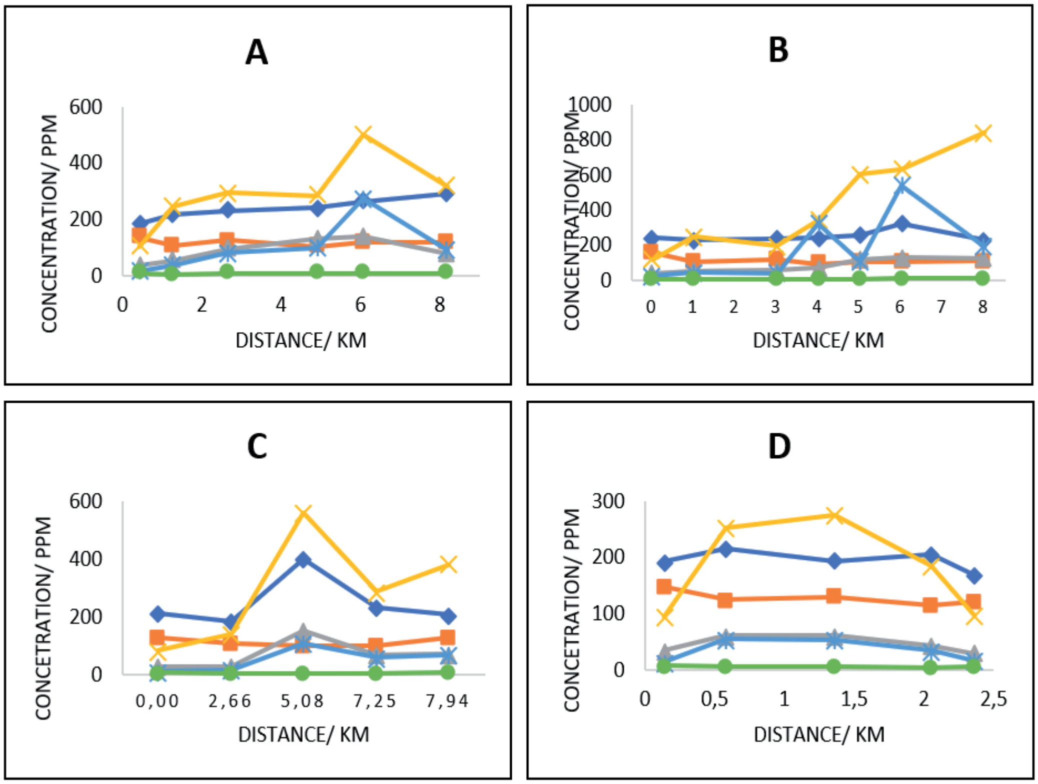

Fig. 5 - Spatial distribution of heavy elements; Cr, Ni, Cu, Zn, Pb, and As in Main Valleys of right bank of Mosul City/ Iraq. A- Ugab Wadi, B- Al-Yamouk Wadi, C- Al-Ein Wadi and D-Al-Mamoun Wadi

agricultural, and industrial sites.

Pb (I_{geo}) ranged between (-1.43-4.16) (uncontaminated-strongly to extremely contaminated). The high values of Pb (I_{geo}) in Al-Yarmouk wadi and Ugab wadi up to (4.16) and (3.19) respectively, and the highest value in Al-Ein wadi is (2.95). While the highest value in Al-Mamoun wadi is (0.87). These values give an indication of the affecting sites of lead contamination, especially those related to industrial sites, while the lower values represent the effect of the domestic wastes, (Fig. 5).

All As (I_{geo}) are below (I_{geo} =0) in all wadis that reflect the sediments are unpolluted and fall in the category (uncontaminated).

Enrichment Factor: EF

Table 9 showing the values of the enrichment factor of heavy metals in the sediments of the studied area. These EF values ranged for; Cr (3.51-10.75), Ni (3.10-5.57), Cu (1.12-7.45), Zn (1.70-21.12), Pb (1.47-76.05) and As (0.66-1.81).

The EF values of Cr appear in Ugab wadi and Al-Yarmouk wadi falls within the category (significant enrichment), while the EF in Al-Ein wadi and Al-Mamoun wadi ranges between the two categories (moderate enrichment-significant enrichment). The EF values of Ni fall within the category of (moderate enrichment) in all wadis. All the samples show EF values less than 4 which reflect that Ni correlated to the clay minerals only as adsorption.

Table 9 shows the EF values of Cu and Zn for Ugab wadi and Al-Yarmouk wadi falls in (moderate enrichment-significant enrichment) categories (except the 1st samples), while they fall in category of (deficiency to minimal enrichment) and (moderate enrichment) (except sample E5) in Al-Ein wadi. The fluctuation in lead EF values ranging (1.47-76.05) (except for the first samples) reflects the variation in the impact of pollution sources along the path of the wadis, and as mentioned previously the effect of industrial areas on the rise in Pb concentrations relative to the effect of residential and agricultural areas. Therefore, the categories of the enrichment factor range between (moderate enrichment) to (extremely high enrichment). The category of EF for As is (deficiency to minimal enrichment) as its values less than 2.

CONCLUSION

The sediments of wadis are a result of the natural processes represented by weathering and transportation from the source rocks of the Fat'ha Formation (limestones, gypsum and marl), the sediments of the Quaternary deposits and the derived soils. In addition to the organic matter resulting from the decomposition of solid and liquid wastes that are dumped from residential, industrial and agricultural sites.

The sources of heavy metals are related to domestic, agricultural and industrial activities. It is noted that the concentrations of lead, chromium, zinc and copper have increased in Ugab wadi and Al-Yarmouk wadi due to the presence of industrial sites represented in plumbing and dyeing workshops, blacksmithing, food productions and detergent factories, in addition to vehicles scrapyards and iron waste. While Al-Mamoun wadi and Al-Ein wadi concentrations of heavy elements decrease because they cross residential and agricultural regions, (except for the sample E5), which placed on the site of vehicle scrapyard, and remains of war.

The first samples in all wadis represent the areas that have been exposed to the impact of pollution at a low level due to their distance far from the sources of pollution.

Factors indicated that Ugab wadi occupies the first place in being affected by pollution, followed by Al-Yarmouk wadi due to the proximity of the sources of pollution to them. Lead and chromium constitute the most polluting elements (strongly contaminated), while the I_{geo} indicates that Al-Mamoun and Al-Ein wadis are moderately contaminated.

In general, it is noted that there is an increase in the concentrations of heavy elements along the path of the wadis due to the factors of erosion, transport and water movement during the year, especially during the period of rain precipitation. Taking into account the high concentrations during the wadis path due to the presence of pollution sites as in the Al-Ein wadi. No change was observed in the degrees of nickel enrichment in all valleys because of its association with clay minerals as an adsorbed element.

The highest values of enrichment factor (EF) appeared that the heavy elements ordered as lead> zinc> chromium> copper> nickel> arsenic.

ACKNOWLEDGEMENT

The authors would like to thank the administration of the college of science and geology department at Mosul University, for support and facilities in the performance of analyses.

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Received July 2021 - Accepted September 2021