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Assessing sediment pollution by applying some geochemical indices for Al-Wind River banks/ East of Iraq

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ABSTRACT

15 sediment samples were collected; 8 samples from the eastern bank, and 7 samples from the western bank of Al-Wind River in Diyala governorate to assess the sediment pollution in some trace elements such as Fe, Ni, Cd, Zr, Zn and Cu in addition to some oxides such as Al_2O_3, CaO, Na_2O and K_2O to find the effect of anthropogenic pollution and the industrial production on the sediment closed especially Naftkhana by using some geochemical pollution indices such as: geoaccumulation factor (I-geo), enrichment factor (EF),contamination factor (CF), pollution loud index (PLI) and to evaluate the degree of weathering by Applying the Chemical Index of Alteration (CIA)in both banks of Al-Wind River. The results of general contamination factors indicate that the eastern bank of Al-Wind River especially that closed by Naftkhana area having quite more concentrations of trace element and oxides from the western bank. The results of I-geo presents unpolluted sediment with Pb and Fe and slightly polluted with Zn, Cu, and Ni in both banks, while the western bank in some locations recorded of moderately polluted sediments with Ni and slightly to moderately polluted sediments with Cu and Zn and reach moderately severely polluted in the eastern bank. The contamination factor (CF) for Ni and Zr classified as class 2 which indicate moderately contamination to severely pollute in both banks, while Fe, Pb, Cu and Zn conbankred unpolluted in both banks. Enrichment factor (EF) for Fe, Pb, Zr and Cu are conbankred deficiency to low enrichment the range of natural variability, while Ni record high values reached to 6.4 indication of anthropogenic inputs. Pollution load Index (PLI) is perfection and classified as class 0 in both banks. Chemical index of alteration (CIA) reflecting the chemical weathering intensity especially for the western bank.

Keywords: Geo-accumulation; Contamination factor; Pollution load index; Chemical Index, Enrichment factor, Al-Wind River, East of Iraq.

تقييم تلوث الرسوبيات بتطبيق بعض معاملات التلوث الجيوكيميائي على جانبي نهر الوند /شرق العراق

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الخلاصة

تم جمع 15 نموذجا رسوبيا من ضفتي نهرالوند 8 من الضفة الشرقية و7 من الضفة الغربية من نهر الوند في محافظة ديالى لتقييم تلوث التربة ببعض العناصر الثقيلة مثل الحديدوالنيكل والكاديميوم والزركون والزنك والنحاس بالاضافة الى بعض الاكاسيد مثل اوكسيدالالمنيوم اوكسيدالكالسيوم اوكسيدالصوديوم واوكسيدالبوتاسيوم ودراسة تأثير الفعاليات البشرية والصناعية بالقرب منها وخاصة النفطخانة وقد تم ذلك بدراسة

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بعض معاملات التلوث الجيوكيميائي مثل (I–geo)و(CF)و (EF) و(PLI)بالاضافة الى تقييم شدة التعرية الكيميائية وذلك بمعرفة قيمة (CIA). بينت النتائج ان الضفة الشرقية من نهر الوند سجلت تراكيز اعلى نسبيا من الضفة الغربية منه كونها قريبة من النفطخانة . اثبتت دراسة (I–geo)عدم تلوث التربة في كلا الجانبين.اما نتائج (CF)سجلت تلوثا من المرتبة الثانية لكل من النيكل والزركون بينما اعتبرت غير ملوثة لكل من الحديدوالرصاص والنحاس والزنك. عامل (EF) اثبت عدم تلوث الرسوبيات بالحديد والرصاص والزركون والنحاس في حين سجل النيكل قيمة عالية بلغت 6.4 مما يعكس التأثير السلبي للفعاليات البشرية والصناعية. أظهرت نتائج (PLI) عدم تلوث رسوبيات المنطقة بالعناصر الثقيلة.أثبتت دراسة (CIA) تعرية كيمائية شديدة خاصة في الضفة الشرقية من نهر الوند.

1. INTRODUCTION

The anthropogenic and the industrial components both represent the main cause of River sediment pollution [1].The common chemicals that causing sediment pollution are: Petroleum hydrocarbons, heavy metals, pesticides, solvents [2]. Many researchers have used many traditional analytical methods to find the pollution in sediments [3, 4] while few of them used the chemical indices like accumulation load index (I-geo), enrichment factor (EF), contamination factor (CF), and pollution load index (PLI) together to assess the pollution in sediment. Trace elements are found in natural soil in a small amounts and its concentration increased in the environment due to human activities and may reach to concentrations up to levels lethal to humans and wildlife both in water pollution or its accumulation in aqueous solutions, medium soil texture helps in contaminants movement to the surface and ground water, therefore; it becomes subject to the chemical and physical processes [5].There are four anthropogenic sources for trace elements in the soil; the first is atmospheric deposition that arising from coal and gasoline burning, nonferrous and ferrous metal mining, smelting, manufacturing, waste ignition, production of phosphate fertilizers, cement, and wood combustion; the second is the land application of sewage sludge, animal manure and other organic wastes and co-products from agriculture and food industries; the third is land disposal of industrial co-products and waste, including paper industry sludge, coal fly ash, bottom fly ash and wood ash; the fourth source for heavy metals in the soil is fertilizers, lime and agrochemicals such as pesticides that used in agriculture activates [6].Trace elements can be found in many forms: as soluble in sediment solution, exchangeable in organic and inorganic components, or as structural components of the lattices of sediment minerals, or as insoluble precipitates with other sediment components as complexes. High concentrations of heavy metals in soil reflect the occurrence of mixture material inputs from different sources**.** In an arid environment such in the study area; physical weathering usually occurs in high rates, while chemical transformation being rather rare because it requires a lot of water, while in a tropical climate environments with high temperature and humidity, chemical weathering is favored, resulting in the formation of more clay minerals [7].

The main aim of this research is to compute and compare the trace elements distribution of some trace elements such as Fe Ni, Cu, Zr, Zn, pb and Cd by using many chemical indices like geo-accumulation index (I-geo), contamination factor (CF), enrichment factor (EF) and Pollution load index (PLI) and study the effect of Nafkhana on the soil quality in the study area, and find the percentage of some oxides such as Al_2O_3, CaO, Na_2O and K_2O to investigate the intensity of chemical weathering by applying the CIA in both banks of Al-Wind River in Khanaqeen area/ Diyala Governorate .

2. Location of the study area

The study area is located in the northeastern part of Iraq at the northeastern part of Diyala provinces between latitudes (34^o14'00"- 34^o16'00") N and longitude (45^o10'40"-45^o30'00")E, Sediment samples are collected during September, 2016 from different sites of Al-Wind River; samples D1, D2, D3, D4, D5, D6 and D7 are from the western bank, while the sediment samples D8, D9, D10, D11, D12, D13, D14 and D15 are from the eastern bank that nearby Naftkhana area (Figure-1)

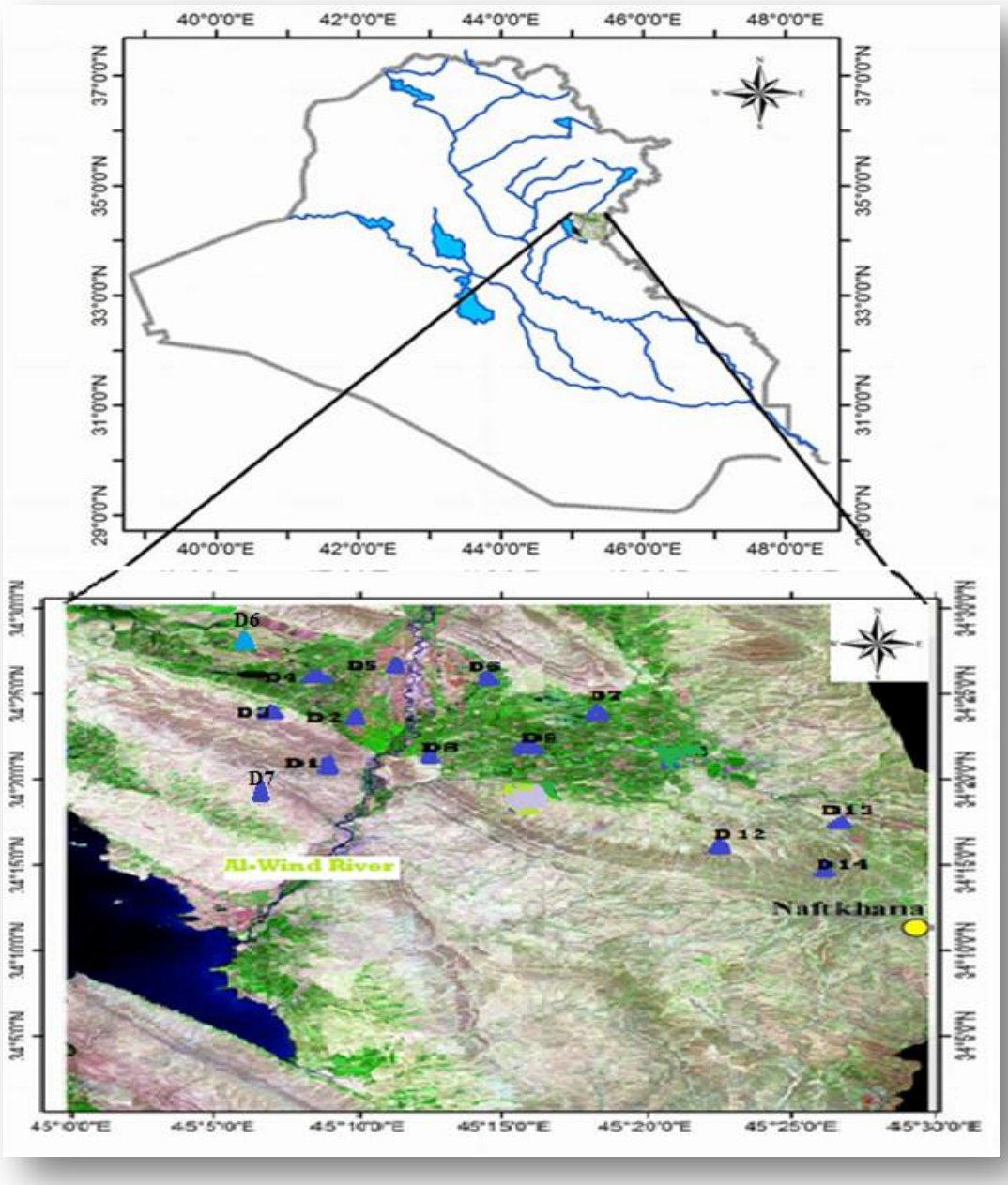

Figure 1-Location map for the study area viewing the water sampling sites

Table1-The concentrations of heavy elements (mg/kg), Percentage of oxides and CIA values measured in the study area,

Bank	Site No.	Fe	Pb	Zr	Ni	Zn	Cu	Al_2O_3 %	CaO %	Na_2O%	K_2O %	CIA
Western bank	D1	1665	7.2	44	88	98	13.1	5.33	14.2	4.5	1.02	21.3
	D2	2015	8.6	40	92	78	12.4	6.11	15.1	3.8	1	23.5
	D3	3420	7.9	43	100	87	11.4	5.8	14.9	4.3	1.2	22.1
	D4	1540	9.2	40	76	78	13.7	4.82	13	3.9	0.9	21.3
	D5	3345	11.7	44	94	68	17.8	7.3	14.5	4.1	0.89	27.3
	D6	3321	8.2	45	84	89	14.5	4.2	13.9	4. 3	1.1	17.8
	D7	2370	9.9	44	89	122	12.7	6.7	15.8	4. 2	1	24.1
	Av.	2525	8.95	42.8	89	88.5	13.6	5.75	14.4	4.12	1.01	22.4
	D8	4355	12.5	49.8	122	133	15.8	6.8	16	4.8	1.6	26.9

Eastern bank	**D9**	**4210**	**11.8**	**52**	**110**	**90**	**16.5**	**5.55**	**15.3**	**4. 4**	**1.5**	**20.5**
	D10	**5730**	**16.9**	**55**	**119**	**117**	**24.2**	**7.21**	**17.1**	**4.9**	**1.2**	**23.4**
	D11	**5321**	**17.3**	**56**	**104**	**92**	**21.9**	**7.10**	**15.2**	**4.9**	**1.2**	**25.3**
	D12	**5318**	**14.2**	**58**	**118**	**112**	**22.2**	**5.23**	**14.8**	**5.1**	**1.5**	**19.6**
	D13	**5330**	**16.9**	**63**	**120**	**115**	**19.3**	**4.76**	**16.7**	**5.4**	**1.3**	**36.2**
	D14	**5750**	**15.9**	**61**	**116**	**100**	**21.6**	**5.21**	**16.8**	**5.6**	**1.5**	**17.9**
	D15	**5266**	**16.6**	**61.3**	**128**	**120**	**22.9**	**6.23**	**15.5**	**4.7**	**1.61**	**22.2**
	Av.	**5160**	**15.2**	**57**	**107.1**	**109**	**20.5**	**6**	**15.9**	**5.1**	**1.4**	**24**
Al- Bassam and Yousif, 2013			**6.02**		**91**	**54**	**16**					

3. MATERIALES AND METHODS

15 sediment samples were selected at depths 0- 30 cm during September 2016. 7 samples from the western bank of Al-Wind River and 8 samples from the eastern bank. All the sediment samples were powdered, then subjected to the drying process by oven at a temperature of 60˚C.Then 5 g powder of size 0.063 μm was analyzed in XRF Spectrometer to find out the element concentrations. Studying trace elements concentration of soil particles of clay fragments size particles less than 2 microns because they contain high concentrations of trace elements and it has high adsorption capability of these elements in the environment. All samples have been analyzed for Fe, Pb, Zr, Zn, Cu and Ni elements using four indices; geo-accumulation index (I-geo), contamination factor (CF), enrichment factor (EF) and pollution load index (PLI) to detected the sediments pollution. The results were established according to [8]. All samples were analyzed in geology department laboratories, College of Science, University of Baghdad. Oxides were analyzed to find the intensity of weathering by computing the chemical index of alteration (CIA) by using [9] formula as follow:

$CIA= (Al_2O_3/ Al_2O_3 + CaO + Na_2O + K_2O) \times 100$

4. RESULTS AND DISCUSSION

Mean concentrations of 6 trace elements analysis were in the order of following: Ni > Zn > Cu> Pb > Fe > Zr and four oxides includes CaO > Al_2O_3> NaO > K_2O. As it is clear, the concentrations of most elements measured in the sediments of the eastern bank of Al-Wind River especially that nearby Naftkhana are record higher rates concentration from that recognized in the western bank (Table-1). Brief Discussion of the heavy metals and oxides concentrations is bellow:

4. A Heavy Metals

4. A.1 Nickel (Ni): is available in the oxidation acidic environment, it has symmetrical characters with Cu and Cd [10]. Its concentration depends on the abundance of organic matter and clay minerals [11]. In sediments, Ni is slightly mobile it's mainly occur in the residual fraction in over of 50% of its total contents in loamy sandy sediment, and in about 70% of its occurrence in estuary muck [12]. Ni concentration in The concentrationsediment of the west bank of Al- Wind River ranges between (76 – 100 ppm) with average (89 ppm), while in the east bank that closed to Naftkhana ranges between (104- 128) ppm with average (107.1 ppm) (Table-1).

4. A.2 Zinc (Zn): Many sources may originate an anthropogenic Zn in agricultural sediments such as atmospheric deposition, fertilizers, pesticides, sewage sludge, manure, waste depending on its chemical species and their affinity to sediment and sediment parameters **[**13**]**. The concentration of Zn ranges between (68- 122) ppm with an average of (88.5ppm) in the western bank of Al-Wind River, while in the eastern bank ranges between (90- 133) ppm with average (109 ppm) (Table-1).

4. A.3 Copper (Cu): is so transitional at pH< 5.5 and becomes with a little transitional at solution basal or equal [14]. Common value for the average total Cu contents in sediments of different types all over the world is reported to range between 20 and 30 mg/kg [15]. The concentration of Cu in the western bank of Al- Wind River ranged between (13.4- 17.8) ppm with average of (13.65 ppm), and it ranged (15.8- 24.2) ppm with average (20.5 ppm) in the east bank (Table-1).

4. A.4 Iron (Fe): Iron is one of the major constituents of the lithosphere, so it plays a vital role in the behavior of several heavy elements, the range of Fe contents in sediments is between 0.1- 10%. Contents of Fe in sediments are innate from parent materials and/or resulted from sediment processes that are controlled by climatic factors[7].In sediments, Fe occurs mainly in forms of oxides and hydroxides, as amorphous compounds, small particles, fillings in cracks and veins and coatings on

other minerals or particles. In sediments, Fe occurs mainly in forms of oxides and hydroxides, as amorphous compounds, small particles, fillings in cracks and veins and coatings on other minerals or particles [16]. Concentration of Fe in the western bank of Al-Wind River ranged between (1665-3420) ppm with average of (2525 ppm), while in the eastern bank ranged between (4210- 5750) ppm with average 5160 ppm (Table-1).

4. A.5 Lead (Pb): is one of four metals that have the most damaging effects on human health. It can enter the human body through the uptake of food (65%), water (20%) and air (15%) [17]. The concentration of Pb in the western bank of Al-Wind River ranged between (7.2-11.7) ppm with average of (8.9 ppm), while in the eastern bank ranged between (11.8- 17.3) ppm with average (15.2 ppm)(Table-1).

4. A.6 Zirconium Zr: is conbankred slightly mobile in soil, the main transporting agents for its mobility is organic acids [18]. It is noted that the average concentration of Zr in the east bank ranged between (49.8- 63) ppm with average (57) ppm slightly higher than the west bank that ranged between (40- 45 ppm) with average of (42.8) ppm. (Table-1)

4. B Oxides:

4. B.1 (Al_2O_3) Aluminum oxide: The concentration of Al_2O_3 in sediment is depended on parent material, degree of weathering, depletion processes. Aluminum is present in the opaque minerals, and in the clay minerals structure such as chlorite, montmorillonite and kaolinite minerals [19]. Al_2O_3 percentage in the western bank of Al- Wind River ranged between (4.2-7.35%) with average of 5.75%, while the east bank ranged between (4.7-7.2%) with average of 6% (Table-1).

4. B.2 Calcium oxide (CaO): CaO percentage ranged between (13- 15.8%) in the western bank of Al-Wind River with an average 14.4 %, and from (14.8- 17.1%) with an average of 15.9% in the eastern bank (Table-1).

4. B.3 Sodium Oxide (Na_2O): Sodium oxide content in sediment combines with clay minerals especially Montmorillonite [20]. Na_2O percentage ranged between (3.8- 4.5%) with an average of 4.12% in the west bank, while it ranged between (4.4- 5.6%) with an average of 5.1% in the east bank of Al-Wind River (Table-1).

4.B.4 Potassium Oxide (K_2O): The percentage of the western bank of Al-Wind River Ranged between(0.9-1.2%) with an average of 1.01%, while it ranged between(1.2- 1.61%) with an average of 1.4% in the east bank of Al-Wind River, the high oxide percentage reflects the negative effect of Naftkhana on the sediment closed (Table-1).

4. C Geochemical Indices:

All the results of geochemical are listed in Table-6. Discussion of these chemical indices as follows:

4. C.1 Geo-accumulation index (I- geo):

In order to compare the analyzed heavy elements in the study area with background levels I- geo can be calculated according to [8] by this equation:

I- geo = $\log_2$ (Cn/1.5 Bn)

Cn: concentration of the heavy metals in the sediments of the study area.

Bn: concentration of heavy metals in the sediment of the background.

The standard of I- geo categories were classified the sediment into six classes [20] (Table-2). I- geo for Fe was negative in both banks; ranged between (-0.39 to -0.73) with an average (-0.54) in the western bank, while they ranged between (-0.16 to -0.44) with an average (-0.24) in the eastern bank indicate that both banks are unpolluted by each of Fe, Ni, Zn, Zr and Cu although they have positive values in some sites but their values not exceed 1 that mean it was practically polluted to slightly polluted sediments Tables-(2, 6).

Table 2-The main classes of the sediments according to I-geo values [21]

I-geo	order	Result
≤ 0	class 0	Practically unpolluted
0 < to ≤ 1	class 1	slightly polluted
1< to ≤ 2	class 2	moderately polluted
2< to ≤ 3	class 3	Moderately Severely polluted
3< to ≤ 4	class 4	Severely polluted
4< to ≤ 5	class 5	Severely extremely Polluted
> 5	class 6	Extremely polluted

4. C.2 Contamination factor (CF) has been computed according to [8] equation.
CF = Cn Sample/ Cn Background
CF: contamination factor.
Cn (Sample): the concentration of metal content in the sample.
Cn (Background): the concentration of the background level of metal.
According to [20]) (Table-3), there are 3 classes of contamination factor, each of Fe, Cu, Zr elements are having CF<1 therefore it represents low contamination so as Pb element in the eastern bank of Al-Wind River; while Pb in the western bank represent class 2 so as Ni and Zn elements Tables-(3, 6).

Table 3-The main class of the sediments according to CF values [20]

CF	class	Quality
<1	class 1	Low contamination
1≤CF< 3	class 2	Moderate contamination
3≤ CF≤6	class 3	Considerable contamination

4. C. 3 Pollution load index (PLI)

Pollution load index (PLI) has been computed according to [21] equation:
PLI = n√CF1 * CF2 * CF3 x …..*CF n
n: number of metals has been analyzed.
CF: contamination factor
Pollution load index (PLI) for studied trace elements indicated that the soil classified as class 0 according to [21], all the sediments samples quality were classified as perfection (Table-4) that mean there is no local pollution. PLI value in the study area ranged from 0.32 to 0.49 with an average of 0.35 in the western bank and from 0.40 to 0.74 with average of 0.54 in the eastern bank Tables-(4, 6).

Table 4-The main class of the sediments according to PLI values [21]

<1	class 0	Perfection
=1	class 1	Baseline level
>1	class 2	Deterioration site

4. C .4 Enrichment Factor (EF)

It represents a powerful instrument for analyzing sediment pollution, and transmission the raw environmental information to the searchers, managers and technicians [22]. To evaluate the source of

the chemical elements; EF has shows for all sediment samples using Zircon (Zr) as a background element. Zircon careful as originated from natural lithogenic sources such as rock weathering contain Zircon bebank it has no significant anthropogenic source it used in geochemical studies of mineral weathering as a 'conservative' lithogenic element, bebank which comparative enrichments have been compared, the EF has been calculated according to the following equation [23]:

EF = (M / Zr) sediment/(M / Zr)earth's crust. … (Zr is a background).

M: Total elemental concentration (mg/kg)

Zr: Total concentration of Zr (mg/kg) in sediment sample/earth's crust.

According to [24- 26]; EF of Fe, Pb and Cu elements is < 2; therefore their quality is deficiency to low enrichment the range of natural variability. The EF of Ni ranging between (4.1-5.1) with average of 4.4 in the eastern bank, while it's ranging between (4.4- 5.1) with an average of 4.7in the western bank, and its quality is low enrichment that almost caused by anthropogenic inputs, there is a significant enrichment in Zn element caused by anthropogenic inputs in sediment sample D1, D7and D8 which indicate human influence Tables - (5, 6).

Table 5-The main class of the sediments according to EF values [23- 26]

EF value	Quality
EF< 2	deficiency to low enrichment the range of natural variability
2 < EF < 5	low enrichment (almost caused by anthropogenic inputs
5 < EF < 20	indication of human influence (significant enrichment caused by anthropogenic inputs)
EF 20 to 40	very high enrichment

4.C.5 Chemical Index of Alteration (CIA) has been measured according to [9] equation: CIA= $[Al_2O_3/ (Al_2O_3+ CaO + Na_2O + K_2O) \times 100]$

the results are listed in (Table-1). By comparing the concentrations of trace elements in this study with those obtained of [27] in their study of Mesopotamian sediment (Table-1), it's noticed that all traces are within the acceptable range except Zn element that record high ranges from Al-Bassam and Yousif study. The high concentration of Zn element in the study area reflects the extensive use of fertilizers, so the Iraqi fertilizers rich in Zinc element [27].

5. CONCLUSION

• Geochemical analysis shows that the soil sample contains a high concentration of Zn element which exceeds the natural limits of Iraqi soil, this refers to the extensive use of fertilizers, the other trace elements were within the natural limits.

By comparing the concentrations of trace element with the previous study of Al-Bassam and Yousif concluded that all traces in the western bank of Al- Wind River were within the acceptable ranges except Zn element, while its values it's the standards in the eastern bank that record higher ranges this reveals the negative effect of the industrial activities.

• The spatial extent of pollution that examined in the area nearby Naftkhana reflects the negative effect of the industrial and anthropogenic process on the sediment.

Table 6- I- geo, CF, EF and PLI values for sediment in the study area

location	Site No.	Fe			pb			Zr		Ni			Zn			Cu			PLI
		CF	EF	Igeo	CF	EF	I-geo	CF	Igeo	CF	EF	Igeo	CF	EF	Igeo	CF	EF	Igeo	
Western Bank	D1	0.02	0.11	-0.70	0.57	0.21	-0.41	0.26	-0.75	1.17	4.4	-0.10	1.4	5.28	-0.02	0.23	0.87	-0.79	0.42
	D2	0.03	0.14	-0.62	0.68	0.28	-0.33	0.24	-0.79	1.22	5.1	-0.08	1.11	4.64	-0,12	0.22	0.93	-0.82	0.34
	D3	0.06	0.23	-0.39	0.63	0.23	-0.37	0.26	-0.76	1.33	5.15	-0.05	1.24	4.8	-0.08	0.20	0.78	-0.85	0.38
	D4	0.02	0.23	-0.73	0.73	0.30	-0.30	0.24	-0.79	1.01	4.2	-0.17	1.11	4.33	-0.12	0.24	1.03	-0.77	0.32
	D5	0.05	0.22	-0.40	0.93	0.34	-0.62	0.26	-0.75	1.25	4.1	-0.07	0.97	3.6	-0.18	0.32	1.21	-0.66	0.42
	D6	0.05	0.21	-0.40	0.65	0.23	-0.35	0.27	-0.74	1.12	4.1	-0.13	1.27	4.69	-0.07	0.26	0.96	-0.75	0.39
	D7	0.04	0.21	-0.5	0.79	0.29	-0.2	0.26	-0.7	1.18	4.4	-0.1	1.74	6.59	0.06	0.23	0.84	-0.8	0.49
Aver.		0.004	0.19	-0.54	0.71	0.26	-0.37	0.25	-0.76	1.18	4.49	-0.1	1.26	4.84	0.07	0.24	0.95	-0.77	0.305
Eastern *Bank*	D8	0.07	0.25	-0.3	1	0.33	-0.2	0.30	-0.7	1.62	5.4	0.03	1.9	6.3	0.102	0.29	0.93	0.28	0.52
	D9	0.074	0.23	-0.30	0.94	0.29	-0.20	0.31	-0.67	1.46	6.4	0	1.28	4.09	-0.06	0.27	0.93	-0.69	0.47
	D10	0.010	0.27	-0.18	1.35	0.31	-0.04	0.33	-0.65	1.58	4.8	0.02	1.67	5	0.04	0.44	1.33	0.45	0.50
	D11	0.094	0.21	-0.44	1.38	0.34	-0.03	0.33	-0.64	1.38	4.1	-0.08	1.31	3.9	-0.05	0.39	1.18	0.41	0.55
	D12	0.094	0.26	-0.20	1.13	0.31	-0.12	0.35	-0.63	1.58	4.5	0	1.6	4.5	0.02	0.40	1.15	-0.57	0.57
	D13	0.094	0.26	-0.19	1.35	0.34	-0.04	0.38	-0.59	1.6	4.2	0.02	1.64	4.3	0.04	0.35	0.90	-0.63	0.59
	D14	0.01	0.26	-0.16	1.27	0.34	-0.07	0.36	-0.60	1.75	4.2	0.01	1.43	3.9	-0.01	0.39	1.06	0.26	0.40
	D15	0.093	0.27	-0.2	1.32	0.27	0	1.32	-0.6	1.57	4.6	0.05	1.7	4.6	0.05	0.41	1.12	-0.5	0.74
Average		0.068	0.25	-0.24	1.21	0.31	-0.83	0.34	-0.63	1.56	4.77	0.006	1.55	4.57	0.016	0.36	1.07	-0.13	0.54

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