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Assessment of heavy metals pollution in the sediments of Haditha reservior and Eupheates River, within Anbar Governorate/Iraq

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***Abstract*---**10 sediment samples were obtained from Haditha reservoir and Anah city in Al-Anbar governorate for this study during (October, 2021). to assess sediment contamination in trace metals like (Cd, Fe, Pb, Zn, Cu, and Ni), from applying geochemical contamination coefficients such as Geo - Accumulation variable I-Geo, Contamination Factor CF, as well as Pollution loud Index PLI. The research area is found in the northwestern region of Al-Anbar governorate, between the longitudes (42°23'.13'' - 42°01'.10'' E). and latitudes (34°10'.22'' - 34°22'.7'' N), The area which is located between Haditha Dam and Anah city. The results of geochemical analyzes showed that it soil sediment has a high value of the elements (Ni, Fe and Cd), which exceeds the limits of local studies, this can be affected by Anthropogenic activities like urbanization, industrialization, agricultural runoff, fertilizers, and also the Haditha dam's electrical station, but the elements (Zn, Pb and Cu), Within the permissible limits of local studies.The results of the I-geo shows that the elements (Ni, Zn, Pb, Fe and Cu), has unpolluted (class- 0). While Cd is (class-1), slightly polluted. The Contamination_Factor CF to (Fe, Ni) was characterized since (classes- 2), moderate pollution. But even so, (Zn, Pb, and Cu) were characterized as (classes- 1), small contamination. As for the last element (Cd), classify as (classes- 3), Considerable contamination. While the Pollution Load Index PLI to (Cd, Fe, Pb, Zn, Cu, and Ni),has been calculated and characterized as (classes- 2),

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Deterioration site. Except for (S1-S2 wet and S2 dry), which is characterized as (classes- 0), Perfection. The principal purposes of this reseaech are to evaluate trace elements contamination within the research site's soils.

***Keywords*---**assessment, Euphrates River, heavy metals, pollution, geo-accumulation, Haditha reservoir.

Introduction

Due to rising population, quick industrialization growth, as well as an availability of contamination safety regulations, sediment trace material pollution has become worldwide issue mostly on it's governmental as well as private stages, especially even though soil samples are an essential part from respectively rural as well as urban conditions (Tang et al., 2014; Rahman et al., 2012; USDA, 2001). Accumulation of trace metals through river soil being effected to industrial as well as mining it's common mostly on underdeveloped nations (Islam et al., 2015). Trace materials can be transported and sourced in the environment by soils (Haiyan et al., 2013). Trace materials throughout river soil pass along a variety of routes, including sources of both point and non-point materials (Shazili et al., 2006).

The allocation of particle sizes has a major influence on soil trace materials value. Numerous studies shown that as the particle size of soils reduces, the metals concetration rise more than that of relatively coarse sediments (Svetlana et al., 2012). This is due to higher total area of smaller grains, like clay fraction soils, That also enables trace minerals to all be kept in high concentrations (Wang et al., 2006). Rocks have a significant impact on soil heavy metal concentration, with concentration range occasionally exceeding significance level (Salonen and Korkka-Niemi, 2007). Previous research within area would include Ali's (1972) discovery Trace materials provinces on recent sediments within Euphrates and Tigris river. Al-Bassam and Al-Mukhtar (2007) researched traces metals within 63m of Euphrates River breaks soils and discovered enhancement of such trace metal ions. (Hussain and Al-Jaberi, 2020) 25 core samples are collected from 8 rivers sediment soil locations to analyze trace metals content for the Euphrates as well as Shatt al-Arab. Anthropogenic activities like urban development, industrialization, agricultural runoff, fertilizers, as well as the electrical station to Haditha dam are really the major sources of pollution within area. The purpose to this study are calculate as well as comparison a traces metal allocation for certain havey minerals like Ni, Zn, Pb, Fe, Cu, and Cd using a number of chemical index values like Geo-Accumulation varable I-Geo, Contamination_Factor CF, as well as the Pollution load index PLI.

The area of research is found in the northwestern part of Al-Anbar governorate, between the longitudes (42°23'13'' - 42°01'10'' E). and latitudes (34°10'22'' - 34°22'7'' N), The area which is located between Haditha Dam and Anah city, (Fig.1),(Table 1). Haditha Lake, with a maximum capacity are (8.2 km3), would be the large lake along Iraqi stretch of a Euphrates River.. The discharge from Haditha dam to Euphrates River {input (623 – 312 m) and output (566 – 386 m)}, during period (2020 – 2021). The water level of Haditha Reservoir is (146 – 142 m), and Euphrates River after the dam is (101 – 100 m), during period (2020 – 2021). The Climatic information of Haditha station during the period (1990-2020), the annual mean rainfall was (126 mm),with the highest and the lowest temperature (35 °C in July – 8.4 °C in January), (Iraqi Meteorological Organization, 2021).

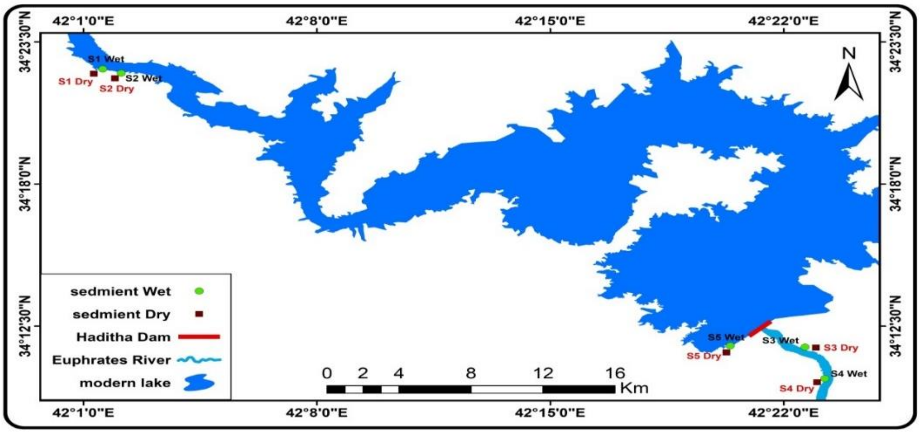

Fig. 1. Site map for sediment sampling.

Table 1. Location and area description of the surface soil and river sediment sampling sites in Euphrates River and Haditha Reservoir

Samples No.	Sampling description site	Longitude	Latitude
S1 Wet S1 Dry	Anah city	E 42˚01' 10"	N 34˚ 22' 7"
S2 Wet S2 Dry	Alrihana village	E 42˚01' 0.9"	N 34˚ 22' 6.96"
S3 Wet S3 Dry	Zwachi (Barawana city)	E 42˚22' 17.2"	N 34˚ 11' 8"
S4 Wet S4 Dry	Al-wasta (Haditha city)	E 42˚23' 13.8"	N 34˚ 10' 22"
S5 Wet S5 Dry	Haditha Reservoir (Al-wasta side)	E 42˚20' 30"	N 34˚ 11' 7.5"

The exposure formations inside the research region are as follows: 1- Anah Formation on age Oligocene, that also composed of very solid limestone and corals; 2- Euphrates Formation on age Lower Miocene, that also composed of highly fossiliferous limestone, dolostone, as well as marl; 3- Fatha Formation on age Middle Miocene, that also composed of cyclic deposits such as (green marl, reddish brown claystone, limestone, gypsum; as well as silt); 4- Quaternary deposits on age Pleistocene to Recent, that also composed of gypsum, limestone, sand, gravel and clay, (Fig.2).

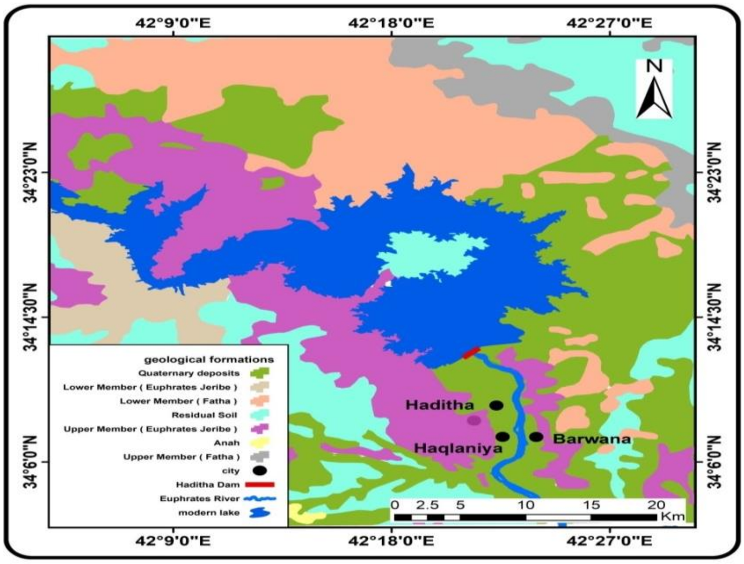

Fig. 2. Regional geology map of study area.

Materials and Methods

Ten sediment samples were collected from Haditha reservoir and Anah city during (October, 2021), These sediment samples were taken that used a hand auger (at depth 0-30 cm). Sediment samples were sieved with nylon mesh inside the laboratory since air drying at rooms temperature. Sample fraction has been ground in an agate pestle and mortar and sieved (2 mm). Heavy minerals such as (Ni, Zn, Pb, Fe, Cu, and Cd), were analyzed using X-ray fluorescence (XRF-140 Micro analyzer) in the Ministry of Science and Technolog Laboratory .

Results

Results for trace minerals analysis in soils samples of Haditha reservoir and Anah city are listed in (Table 2). The Ni concentration varies from 125-209 ppm, with an average value of 176.5 ppm, exceeding its permissible limits of local studies (Ali, 2012). The highest concentration of Ni because of the dominance of montmorillonite over the other clay minerals in these areas can be causes the higher value of Ni (Forstner and Wittman, 1981; Mu'azu et al., 2018). While Zn value varied between 67-103 ppm with an average reached to 87 ppm, which is less than the permissible limits of local studies in (Ali, 2012). The explanation for existence the zinc within research site's sediments could be attributed to human activity (Yan et al., 2018). Furthermore, Zinc can noticed on metals such as ilmenite as well as magnetite, that are primarily found through Euphrates River sediments; Zinc discharged into sediment throughout weathering methods as well as later accumulated (Benni, 2014; González-Costa et al., 2017). The Pb concentration inside the study stations ranged from 17 - 22 ppm, with an average of 19.6 ppm, that is lower than the permissible limits of local studies (Ali, 2012).

The presence of Pb in the study region sediments is due to lead as ($Pb2+$) forming carbonates during weathering and being absorbed in clay minerals, (Fe – Mn) oxides, and organic material. Parent rocks have a strong influence on its concentration in soil (Kapata – Pendias and Pendias, 2001). The Fe concentration from 8765-9765 ppm with average 9288 ppm, it exceeds the permissible limits of local studies in (Ali, 2012). The explanation for existence the Fe within soils of the study region may be due to human activities. The Cu concentration from 25-59 ppm with average 37.2) ppm, it is within the permissible limits of local studies in (Ali, 2012).except (S5 wet),is exceed. The influence of Cu explains the effect of human activity.And the last elements the Cd concentration from 3.5-4.3 ppm with average 3.92 ppm, it exceeding the permissible limits of local studies in (Ali, 2012). The highest concentration of Cd due to natural weathering processes, agricultural use, fertilizers and pesticides.As well demonstrated that Cd can also be absorbed by clay minerals' surfaces.

Table 2. Trace elements concentration in (ppm) in sediments of the study are and compare it with local studies

Sample NO.	Ni	Zn	Pb	Fe	Cu	Cd
S1 Wet	125	73	19	9675	25	4.2
S1 Dry	147	94	22	9123	34	3.8
S2 Wet	134	97	18	9300	28	4.3
S2 Dry	156	67	19	9221	30	3.8
S3 Wet	197	92	19	9765	40	3.8
S3 Dry	202	85	22	9213	40	4.1
S4 Wet	200	82	19	9342	38	4.2
S4 Dry	209	93	17	8976	37	3.5
S5 Wet	192	84	21	8900	59	4
S5 Dry	203	103	20	8765	41	3.5
Min	125	67	17	8765	25	3.5
Max	209	103	22	9765	59	4.3
Average	176.5	87	19.6	9228	37.2	3.92
(Ali, 2012)	135.8	116.4	66.8	6800	41.9	<1

Assessment of Trace Minerals

Situation for trace Minerals pollution within study region to assessed using various quantitative contamination indices. Sediment geochemistry is a good indicator of human sources in river sediments.Many of the environmental index was using to calculate the extent of human impact include like the Contamination_Factor CF, Pollution Load Index PLI, as well as Geo-Accumulation Varaible (I-Geo), (Wojciechowska et al., 2019).

Geo-Accumulation Varaible (I- Geo)

To comparing teace metals within research region with background concentrations, use the formula by (Taylor and McLennan, 1985) ,to measure I-geo.

$$I\text{- }Geo = Log2\,(Cn/1.5\;Bn)$$

Where:

Cn: Values for trace minerals within research site's soils.
Bn: Values for trace minerals within back - ground sediments.

Contamination factor (CF)

(Taylor and McLennan, 1985), has been calculated by utilised equation:
Cf = Cn Sample/ Cn Background
Where:
Cf: Contamination_factor.
Cn Sample: Values for trace minerals within research site's soils.
Cn Background: Values for trace minerals within back - ground sediments.

Pollution Load Index (PLI)

(Thomson et al., 1980) measured pollution load index (PLI) through using formula:
$PLI = \sqrt[n]{Cf1 * Cf2 * Cf3 \times \ldots * Cf n}$
Where:
n: Numbers for materials examined.
Cf: Contamination_factor.

Discussion

Geo-Accumulation Varaible is utilised to assess the human activity effect. The sediment was divided into six classes using the I- geo categories (Weaver and Pollard, 1974), (Table 3 and Table 6). I-geo values for the elements (Ni, Zn, Pb, Fe and Cu), was unpolluted (class- 0). While I-geo values for the (Cd),was slightly polluted (class- 1), Cd levels are low because of of industrial processes, agricultural runoff, as well as other human activity inputs (Fig 3).

Table 3. Major sediment classes based on I-geo values (Thomilson et al., 1980)

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

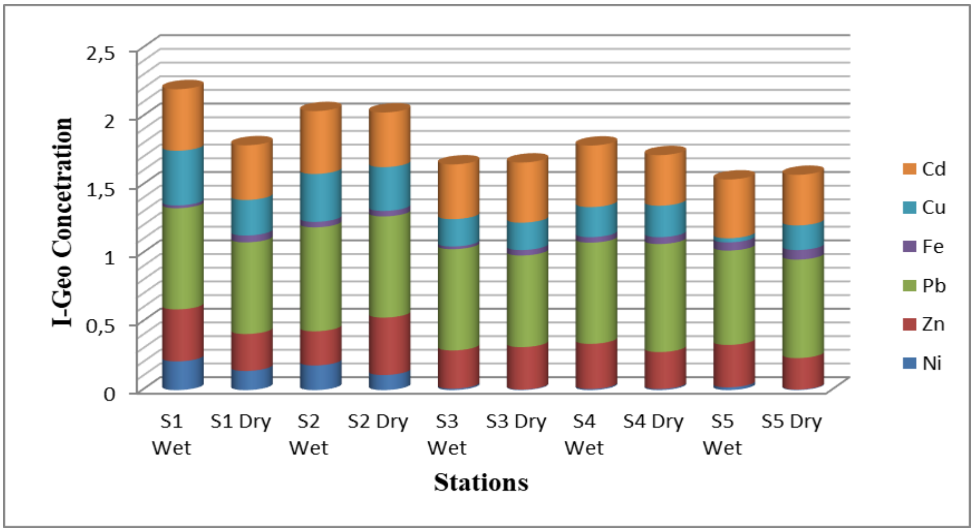

Fig. 3. I-Geo values of soil samples.

Contamination_factor CF, defines a pollutions for a specific poisonous actual content inside the lake or sub-basin. There are 3 classes of contamination_factors, according to (Weaver and Pollard, 1974), (Table 4 and Table 6). Within research site , contamination_factor CF, to (Cu, Zn, as well as Pb) was determined to be (class- 1), indicating low contamination, except (S5 wet), for element Cu is moderate contamination (class- 2). While CF values for the (Ni and Fe),was moderate contamination (class- 2). This is may be due to the human activities. But the (Cd), was Considerable contamination (class- 3). Cd levels are extremely high, suggesting severe human activity contamination. Numerous sites can be characterize as polluted sites (Fig 4).

Table 4. Major sediment classes based on CF values (Weaver and Pollard, 1974)

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

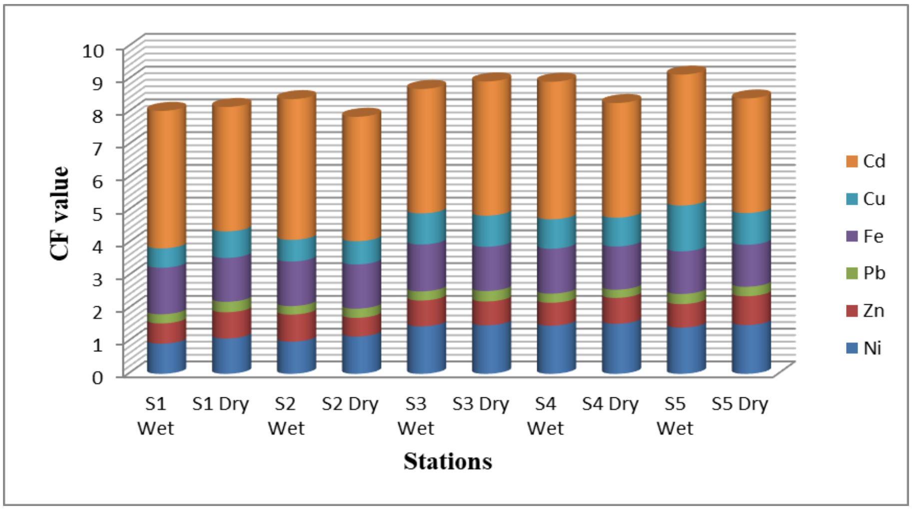

Fig. 4. CF values of soil samples.

The Pollution Load Index was measured by numerous Contamination_Factor values. The Pollution Load Index to (Cd, Fe, Pb, Zn, Cu, and Ni) has been measured as Class- 2 classification (Deterioration site), except (S1-S2 wet and S2 dry), is classify as Class- 0 (Perfection), However according (Thomson et al., 1980), (Table 5). PLI concetration within research site varying from (0.74 - 1.51), average (1.12). (Tables 6), (Fig 5).

Table 5. The major sediment classes based on PLI values (Thomilson et al., 1980)

PLI	Order	Result
<1	Class- 0	Perfection
1	Class- 1	Baseline level
>1	Class- 2	Deterioration site

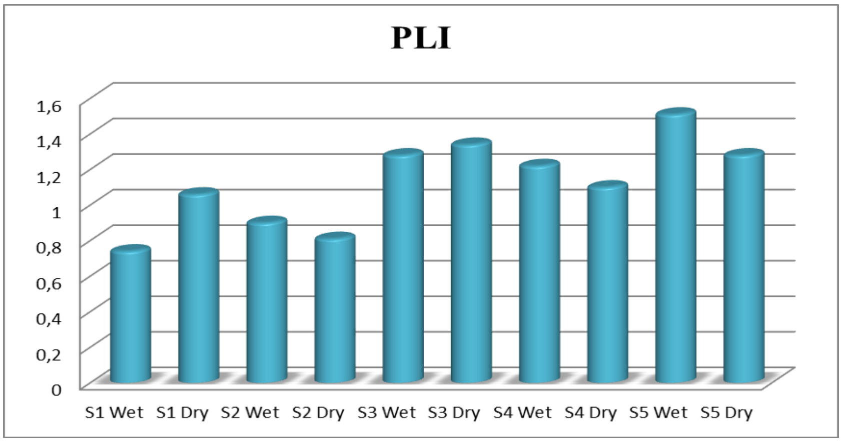

Fig. 5. PLI values of soil samples.

Table 6. The concentration of (CF, I- Geo, and PLI) within research site's

Sample		Ni		Zn		Pb		Fe		Cu		Cd	
	I-Geo	CF	I-Geo	CF	I-Geo	CF	I-Geo	CF	I-Geo	CF	I-Geo	CF	PLI
S1 Wet	-0.21	0.92	-0.38	0.62	-0.74	0.28	-0.02	1.42	-0.4	0.59	0.45	4.2	0.74
S1 Dry	-0.14	1.08	-0.27	0.8	-0.67	0.32	-0.05	1.34	-0.26	0.81	0.4	3.8	1.06
S2 Wet	-0.18	0.98	-0.25	0.83	-0.76	0.26	-0.04	1.36	-0.35	0.66	0.46	4.3	0.9
S2 Dry	-0.11	1.14	-0.42	0.57	-0.74	0.28	-0.04	1.35	-0.32	0.71	0.4	3.8	0.81
S3 Wet	-0.01	1.45	-0.28	0.79	-0.74	0.28	-0.02	1.43	-0.2	0.95	0.4	3.8	1.28
S3 Dry	-0.004	1.48	-0.31	0.73	-0.67	0.32	-0.04	1.35	-0.2	0.95	0.44	4.1	1.34
S4 Wet	-0.008	1.47	-0.33	0.7	-0.74	0.28	-0.04	1.37	-0.22	0.9	0.45	4.2	1.22
S4 Dry	0.008	1.53	-0.27	0.79	-0.79	0.25	-0.05	1.32	-0.23	0.88	0.37	3.5	1.1
S5 Wet	-0.02	1.41	-0.31	0.72	-0.69	0.31	-0.06	1.3	-0.03	1.4	0.43	4	1.51
S5 Dry	-0.004	1.49	-0.23	0.88	-0.72	0.29	-0.07	1.28	-0.18	0.97	0.37	3.5	1.28
Min	-0.21	0.92	-0.42	0.57	-0.79	0.25	-0.07	1.28	-0.4	0.59	0.37	3.5	0.74
Max	0.008	1.53	-0.23	0.88	-0.67	0.32	-0.02	1.43	-0.03	1.4	0.46	4.3	1.51
Average	-0.06	1.29	-0.3	0.74	0.72	0.28	-0.04	1.35	-0.23	0.88	0.41	3.9	1.12

Conclusion

Several tools would be used to assess havey materals value within soils of Haditha reservoir as well as Anah city. including comparison with of local studies, and calculation of different indices by using geochemical pollution index like geo-accumulation variable (I-Geo), contamination_factor (CF), as well as pollution loud index (PLI). Trace minerals found within study research gradual difference in their background range and median values, which are influenced by parent or source rocks, climatic conditions, pedogenic processes, and drainage. The results of (I-geo), values for all elements was unpolluted except the element (Cd),shows low polluted because of the impact of industrial activities, agricultural runoff, as well as other human activity sources. While the contamination_factor (CF), indicates low to moderate contamination except for (Cd), there was considerable contamination, suggesting severe human activity contamination. While the Pollution Load Index (PLI) for all elements was estimated and classified Deterioration site (low polluted), except afew stations is classify Perfection (unpolluted).

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