Assessment of some heavy metals contamination in sediments of Tigris River in Kut City, Wasit Governorate, Iraq

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Abstract. The grade of contamination in the Tigris River sediments in the Kut City by heavy metals Co, Cu, Cr, Mn, Ni, Pb, Zn and Cd has been evaluated by using some pollution indices like Enrichment factor (EF), geo-accumulation (I-geo), contamination factor (CF) and pollution load (PLI). The (EF, enrichment factor) is one of the most factors applied as a way to describe the degree of anthropogenic pollution to find enrichment ratios, whereas on the geo-accumulation has been mostly applied as a measurement of contamination in freshwater sediment. Whereas, the index of pollution load (PLI), appear the sum of times by which the heavy metals concentrations in the sediment exceed the level, concentration and accord a guide to the total level of heavy metals is toxicity in a special sample. By using these numerical sediments indices we found that the sediments of Tigris River in the Kut city are polluted by the metals of Lead and Cadmium, and moderately polluted by the metals of Nickel, Zinc and Copper, while the sediments of Tigris River are not polluted by the metals of Manganese, Cobalt and Chromium.

Keywords: Kut City, Tigris River, heavy metals, Pollution Indices, Sediments.

1. Introduction
The Tigris River is one of the largest rivers in Iraq. The basin of the river is distributed by: Iraq, Iran, Syria and Turkey. The length of the Tigris in Iraq is approximately 1400 km, whereas, in Wasit province about 327 km therefore it is considered the main source of water. Where most of the districts and areas of the province on both banks of the river. The analysis of sediments in the rivers is a good method of research ecological pollution by heavy metals [1, 2]. Heavy metal accumulations in the sediments via complex chemical adsorption and physical mechanisms which, depending on the properties of the adsorbed compounds and nature of the sediment mold [3]. High concentrations of heavy metals in sediments at the lower of the water column can be a perfect index of human contamination rather than natural enrichment of sediments by erosion and weathering [4]. Heavy metals normally entered into the river come mainly from sources such as weathering, soil erosion, decay of soluble salts in water and anthropogenic sources entering river waters [5]. The contamination of the water environment by heavy metals is a global problem because the toxic effect of heavy metals on living organisms (when permissible concentration standards are exceeded), and indestructible [6]. River sediments are commonly regarded as the final basin for heavy metals discharged into the environment [7]. Contaminated river sediments can threaten life in the Benthic environment, exposing organisms to hazardous concentrations of toxic chemicals.
In this paper, the indices of pollution have been used to estimate the intensity and presence of anthropogenic pollution deposition on river sediment, indices are:

1. Enrichment Factor (EF)
2. Geo-accumulation Index (I-geo)
3. Contamination factor (CF)
4. Pollution load index (PLI).

This research aimed to estimate the pollution of some heavy metals in the sediment of the Tigris River in Kut City, Wasit Governorate, Iraq.

2. Methodology

2.1 Case Study
The Tigris River within Kut city is located between latitudes, 32°30'30", 32°31'36" N and longitudes 45°50'20", 45°48'25"E as shown in table 1 and figure 1. Tigris River is important rivers in Iraq, enters the city of Kut is coming from Baghdad and surrounded by the three sides component peninsula, so it is the main source of daily use and drinking of human, increased the amount of pollutants entered into the Tigris river as a result of industry and agriculture that depend on irrigating land and the use of pesticides, fertilizers, poor sanitation and garbage collection methods led to pollution of the river [8].

Table 1. Location of all sites Samples in Tigris River sediments in Kut City, October 2018

| Site | Coordinate               |
|------|--------------------------|
| S.1  | 45°48'25"E, 32°30'30"N   |
| S.2  | 45°49'53"E, 32°29'19"N   |
| S.3  | 45°50'48"E, 32°29'35"N   |
| S.4  | 45°50'08"E, 32°30'32"N   |
| S.5  | 45°50'20"E, 32°31'36"N   |

2.2 Collection Samples and Analysis
Five sites were selected by using (Peterson Grab) to take sediment samples along the Tigris River within the city of Kut (figure 1), and (table.1). Site sample was localized by GPS. The samples of sediment were collected for one month (October 2018). The collected samples have been assessed for nine heavy metals such as Mn, Cr, Co, Zn, Ni, Cu, Pb, Cd and Zr, heavy metals detect the sediment pollution in the Tigris River by using four of main indices; EF, I-geo, CF and PLI. All samples have been transferred to the XRF (in the laboratory of the Baghdad University, College of Science, Department of Geology), the soil samples are exposed to oven drying at a temperature of 60 °C, the weight of the sample in powder form is 10 g, to detect the Mn, Cr, Co, Zn, Ni, Cu, Pb, Cd and Zr metals by using the XRF method (table 2).
Figure 1. Sampling map of the Tigris River sediments in Kut City

Table 2. Heavy metals Concentrations (ppm) of sediments in Tigris River in Kut City, October 2018, and Background values of the earth's crust according to [9] in [10]

| Sample No. | Mn (ppm) | Cr (ppm) | Co (ppm) | Zn (ppm) | Ni (ppm) | Cu (ppm) | Pb (ppm) | Cd (ppm) | Zr (ppm) |
|------------|----------|----------|----------|----------|----------|----------|----------|----------|----------|
| S.1        | 547.5    | 87.6     | 17.4     | 108.4    | 90.7     | 115.4    | 35.3     | 0.95     | 78.2     |
| S.2        | 615.3    | 90.8     | 20.2     | 112.6    | 93.5     | 121.5    | 39.6     | 0.97     | 85.4     |
| S.3        | 656.6    | 96.5     | 22.6     | 117.1    | 101.2    | 124.8    | 41.2     | 1.01     | 86.5     |
| S.4        | 695.8    | 98.7     | 24.4     | 123.5    | 110.7    | 132.2    | 45.5     | 1.02     | 88.1     |
| S.5        | 596.4    | 89.2     | 18.5     | 112.4    | 91.3     | 118.6    | 38.9     | 0.97     | 80.5     |
| [9] in [10]| 950      | 100      | 25       | 70       | 75       | 55       | 12.5     | 0.2      | 165      |
2.3 **Assessment of Pollution in Heavy Metals**

The four indices EF, I-geo, CF and PLI were utilized for evaluation the pollution in Tigris River sediments by heavy metals, as follows:

2.3.1 **Enrichment Factor (EF):** An enrichment factor is used to assess the deposition intensity and presence of anthropogenic pollutants in river sediments. This index of possibility pollution is estimated via the adjusting the concentration of one element in soil to the concentration of the background element. The background element is indicated as a stable element in the soil, which is characterized by non-attendance of decay phenomena and vertical mobility. Contamination indices such as (Enrichment Factor) are strong material for analysing, processing and transport raw environmental information to technicians, public, managers and the decision- makers [11].

In arrangement to assess if the chemical element content in the sediments comes from anthropogenic or natural sources, the (EF) was calculated for all sediment models studied by using (Zr) as a reference metal. The EF is the relative multiplicity of a chemical element in the sediment sample to compare with bedrocks. Zircon is a result of the weathering of rocks and not of human resources. Zircon was widely utilized in Geochemical studies as a moderate component compared to relative enrichment [12]. The calculated of EFs were, according to:

\[
EF = \frac{M}{Zircon} \text{ for sediment} \div \frac{M}{Zircon} \text{ for earth’s crust}
\]

Where: M, are heavy metal concentration (ppm) and, zircon concentration (Zr), the concentration of Zircon (ppm) measured in (sample of sediment / earth’s crust). The (EF) was classified into five grades, according to [13] [14], (table 3).

| Value | Soil dust quality of enrichment |
|-------|---------------------------------|
| EF>40 | Extremely high                  |
| 20<EF<40 | Very high                      |
| 5<EF<20 | Significant                    |
| 2<EF<5 | Moderate                        |
| EF<2  | Deficiency to minimal           |

Men EF values of metals in Tigris River sediments were in the order Cd > Pb > Cu > Zn > Ni > Cr > Co > Mn. EF values of metals in the Sediments of the Tigris River in Kut City are shown in (table 4, figure 2).

**Table 3.** The EF categories according to [13] [14]

| Site /Metals | Mn  | Cr  | Co  | Zn  | Ni  | Cu  | Pb  | Cd  |
|--------------|-----|-----|-----|-----|-----|-----|-----|-----|
| S.1          | 1.21| 1.85| 1.46| 3.26| 2.55| 4.43| 5.96| 10.02|
| S.2          | 1.25| 1.75| 1.56| 3.11| 2.41| 4.27| 6.12| 9.37 |
| S.3          | 1.32| 1.84| 1.72| 3.19| 2.57| 4.33| 6.28| 9.63 |
| S.4          | 1.37| 1.85| 1.83| 3.30| 2.76| 4.50| 6.82| 9.55 |
| S.5          | 1.28| 1.83| 1.52| 3.29| 2.49| 4.42| 6.37| 9.94 |
| Mean         | 1.28| 1.82| 1.62| 3.23| 2.55| 4.39| 6.31| 9.70 |
2.3.2 Geo-accumulation Index (I-geo): The I-geo was primarily defined by [15], for element concentrations in the 2-part micron. This guide is expressed as follows:

$$I_{-geo} = \log_2 (\frac{C_n}{1.5 * B_n})$$

Cn: the concentration of the element measured in the soil, Bn: Geochemical background value, 1.5: constant for variations in the substance contained in the environment and anthropogenic influence. [16] has defined seven levels of the Geo-accumulation Index (as shown in Table 5) ranging from Class 6 (I-geo > 5, extremely polluted) to class 0 (I-geo=0, unpolluted).

| Soil dust quality of contamination | Value       | Class |
|-----------------------------------|-------------|-------|
| Extremely                         | I-geo≥5     | 6     |
| Heavily to extremely              | 4< I-geo <5 | 5     |
| Heavily                           | 3< I-geo <4 | 4     |
| Moderately to heavily             | 2< I-geo <3 | 3     |
| Moderately                        | 1< I-geo <2 | 2     |
| Uncontaminated to moderately      | 0< I-geo <1 | 1     |
| Uncontaminated                    | I-geo≤0     | 0     |

Mean (I-geo) Accumulation Index values of heavy metals in Tigris River sediments were in the order Cd > Pb > Cu > Zn > Ni > Cr > Co > Mn. (Table 6, Figure 3).

| Site /Metals | Mn     | Cr     | Co     | Zn     | Ni     | Cu     | Pb     | Cd    |
|--------------|--------|--------|--------|--------|--------|--------|--------|-------|
| S.1          | -1.38  | -0.77  | -1.11  | 0.03   | -0.21  | 0.48   | 0.91   | 1.66  |
| S.2          | -1.21  | -0.72  | -0.89  | 0.10   | -0.26  | 0.56   | 1.07   | 1.69  |
| S.3          | -1.12  | -0.64  | -0.073 | 0.15   | -0.15  | 0.59   | 1.13   | 1.75  |
| S.4          | -1.03  | -0.60  | -0.62  | 0.23   | -0.02  | 0.68   | 1.28   | 1.76  |
| S.5          | -1.25  | -0.75  | -1.02  | 0.09   | -0.30  | 0.52   | 1.05   | 1.69  |
| Mean         | -1.19  | -0.69  | -0.87  | 0.12   | -0.19  | 0.56   | 1.09   | 1.71  |
2.3.3 Pollution load index (PLI): The (PLI) depended on Contamination Factors (CF). According to [17], this index is used to classify the contamination of metals in the river sediment samples or lake it is defined as:

\[
\text{Contamination Factors (CF)} = \frac{\text{metals concentration (C)}}{\text{background value (C)}}.
\]

The CF (Contamination Factor) was classified according to [18], into:
- Low contamination, (class 1), if CF < 1
- Moderate contamination, (class 2), if 1 ≤ CF ≤ 3
- Considerable contamination, (class 3), if 3 ≤ CF ≤ 6
- Very high contamination (class 4), if CF > 6

The Pollution Load Index (PLI) for a one site is the (n) root of (n) number multiplying the contamination factors (CF values) with one another. Generally, the pollution load index (PLI) was well-educated by [19] which is as follows:

\[
\text{PLI} = (\text{CF}_1 \times \text{CF}_2 \times \text{CF}_3 \times \text{CF}_4 \ldots \text{CF}_n)^{1/n}
\]

Where:
- n= the number of study heavy metals at every site, (table 7).

The Classified grade of PLI indices, after [19], into:
- Perfection (class 0), if PLI < 1.
- Baseline Level (class 1), if PLI = 1.
- Deterioration (class 2), if PLI > 1.

Figure 4 is presented the values of Contamination Factor (CF) and PLI level in Tigris River sediments in the Kut City for heavy metals.

Table 7. CF values and the PLI Value of Heavy metals in the Tigris River sediments in Kut City, October, 2018

| Site /Metals | Mn  | Cr  | Co  | Zn  | Ni  | Cu  | Pb  | Cd  | PLI |
|-------------|-----|-----|-----|-----|-----|-----|-----|-----|-----|
| S.1         | 0.57| 0.87| 0.69| 1.55| 1.21| 2.09| 2.84| 4.75| 1.44|
| S.2         | 0.64| 0.91| 0.81| 1.61| 1.24| 2.21| 3.17| 4.85| 1.54|
| S.3         | 0.69| 0.96| 0.90| 1.67| 1.35| 2.27| 3.29| 5.05| 1.63|
| S.4         | 0.73| 0.98| 0.97| 1.76| 1.47| 2.40| 3.64| 5.10| 1.73|
| S.5         | 0.63| 0.89| 0.74| 1.61| 1.22| 2.15| 3.11| 4.85| 1.51|
| Mean        | 0.65| 0.90| 0.82| 1.64| 1.29| 2.22| 3.21| 4.92| 1.57|
2.4 Results and Discussion

To determine the heavy metal content in Tigris River sediments in Kut City, it is significant to determine the normal grade of these metals; heavy metals may be joint in the hydrous system from anthropogenic source such as sewage and solid waste industries. Using the Enrichment Factor (EF) investigate as an active instrument to assess the quantity of metal contamination in soil [20], however, according to the results of enrichment factor (EF) on record in (table 8). The Enrichment factor (EF) of Pb and Cd in the Tigris River sediments at (EF= 9.70 and 6.31) respectively ability be said to come from Significant human influence [21]. Metals of Zn, Ni and Cu with EF value 3.23, 2.55 and 4.39 respectively having Moderate Enrichment which is reflected that sewage sludge, phosphate fertilizers and irrigation influence, but metals Mn, Cr and Co with EF value 1.28, 1.82 and 1.62 having Deficiency to Minimal Enrichment which is reflected no human influence on the Tigris River sediments by these metals [22].

Table 8. Range and mean of EF values and Category for metals in Tigris River Sediments in Kut City, 2018

| Heavy metals | EF value of Tigris River Sediments | EF Category           |
|--------------|-----------------------------------|-----------------------|
| Mn           | 1.21-1.37                         | 1.28                  | Deficiency to Minimal Enrichment |
| Cr           | 1.75-1.85                         | 1.82                  | Deficiency to Minimal Enrichment |
| Co           | 1.46- 1.83                        | 1.62                  | Deficiency to Minimal Enrichment |
| Zn           | 3.11 – 3.30                       | 3.23                  | Moderate Enrichment             |
| Ni           | 2.41- 2.76                        | 2.55                  | Moderate Enrichment             |
| Cu           | 4.27- 4.50                        | 4.39                  | Moderate Enrichment             |
| Pb           | 5.96 – 6.82                       | 6.31                  | Significant enrichment          |
| Cd           | 9.37- 10.02                       | 9.70                  | Significant enrichment          |

Depended on geo-accumulation Index to find out the Enrichment of metal concentration above baseline concentrations, sediments were classified as Uncontaminated by Mn, Cr, Co and Ni, while the sediments were classified as moderately contaminated to Uncontaminated by Cu and, Zn, but the sediments in Tigris River were classified as Moderate polluted by Pb and Cd, (table 9).
Table 9. Range and Mean of I-geo values and Grades for Metals in Tigris River Sediments in Kut City, 2018

| Heavy metals | I-geo value of Tigris River Sediments | I-geo Grade of contamination |
|--------------|--------------------------------------|-----------------------------|
|              | Range                                | Mean |                      |
| Mn           | -1.03 - -1.38                        | -1.19| Uncontaminated       |
| Cr           | -0.77 - -0.60                        | -0.69| Uncontaminated       |
| Co           | -1.11 - -0.62                        | -0.87| Uncontaminated       |
| Zn           | 0.03 - 0.23                          | 0.12 | Uncontaminated to moderately |
| Ni           | -0.02 - -0.30                        | -0.19| Uncontaminated       |
| Cu           | 0.48 - 0.68                          | 0.56 | Uncontaminated to moderately |
| Pb           | 0.09 - 1.28                          | 1.09 | Moderately           |
| Cd           | 1.66 - 1.76                          | 1.71 | Moderately           |

To detect the polluted in each site utilize the contamination factor (CF) to estimate Pollution Load Index (PLI), where at the heavy minerals of Cd and Pb with contamination factor values of 4.92, 3.21 Considerable contamination (class 3), respectively, show that these metals are above its background and reflect the influence of anthropogenic inputs and external discrete sources like industrial activities and agricultural runoff. While, the heavy minerals of Zn, Ni and Cu with contamination factor values of 1.64, 1.29 and 2.22 Moderate pollution (class 2), show that these metals are slightly above its background average and reflect both anthropogenic and natural sources. The metals of Mn, Cr and Co with contamination factor values of 0.65, 0.90 and 0.82, low contamination, (class 1) reflect these metals are from lithological sources, (table 10). PLI in all sites more than 1, The quality of the site is deteriorating.

Table 10. Range and mean of CF values, and Grade for the minerals in Tigris River Sediments in Kut City, 2018

| Heavy metals | CF value of Tigris River Sediments | CF Grade                        |
|--------------|-----------------------------------|---------------------------------|
|              | Range                             | Mean                            |
| Mn           | 0.57 - 0.73                        | 0.65 | Low contamination, (class 1). |
| Cr           | 0.87 – 0.98                        | 0.90 | Low contamination, (class 1). |
| Co           | 0.69 – 0.97                        | 0.82 | Low contamination, (class 1). |
| Zn           | 1.55 – 1.76                        | 1.64 | Moderate contamination, (class 2). |
| Ni           | 1.21 – 1.47                        | 1.29 | Moderate contamination, (class 2). |
| Cu           | 2.09 – 2.40                        | 2.22 | Moderate contamination, (class 2). |
| Pb           | 2.84 – 3.64                        | 3.21 | Considerable contamination, (class 3). |
| Cd           | 4.75 – 5.10                        | 4.92 | Considerable contamination, (class 3). |

3. Conclusion
Anthropogenically impacted on the sediments of the Tigris River in Kut City were estimate utilize enrichment factor, I-geo index, contamination factors (CF) and the pollution load index (PLI) for the metals Co, Cr, Zn, Mn, Cu, Ni, Pb, and Cd. Enrichment factor ratios showed that heavy metals of Co, Mn and Cr were Deficiency to Minimal Enrichment, while the metals of Zn, Ni and Cu, were moderately enriched, but the metals of Pb and Cd are significant enrichment.

The I-geo index showed the Tigris River sediments in Kut City are Uncontaminated by metals of Mn, Cr, Co and Ni, uncontaminated to moderately contaminated by the metals of Cu and Zn, while the sediments is Moderately contaminated by metals of Pb and Cd. The contamination factors showed that sediments of the Tigris River in Kut City are Low contamination by metals of Mn, Cr and Co, Moderate contamination by the metals Zn, Ni and Cu while, Considerable contamination by the Pb and Cd.
4. References

[1] Batley G.E., 1989, “Trace Metal Speciation: Analytical Methods and Problems”, CRC Press, Boca Raton, Florida.

[2] Goorzadi A., Vahabzadeh G., and Carbassi A. R., 2009, “Assessment of heavy metals pollution in Tilebon River sediments”, Iran Journal of Applied Science, Vol. 9, No. 6, 2009, pp.1190-1193.

[3] Ankley G.T, Lodge K., Call D.J., Balcer M.D., and Smith B. J., 1992, “Heavy metal concentrations in surface sediments in a near shore environment, Jurujuba Sound, Southeast Brazil”, Environmental Pollution, Vol. 109.

[4] Wakida. F. T. D., Lara-Ruiz. E. J., and Temores P., 2008 “Heavy metals in sediments of the Tecate River, Mexico”, Environmental Geology, Vol. 54, pp. 637–642.

[5] Sattar O. M. AL-Mayyahi, 2016. “Assessment of Dujaila River Water and its relationship with the agricultural soils of Dujaila project Wasit Governorate Central of Iraq”. M. Sc. Thesis. College of Science, University of Baghdad, Iraq. 138 p.

[6] Mmolawa, K., Likuku, A., and Gaboutloeloe, G. 2011. Assessment of Heavy Metal Pollution in Soils along Roadside Areas in Botswana. African Journal of Environmental Science and Technology, 5 (3): 186–196.

[7] Banat, K.M., Howari, F.M. & Al-Hamada, A.A. (2005), “Heavy Metals in Urban Soils of Central Jordan: Should We Worry about Their Environmental Risks?”, Environmental Research, 97: 258–273.

[8] Moutaz A. Al-Dabbas & Sattar O. M. Al-Mayyahi, 2016: Validity of Dujaila River Water within Wasit Governorate-Central Iraq, Iraqi Journal of Science 01/2016; 57(2C):1452-1461.

[9] Taylor, S. R., and S. M. McLennan (1985). The continental crust: its composition and evolution, Blackwell, Oxford.

[10] Krauskoff, K.B. & Bird, D.K. (1995), “Introduction to Geochemistry”, 3rd Edition, McGraw-Hill Inc., USA. 647p

[11] Caeiro, S., Costa, M. H. & Ramos, T.B. (2005), “Assessing Heavy Metal Contamination in Sado Estuary Sediment: An Index Analysis Approach”, Ecological Indicators, 5: 151–169.

[12] Blaser, P., Zimmermann, S. & Luster, J. (2000), “Critical Examination of Trace Element Enrichments and Depletions in Soils: As, Cr, Cu, Ni, Pb, and Zn in Swiss Depletions in Soils: As, Cr, Cu, Ni, Pb, and Zn in Swiss Forest Soils”, The Science of the Total Environment, 249: 257–280.

[13] Hernandez, L., Probst, J.L. & Urich, E. (2003), “Heavy Metal Distribution in some French Forest Soils, Evidence for Atmospheric Contamination”, Sci, Total Environ. 312(1-3): 195-219.

[14] Fong, F.T., Chee, P.S., Mahmood, A.A. & Tahir, N.M. (2008), “Possible Source and Pattern Distribution of Heavy Metals content in urban soil at the Terengganu town center”, Malay. J. Anal. Sci. 12:458-467.

[15] Müller G (1979), Schwermetalle in den sedimenten des RheinseVeranderungen seit 1971. Umschau 79: 778-783.

[16] Müller G (1981), Die Schwermetallbelastung der sedimente des Neckars und seiner Nebenflusse: eine Bestandsaufnahme. Chem Ztg 105: 157-164.

[17] Hakanson, L. 1980. An ecological risk index of aquatic pollution control. A sedimentological approach. Water Research, 14, pp: 975–1001.

[18] Gong, Q., Deng, J., Xiang, Y., Wang, Q., Yang, L. 2008. Calculating pollution indices by heavy metals in ecological geochemistry assessment and a case study in the parks of Beijing. J. Chin. Univ. Geosci. 19 (3), 230–241.

[19] Tomlinson, D.L., Wilson, J.G., Harris, C.R., and Jeffrey, D.W. 1980. Problems in the assessment of heavy metal levels in estuaries and the formation of a pollution index, Helgol. Wiss. Meeresunters, 33, pp: 566-572.
[20] Franco-Uria A., Lopez-Mateo C., Roca E., Fernandez-Marcus M. L. 2009. Source identification of heavy metals in pasture land by multivariate analysis in NW Spain, *J. Hazard. Mater.* 165:1008-1015.

[21] Liu, W.H., Zhao, J.Z., Ouyang, Z.Y.2005. Impacts of sewage irrigation on heavy metal distribution and contamination in Beijing, China. *Environ. Int.* 31:805–812.

[22] Kabata-Pendias, A., and Mukherjee, A.B. 2007. *Trace Elements from Soil to Human.* Springer-Verlag Berlin Heidelberg. pp:561.