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# MULTIVARIATE ANALYSIS AND GEOCHEMICAL ASSESSMENT OF HEAVY METALS POLLUTION IN SURFACE SEDIMENT FROM EUPHRATES RIVER, IRAQ

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## ABSTRACT

**Heavy metals and physical-chemical parameters in surface sediment were collected from twelve sites in the Euphrates river, Iraq, during October, and November of 2018. The high level of Cd and Pb concentrations were recorded in Basrah city and the highest Zn concentration was found in Shamiyah city, in case the Cu level was high in Kafel city. The pollution load index (PLI) for heavy metals concentrations in surface sediment refers to the high levels of attention, suggests baseline polluted conditions for all sites river. The multivariate analysis showed a different relationship between heavy metals, TOM, and pH which was TOM play role in increasing the Zn, Pb, and Cu, and these elements were from different sources such as anthropogenic and agriculture activities.**

**KEY WORDS :** Multivariate analysis, Geochemical assessment, Metals, Euphrates river, Sediment

## INTRODUCTION

In recent years, metal pollution in the riverine systems has received much concern because of its toxicity, abundance, biogeochemical recycling, ecological risks, ubiquitous and persistence, and non-degradability in the environment (Huang *et al.*, 2013; Varol, 2011). It is usually understood that the metals in the polluted aquatic environment may accumulate in the sediment through material exchange processes that are affected by physical, chemical, and biological processes, eventually precipitating in the sediments (Khadse *et al.*, 2008; Venugopal *et al.*, 2009). With the changes in the environmental conditions, metals contamination is released from sediment to the column water which causes to rise in the concentration of trace elements in river water (Mendil *et al.*, 2010).

Trace elements pollution and metalloids are introduced into an aquatic system through anthropogenic and natural sources which are contributing contamination for water, sediment and biota along the river (Waqar, 2006; Terra *et al.*, 2008).

Multivariate statistical analysis is important in the geochemical studies due to being a powerful tool and identifying concealed factors that may indicate sources of trace elements in the ecology (Mostert *et al.*, 2010). The treatment of complicated data sets requires exceptional techniques. Due to these data likely made up of some internal relationships among the variables, especially in partially concealed structures. Thus, the use of multivariate techniques is crucial to understand and interpreting complicated data sets. In addition, multivariate techniques can be used to model and scrutinize raw data, so as to demonstrate the important trends, groupings, and origins of data for instance spatial and temporal variations (Saim *et al.*, 2009). Multivariate analysis methods were exceedingly used to identify the source of trace elements in the sediments (Yalcin ***et al.,*** 2008; Ferati *et al.,* 2015).

Though limited studies were performed to study the heavy metal pollution in the Euphrates River from Iraq (Salah and Al-Rawi, 2012; Issa and Qanbar, 2016), most of these studies were focused on either the urban and rural area or other polluted sections of the river. However, the study and evaluated sources and distributions of metals in surface sediments throughout along the Euphrates River were rarely reported. Therefore, the objectives of this study were (i) to guess the heavy metals pollution in the surface sediments of Euphrates River (ii) to discover the probable sources of heavy metals in surface sediment based on multivariate analysis

## MATERIALS AND METHODS

### Study area

Euphrates River is an important river in Asia, which is expanded from Turkey to Syria and across Iraq to join with the Tigris in the Shatt al-Arab, which empties into the Arab Gulf. The total length of the river from its origin in Turkey to Al Qurna in Iraq is 3,065 km (Rahi and Halihan, 2010). It is the elementary source for different purposes such as for agricultural, municipal, and electrical power generation.

The climate of Iraq in summer, is dry and very hot with temperature of 50 $^{o}$C during July and August. The winter in Iraq is cold with temperature of 4 $^{o}$C (Kadhum, 2020). The samples were collected from the following locations: Hindiyah (S1), Hillah (S2), Kafel (S3), Hashimiyah (S4), Saniya (S5), Diwaniyah (S6), Shamiyah (S7), Samawah (S8), Khidhir (S9), Nasiriyah (S10), Suq Al-Shuykh (S11), Basrah (S12) Figure 1.

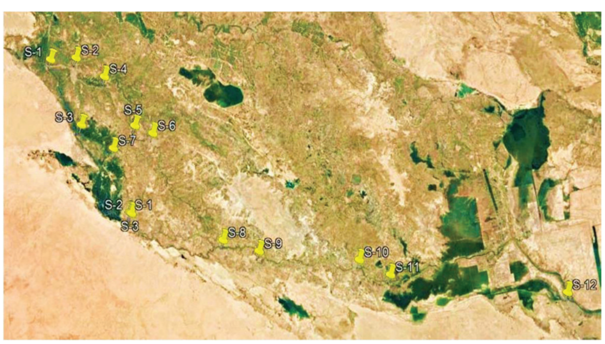


**Fig. 1.** Map of Euphrates River area and sampling collection

### Sampling collection

A total of 36 surface sediment (0-5 cm) samples were collected at 12 locations from upstream to downstream of Euphrates River between October and November 2018. Samples were collected through (PTFE) spatula. The human activities from different locations of Euphrates River are presented in the Table 1. All samples from surface sediments were kept in polyethylene plastic bags, and labeled, the samples put in an ice box and transported to the laboratory.

### Samples analysis

The dried sediment samples (0.5 g) were sieved through a 75 µm mesh nylon sieve in order to remove stones, plant fragments and plastic debris, and then the sieved samples were digested into 10 ml solution of a mixture $HNO_3$ and $HClO_4$ by prepared ratio (4:1), put in a pre-heated block digester at low temperature (40 $^{o}$C) for 1 h and then at 140 $^{o}$C for 3 h (Ismail, 1993). The digested samples were then diluted to 40 mL with double-distilled water (DDW) and filtered through Whatman No.1 filter paper into pre-cleaned 40 mL volumetric flasks. The samples were measured for metals concentrations using Atomic Absorption Spectrophotometer (AAS).

### Physicochemical analysis

The physicochemical properties such as pH and total organic matter were determination for 36 sediment samples were analyzed via standard methods. The pH was calculated in sediment based on (McLean, 1982). The organic matter was calculated based Arain *et al.,* (2008) and Kazi *et al*. (2005) as a loss on ignition through measured the difference between the dry weight of sediment samples before and after ashing in a muffle furnace at 550 °C for 5 h.

### Pollution indices

The pollution load index (PLI) to know the degrees and levels of pollution in surface sediment of Euphrates River (Tomlinson *et al.,* 1980) through used background value for each element in the current study was based on Turekian and Wedepohl (1961).

The pollution load index (PLI) was determined for every site by using the following equation:

$$PLI=\sqrt[n]{CFxCFx\ldots xCFn}$$

Where $CF_{metal} = C_{metal} / C_{background}$

The PLI value if equal or less to 1 suggests the absence of baseline pollution, while PLI if larger than 1 suggests that the site is considered baseline polluted (Tomlinson *et al.,* 1980).

The contamination factors (CF) was refer to the level of each metal with the background value in sediment as follows (CF < 1) low degree, (1 ≤ CF < 3) moderate degree, (3 ≤ CF < 6) considerable degree, and (CF ≥ 6) very high degree (Hakanson, 1980).

## RESULTS AND DISCUSSION

### Total of heavy metals and physicochemical parameters levels

The total average levels of heavy metals (Cd, Cu, Pb and Zn) in surface sediment of Euphrates river from all the locations are shown in Table 2. The zinc (Zn) was the high polluted metals in the surface sediment followed by Cu, Pb and Cd, it has showed that surface sediment in Euphrates River was significantly contamination by heavy metals in urban areas. The results also revealed increasing direction in metal concentrations from Basra and Nasiriyah to Ḍiwaniyah and Kafel cities. Therefore, heavy metals were highest in downstream while lowest in middle and upper stream due to run off industries wastes such as Oil refinery, Petrochemical process which are impacted the directly or in directly to the River (Kadhum *et al.,* 2015).

In this investigation, heavy metal concentrations in surface sediment of the Euphrates river were compared with previous studies such as a study by Varol (2011) which was heavy metals in surface sediment of the Tigris River in Turkey much higher than in the current study.

Variation of physicochemical parameters in sediment of Euphrates river were presented in Table 2 and the results have showed different levels for pH and TOM where the TOM was highest in downstream and pH was likely trend to acidity in the river.

### Geochemical Assessment

Geochemical assessment in surface sediment of Euphrates river was listed in Table 3. The high contamination factors (CF) of heavy metals in surface sediment of the river are outcomes of pollution in the river that may be exposed to different environmental factors such as human pollution activities. In spatial distributions in the river for heavy metals, the contamination factors (CF) values varied between low to high contamination for Cd were concentrated in Basra,

**Table 1.** The anthropogenic activities for each sampling station

| No. | Sites | Coordinates | | Human activities |
|---|---|---|---|---|
| 1 | Hindiyah | N 32°32'17.08" | E 44°13'51.31" | Agriculture area |
| 2 | Hillah | N 32°31′3.15" | E 44°25′32.24" | Industrial area |
| 3 | Kafel | N 32°07'52.06" | E 44°23'03.93" | Agriculture area |
| 4 | Hashimiyah | N 32°22'36.35" | E 44° 36'57.30" | Agriculture area |
| 5 | Saniya | N 32° 3′50.48" | E 44°46′57.83" | Agriculture area |
| 6 | Diwaniyah | N 31°59′55.17" | E 44°54′23.87" | Agriculture area |
| 7 | Shamiyah | N 31°57'39.45 | "E 44°35'42.08" | Agriculture area |
| 8 | Samawah | N 31°18'53.63" | E 45°17'29.44" | Agriculture area |
| 9 | Khidhir | N 31°12′35.03" | E 45°32′30.76" | Agriculture area |
| 10 | Nasiriyah | N 31° 2′14.10" | E 46°15′45.67" | Industrial area |
| 11 | Suq Al-Shuyukh | N 30°54′50.07" | E 46°28′12.77" | Industrial area |
| 12 | Basrah | N 30°34′33.09" | E 47°44′45.46" | Industrial area |

**Table 2.** Physicochemical parameters and heavy metals levels in surface sediment of Euphrates river

| Elements | Unit | Min | Max | Mean | SD | Var |
|---|---|---|---|---|---|---|
| pH | | 5.69 | 8.21 | 7.19 | 0.13 | 0.6 |
| TOM | % | 1.12 | 9.08 | 3.43 | 0.09 | 5.45 |
| Cd | mg/kg | 0.10 | 3.27 | 1.29 | 0.96 | 0.93 |
| Zn | mg/kg | 47.10 | 311.90 | 156.15 | 88.94 | 7910.41 |
| Pb | mg/kg | 22.38 | 122.56 | 63.23 | 27.88 | 848.48 |
| Cu | mg/kg | 46.20 | 93.23 | 67.52 | 21.86 | 478.21 |

Samawah, and Khidhir, these areas likely polluted by petrochemical and oil refinery process and agriculture activities. For Pb element was very high polluted in Basra city, and contamination factors (CF) for Zn and Cu were located close to industrials cities (Basra, and Nasiriyah with high other activities such as domestic sewage, pesticides from agriculture areas. The highest contamination factors (CF) levels for heavy metals were found in the downstream of river, the contamination factors (CF) of the four metals in surface sediment decreased in the following sequence: Cd > Pb > Zn > Cu.

The results of the pollution load index (PLI) are shown in Table 3, The pollution load index (PLI) values were between 1.21 to 4.20 indicating that the Euphrates river is baseline polluted based on Tomlinson *et al.* (1980) which is if PLI larger than 1 suggests that the locations are considered as baseline polluted. Thus, the river needs more attention to be controlled and manage for future studies. Increasing levels of metals in surface sediment definitely impact aquatic and contributed to making a risk to human health over the consumption of fish (Siddique *et al.,* 2009; Kadhum *et al.*, 2016).

**Multivariate analysis**

In order to found the impact of the physical-chemical parameters on heavy metal distributions in surface sediment of the Euphrates river, the Pearson correlation was used for this purpose (Table 3). The results showed that TOM had the most impact to increase the heavy metal in surface sediment through the strong correlation with Zn ($P \le 0.01$) and a weak correlation with Pb and Cu ($P \le 0.05$). Moreover, pH also can play a role to increase the heavy metals in surface sediment where the weak correlation with Pb ($P \le 0.05$). Moreover, the results revealed that heavy metals had a weak relationship between Cd and Zn ($P \le 0.05$); Pb and Cu ($P \le 0.05$). indicating these metals are the same sources.

Principal component analysis (PCA) was applied to identify factors influencing heavy metals and physical-chemical parameters in surface sediment. Kaiser-Meyer-Olkin Measure of Sampling Adequacy was 0.5 and Bartlett's Test of Sphericity was as statistically significant ($p < 0.000$), heavy metals, and physical-chemical parameters in surface

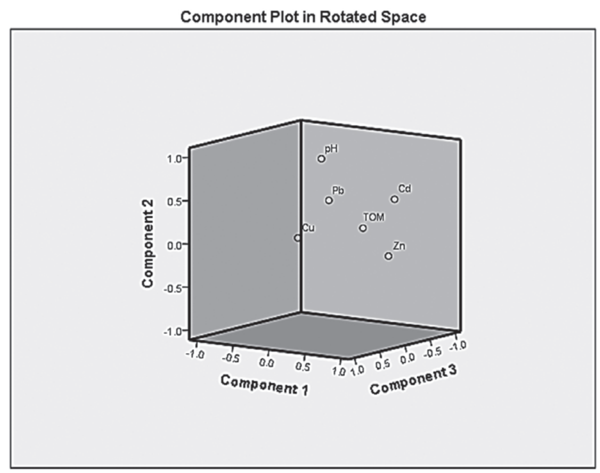


**Fig. 2.** PCA loading plot of physical-chemical parameters and heavy metals in surface sediment (PCA loadings > 0.7).

**Table 3.** Geochemical assessment including contamination factors (CF) and pollution load index (PLI)

| Sites | Contamination Factors (CF) | | | | *Pollution level | | | | Pollution load | |
|---|---|---|---|---|---|---|---|---|---|---|
| | Cd | Pb | Zn | Cu | Cd | Pb | Zn | Cu | PLI | Status |
| 1 | 0.48 | 3.87 | 1.13 | 1.02 | L.D | C.D | M.D | M.D | 1.21 | Baseline |
| 2 | 0.81 | 2.87 | 2.16 | 1.44 | L.D | M.D | M.D | M.D | 1.64 | Baseline |
| 3 | 1.87 | 2.23 | 0.30 | 2.07 | M.D | M.D | L.D | M.D | 1.27 | Baseline |
| 4 | 4.82 | 4.66 | 0.63 | 1.88 | C.D | C.D | L.D | M.D | 2.27 | Baseline |
| 5 | 5.41 | 2.06 | 0.49 | 0.75 | C.D | M.D | L.D | L.D | 1.42 | Baseline |
| 6 | 0.33 | 4.03 | 1.87 | 1.70 | L.D | C.D | M.D | M.D | 1.44 | Baseline |
| 7 | 5.14 | 3.05 | 3.28 | 2.00 | C.D | C.D | C.D | M.D | 3.04 | Baseline |
| 8 | 9.23 | 1.97 | 2.67 | 0.99 | H.D | M.D | M.D | L.D | 2.64 | Baseline |
| 9 | 6.13 | 1.11 | 0.89 | 0.66 | H.D | M.D | L.D | L.D | 1.41 | Baseline |
| 10 | 3.03 | 1.69 | 1.46 | 1.9 | C.D | M.D | M.D | M.D | 1.94 | Baseline |
| 11 | 3.66 | 4.22 | 2.00 | 1.86 | C.D | C.D | M.D | M.D | 2.74 | Baseline |
| 12 | 10.92 | 6.12 | 2.79 | 1.68 | H.D | H.D | M.D | M.D | 4.2 | Baseline |
| Average shale | 0.30 | 20 | 95 | 45 | | | | | | |

*($CF < 1$) low degree (L.D), ($1 \le CF < 3$) moderate degree (M.D), ($3 \le CF < 6$) considerable degree (C.D), and ($CF \ge 6$) very high degree (H.D) (Hakanson, 1980).).

**Table 3.** Pearson correlation of physical-chemical parameters and heavy metals in surface sediment.

| | Cd | Pb | Zn | Cu | TOM | pH |
|---|---|---|---|---|---|---|
| Cd | 1 | | | | | |
| Pb | 0.147 | 1 | | | | |
| Zn | 0.363* | 0.300 | 1 | | | |
| Cu | -0.187 | 0.382* | 0.190 | 1 | | |
| TOM | 0.277 | 0.370* | 0.465** | 0.358* | 1 | |
| pH | 0.307 | 0.379* | -0.031 | 0.179 | 0.229 | 1 |

sediment from Euphrates river three components Fig. 2. The first component was including TOM and Zn indicating that Zn influence by TOM and was origin from human activities. The second component had the only pH and the third component had Cu suggested that the element was a different source.

Cluster analysis (CA) was also analyzed to identify the sources of heavy metals in surface sediment of the Euphrates river based on spatial samplings Fig. 3. A similar sampling of the river sediment was grouped into three statistically significant were group 1 containing Hindiyah, Kafel, Hashimyah, Saniya, Khidhir, and Nasiriyah indicating these cities may be impacted through agriculture activities such as pesticides. The second group was included the anthropogenic and agriculture activities for the Hillah, Diwaniyah, and Suq Al-Shuyukh, while the third group was high influent with the petrochemical process and other activities for Basrah, Samawah, and Shamiyah.

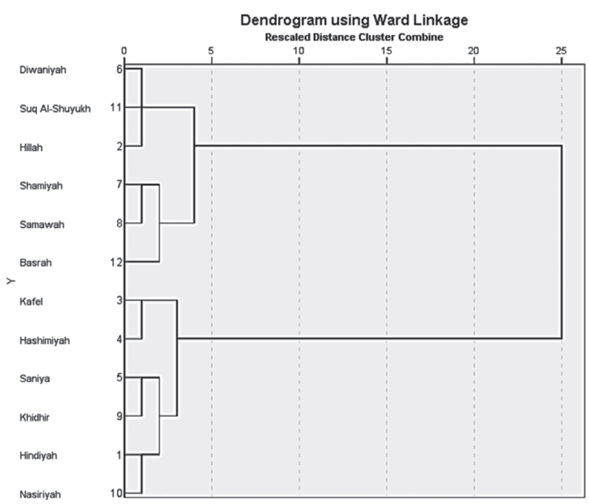


**Fig. 3.** Dendrogram showing clustering of the sampling stations

## CONCLUSION

This study has revealed that the surface sediment of the Euphrates river was highly polluted for four heavy metals and was recorded as baseline pollution in the river. The physical-chemical results involved that TOM was highest downstream of river and pH was likely to be acidic in surface sediment. The Pearson correlation showed that Zn, Pb, and Cu increasing were impacted by TOM. PCA analysis revealed that the elements were from different sources. The cluster analysis divided the sampling locations into agriculture and anthropogenic activities. These data can be used for environmental river management for controlling pollution.

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