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# Assessment of Some Heavy Metal Concentrations in Drilling Mud samples in Az Zubair Oil Field, Basra, Iraq

***Abstract-*** *Analysis of eight heavy metal concentrations (Cd, Cr, Cu, Fe, Mn, Ni, Pb and Zn) of 14 drilling mud samples collected from oil well at different depths which is located in AZ Zubair oil field-Basra was done in this study . The samples were measured using atomic absorption spectrophotometry. Obtained results indicated that the heavy metal concentrations range from the lowest value of 1.66mg/kg for Cd to the highest value of 1235.86mg/kg for Fe. The abundance trend for the heavy metals concentration was in the descending order of Fe, Mn, Ni, Cu, Cr, Zn, Pb, and Cd. Four parameters: Enrichment Factor (EF), Contamination Factor (CF), Geo-accumulation Index (Igeo) and Pollution Load Index (PLI) were assessed in order to evaluate the degree of contamination.*

***Keywords-*** *Heavy metals, Drilling mud, Spectrophotometry, Oil Well, Az Zubair*

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## 1. Introduction

Exploration and production operations in oil exploration fields can cause enormous and unavoidable environmental effects. It is reported that the impacts resulting from oil drillings mud and fluid are of great concern because of their toxicity to all forms of life. However, the problems range from soil degradation to pollution of surface water and ground water [1].

Drilling mud in oil exploration can be a possible source of heavy metals, and their contamination is of major concern in the environment because of their toxicity and threat to human life and the ecosystems [2, 3, 4]. Metal interaction in soil varies significantly with the nature of soil types. Furthermore, many environmental factors influence metals availability such as the nature of the metal species, their interaction with soil colloids, the soil characteristics and duration of contact with surface binding [5].

The aim of the present work is to assess heavy metal concentrations in drilling mud samples collected from different depths of the ZB-269 well at Az Zubair oilfield in southern Iraq.

## 2. Definitions

Drilling mud is a mixture of clays, chemicals and water pumped down the drill pipe to lubricate and cool the drilling bit and to flash out the cuttings and to strengthen the sides of the hole [6].

Formation is the fundamental unit of lithostratigraphy which is a body of rock that is sufficiently distinctive and continuous and can be mapped [7].

## 3. Formation's Description [8]

- **Dibdibba:** It contains sand and gravels with some cementing material such as silt and clay, lenticels of sandstone and silty marl with fibrous gypsum veins.
- **Lower Fars:** Composed of anhydrite, gypsum, marls and shallow water limestone and relatively fine grained clastics.
- **Ghar:** Composed of sandstone with subordinate gravels and occasional clay, silty beds, limestone and marl interbeds.
- **Damamm:** Composed of limestones (partly chalky, organodetrital or dolomitic), dolomites, marls, and shales.

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- **Rus:** Consists of anhydrites alternating with marls, blue shale, and unfossiliferous limestone, In Its middle parts, and of dolomitized limestone below, and soft, chalky limestone above them.
- **Umm Radhuma:** Composed of anhydritic and dolomitic limestones, mostly dull, white, or buff microcrystalline and porous. Chert occurs in the higher part of the formation.
- **Tayarat:** Consists of rubbly porous limestone that is white, buff, and pink; it is rather chalky, fossiliferous, recrystallized, dolomitized, locally sandy, and is conspicuously more massive at the base.
- **Shiranish:** Composed of blue marls in its upper parts and of thin bedded marly limestones in the lower division. The sediments are pelagic marls, sometimes dolomitic and of occasional marly limestone beds, with rich microfauna.
- **Harthe:** Composed of 200-250m in thickness of bioclastic-detrital, glauconitic limestone with green or gray, shale beds. In some places, the limestone is strongly dolomitized.
- **Sa'adi:** Composed of white, chalky, marly, globigerinal limestones with one well developed marl bed of 60m thickness. The upper part of the formation includes organic detrital limestones too.
- **Tanuma:** Consists of black shale with streaks of detrital limestone. The shales are fissile and the limestones are gray, marly, microcrystalline, pyritespotted, and detrital; glauconite and dolomite crystals occur throughout. An oolitic limestone streak appears in the upper part of the formation; the ooliths have a core of pyrite or glauconite.
- **Khasib:** The lower part is composed of dark grey and greenish; grey' shales, alternating with grey; fine grained, marly-limestones. The upper division consists of grey; fine grained marly-limestones only.

**Mishraf:** Represents a heterogeneous formation originally described as organic detrital limestones, capped by limonitic fresh water limestones.

## 4.Material and Methods

*I.Samples Collection and Analyses*

Fourteen drilling mud collected from ZB-269 oil well in Az Zubair oil field from different formations. Formations and depths, from which the samples were collected, are listed in Table 1.

**Table 1: Formation and depths (m) from which the samples were taken from**

| Formation | Depth (m) |
|---|---|
| Dibdibba | 140-150 |
| Lower Fars | 390-400 |
| Ghar | 590-600 |
| Damamm | 720-730 |
| Rus | 790-800 |
| Umm Radhuma | 1130-1140 |
| Tayarat | 1680 |
| Shiranish | 1747 |
| Harthe | 1850-1880 |
| Sa'adi | 2100-2110 |
| Tanuma | 2180-2190 |
| Khasib | 2200-2210 |
| Mishraf | 2290-2400 |

The collected samples were air dried, crushed and milled to a fine powder, then sieved with 0.3mm mesh size. A weight of 0.2gm from each sample was transferred into 100 ml, Pyrex beaker, 40 ml
of Aqua Regia (1:3 $HNO_3$: HCl) was added in order to digest the samples. The percentages of $HNO_3$ and HCl are 69.0-71.0% supplied from fine-CHEM limited, MUMBAI, India and 35.0-38.0% supplied from Thomas Baker PVT limited, MUMBAI, India, respectively. The solutions were evaporated to near dryness on a hot plate at a temperature of 105ºC. When the solutions become cold they were transferred to a 100 ml volumetric flask and made up to 100ml volume using deionized distilled water. The solutions were kept for 24 hours to allow sand grains to settle. Heavy metal samples were analyzed using Atomic Absorption Spectrophotometer (AA-6300 SHIMADZU – Japan) according to standard method 3030E in the Environmental Research Center laboratory, University of Technology, Baghdad [9].

*II.Assessment of Metal Contamination*

In order to evaluate anthropogenic impact and contamination level due to petroleum processing activities, many factors were calculated such as (Enrichment Factor (EF), Contamination Factor (CF), Pollution Load Index (PLI) and Geo-accumulation Index (Igeo)).

*a. 1.Enrichment Factor (EF)*

Enrichment Factor was calculated using Zoller et al. equation [10]:

$EF(C_M/C_{Fe})_{sample}$ / ($C_M$ / $C_{Fe})_{Background}$ (1)

Where $(C_M/C_{Fe})_{sample}$ is the metal to Fe ratio in the sample of interest; $(C_M/C_{Fe})_{background}$ is the background value of the metal to Fe ratio.

Fe was used as a reference element in order to determine the relative degree of metal contamination because its concentration in the earth crust has not been affected by anthropogenic activity. Fe has been selected as a normalization element because its input is immensely dominated by natural sources (98%) [11].

*2.Contamination Factor (CF)*

The level of contamination of sediment by metal is expressed in terms of a contamination factor (CF) calculated using equation (2):

$$CF = (C_M)Sample\ /\ (C_M)Background \quad (2)$$

Where, $(C_M)_{Sample}$ is the concentration of a given metal in the sample, and $(C_M)_{Background}$ is the value of the metal equals to the world surface rock average given by [12].

*3.Geo-accumulation Index (Igeo)*

Geo-accumulation index (Igeo) means the buildup of the metal concentration above the background concentrations and it was calculated using equation (3):

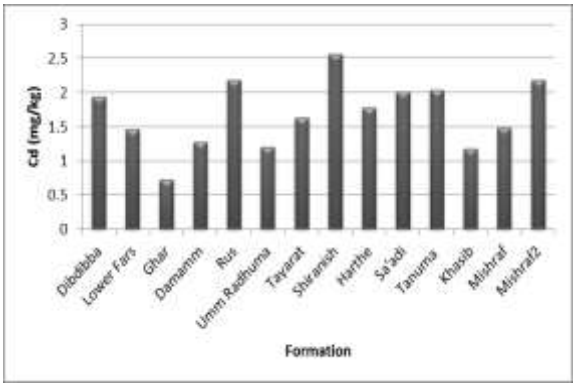
$$I_{geo} = Log_2[C_{M_{Sample}}/(1.5 \times B_M)_{Background}] \quad (3)$$

Where $(C_M)_{Sample}$ is the measured concentration of element n in the sample and $B_{MBackground}$ is the geochemical background value. The factor 1.5 is the variations in the background values due to lithogenic effect.

*4.Pollution Load Index (PLI)*

Pollution load index (PLI), for a particular formation, has been calculated using equation (4):

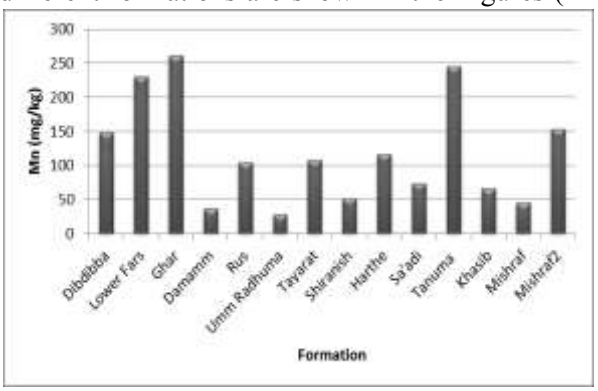
$$PLI = (C_{M1} + C_{M2} + \cdots + C_{Mn})(1/n) \quad (4)$$




Where, $C_M$ is the measured concentration of element n in the sample and n is the number of metals.

## 4.Results and Discussion

The concentrations of the investigated heavy metals (Cd, Cr, Cu, Fe, Mn, Ni, Pb and Zn) in different formations are shown in the Figures (1-




8), respectively

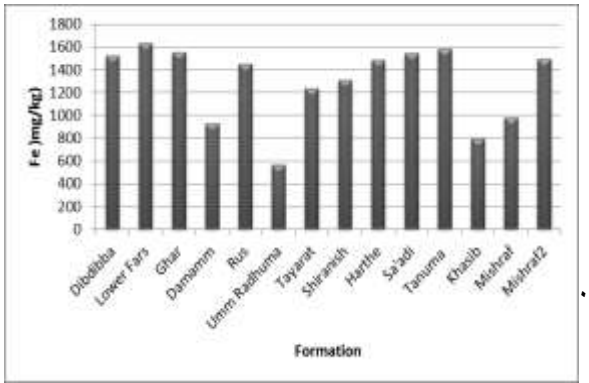
**Figure 1: Cd concentrations in different formations**

**Figure 2: Cr concentrations in different formations**

**Figure 3: Cu concentrations in different formations**

**Figure 4: Fe concentrations in different formations**

**Figure 5: Mn concentrations in different formations**



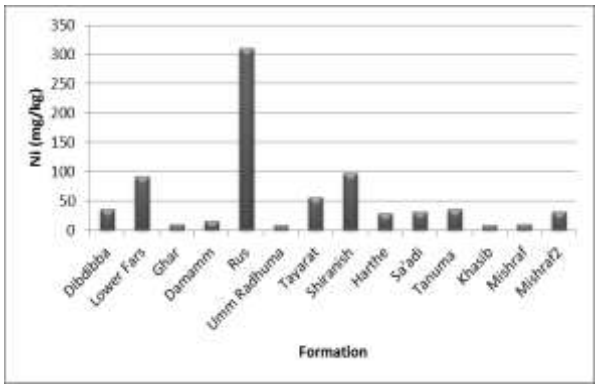



**Figure 6: Ni concentrations in different formations**

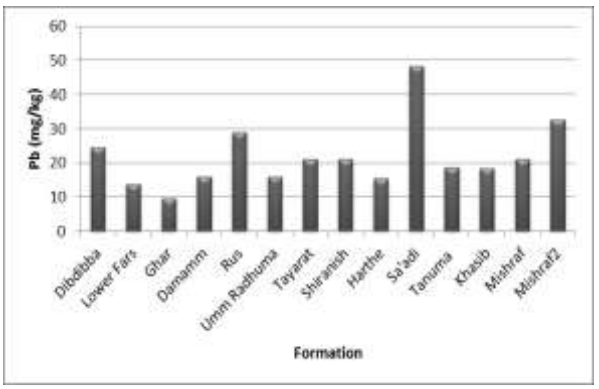



**Figure 7: Pb concentrations in different formations**

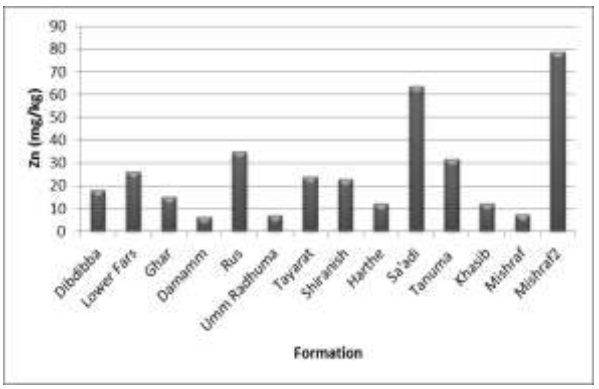



**Figure 8: Zn concentrations in different formations**

Minimum, maximum, formation and mean values of metal concentrations of the investigated samples are listed in Table 2. The descending order of the concentrations of the investigated heavy metals in in the investigated drilling mud samples is Fe, Mn, Ni, Cu, Cr, Zn, Pb and Cd. Table 3 shows the present results compared with the results of published works. Therefore, the discrepancies might be due to type of soil, geological structure, human activities and some environmental conditions [15].

**Table 2 Descriptive statistics of the heavy metals in the investigated samples**

| Elements | Min mg/kg | Formation | Max mg/kg | Formation | Mean mg/kg |
|---|---|---|---|---|---|
| Cd | 0.7 | Ghar | 2.6 | Shiranis | 1.7 |
| Cr | 21.1 | Umm | 46.9 | Sa'sdi | 28.6 |
| Cu | 4.2 | Umm | 304.0 | Rus | 41.2 |
| Fe | 565. | Umm | 1638. | L. Fars | 1292. |
| Mn | 28.2 | Umm | 261.4 | Ghar | 119.4 |
| Ni | 8.8 | Umm | 311.0 | Rus | 55.5 |
| Pb | 9.7 | Ghar | 48.3 | Sa'adi | 21.8 |
| Zn | 6.3 | Damma | 78.8 | Mishraf | 25.7 |

**Table 3 Comparison of the present work with published work**

| Element | Average Concentrations | | | |
|---|---|---|---|---|
| | Present work | Soil Nigeria [1] | Drilling muds Nigeria [13] | Iraq[14] |
| Cd | 1.645 | 0.495 | ------- | ------ |
| Cr | 33.99 | 83.15 | ------- | 180 |
| Cu | 154.1 | 27.2 | ------- | ------ |
| Fe | 1101.9 | 911.6 | 349.50 | 25000 |
| Mn | 119.4 | -------- | 3.52 | 500 |
| Ni | 159.9 | 7.7 | ------ | ------ |
| Pb | 29 | 51.4 | 2.38 | 90 |
| Zn | 42.55 | 142.55 | <0.1 | 188 |

Enrichment factor values of the heavy metals in the investigated Formations and their categories are listed in Table 4. EF categories are classified according to the EF categories given by Mmolawa et al. [16].

The determined CF for the investigated heavy metals in the samples of different formations of Az Zubair oil well is presented in Table 5. According to the four categories of Contamination Factors (CF) defined by [18], the calculated CF values shows that the drilling-mud samples from all formations are low to moderately contaminate for all metals except for Cd which are between considerable to very high contaminated.

Muller [19] identified six classes of the geoaccummulation index. It was observed that the $I_{geo}$ values of Cu, Fe, Ni, Mn, Pb and Zn in all formations are extremely polluted, while its value of Cd is strongly polluted and that of Cr is unpolluted. Calculated $I_{geo}$ values are given in Table 6.

Values of PLI gives simple but comparative means to estimate the site quality, where a value of PLI <1 indicate perfection; PLI = 1 presents that only baseline levels of pollutants are presented and PLI

>1 would indicate degradation of site quality [20]. The PLI values for heavy metals in the samples of the investigated Formations are listed in Table 7 which indicates that PLI is greater than 1 in all types of Formations.

**Table 4: Enrichment Factor (EF) values of heavy metals in the investigated samples**

| Formation Layer | Cd | Cr | Cu | Mn | Ni | Pb | Zn |
|---|---|---|---|---|---|---|---|
| Dibdibba | 229.03 | 8.97 | 8.46 | 4.66 | 17.64 | 36.22 | 3.35 |
| Lower Fars | 160.47 | 10.21 | 44.69 | 6.74 | 41.09 | 18.96 | 4.52 |
| Ghar | 83.88 | 7.71 | 4.83 | 8.07 | 4.97 | 13.98 | 2.77 |
| Damamm | 245.60 | 12.97 | 16.14 | 1.87 | 12.19 | 38.62 | 1.92 |
| Rus | 269.32 | 13.35 | 234.73 | 3.45 | 156.80 | 44.77 | 6.79 |
| Umm Radhuma | 382.78 | 18.87 | 8.26 | 2.39 | 11.45 | 63.69 | 3.49 |
| Tayarat | 237.18 | 0.40 | 1.31 | 0.14 | 1.15 | 1.31 | 0.19 |
| Shiranish | 351.68 | 11.87 | 57.01 | 1.91 | 54.66 | 36.03 | 4.94 |
| Harthe | 214.51 | 8.33 | 13.89 | 3.76 | 14.36 | 23.33 | 2.30 |
| Sa'adi | 234.05 | 15.34 | 8.61 | 2.27 | 15.17 | 70.16 | 11.64 |
| Tanuma | 231.13 | 8.81 | 6.39 | 7.40 | 16.49 | 26.38 | 5.64 |
| Khasib | 265.49 | 14.50 | 11.31 | 3.99 | 8.35 | 51.83 | 4.36 |
| Mishraf 1 | 272.91 | 13.78 | 5.54 | 2.24 | 8.17 | 48.12 | 2.13 |
| Mishraf 2 | 262.16 | 8.59 | 8.27 | 4.92 | 15.32 | 48.97 | 14.92 |
| Enrichment Category | Extremely high | Significant | Moderate & extremely high | Minimal-moderate | Significant to extreme | Significant to extremely high | Minimal-significant |
| Crieteria | EF ≥ 40 | 5≤EF≤20 | 2≤EF≥40 | 2>EF<5 | 5≤EF≥40 | 5≤EF≥40 | 2>EF<20 |

**Table 5 Contamination factor (CF) for the heavy metals in the investigated samples**

| Formation Layer | Cd | Cr | Cu | Fe | Mn | Ni | Pb | Zn |
|---|---|---|---|---|---|---|---|---|
| Dibdibba | 9.725 | 0.38 | 0.36 | 0.04 | 0.20 | 0.75 | 1.54 | 0.14 |
| Lower Fars | 7.325 | 0.47 | 2.04 | 0.05 | 0.31 | 1.88 | 0.87 | 0.21 |
| Ghar | 3.625 | 0.33 | 0.21 | 0.04 | 0.35 | 0.22 | 0.60 | 0.12 |
| Damamm | 6.375 | 0.34 | 0.42 | 0.03 | 0.05 | 0.32 | 1.00 | 0.05 |
| Rus | 10.9 | 0.54 | 9.50 | 0.04 | 0.14 | 6.35 | 1.81 | 0.27 |
| Umm Radhuma | 6.025 | 0.30 | 0.13 | 0.02 | 0.04 | 0.18 | 1.00 | 0.05 |
| Tayarat | 8.17 | 0.40 | 1.32 | 0.03 | 0.14 | 1.15 | 1.31 | 0.19 |
| Shiranish | 12.825 | 0.43 | 2.08 | 0.04 | 0.07 | 1.99 | 1.31 | 0.18 |
| Harthe | 8.875 | 0.34 | 0.57 | 0.04 | 0.16 | 0.59 | 0.97 | 0.10 |
| Sa'adi | 10.075 | 0.66 | 0.37 | 0.04 | 0.10 | 0.65 | 3.02 | 0.50 |
| Tanuma | 10.2 | 0.39 | 0.28 | 0.04 | 0.33 | 0.73 | 1.16 | 0.25 |
| Khasib | 5.9 | 0.32 | 0.25 | 0.02 | 0.09 | 0.19 | 1.15 | 0.10 |
| Mishraf 1 | 7.45 | 0.38 | 0.15 | 0.03 | 0.06 | 0.23 | 1.31 | 0.06 |
| Mishraf 2 | 10.9 | 0.36 | 0.34 | 0.04 | 0.20 | 0.64 | 2.04 | 0.62 |

**Table 6: Geo-accumulation indices ($I_{geo}$) of heavy metals in investigating samples**

| Formation Layer | Cd | Cr | Cu | Fe | Mn | Ni | Pb | Zn |
|---|---|---|---|---|---|---|---|---|
| Dibdibba | 3.87 | -0.81 | 7.94 | 25.12 | 16.18 | 10.23 | 8.04 | 10.58 |
| Lower Fars | 3.46 | -0.52 | 10.44 | 25.23 | 16.82 | 11.55 | 7.21 | 11.12 |
| Ghar | 2.44 | -0.99 | 7.16 | 25.15 | 16.99 | 8.43 | 6.69 | 10.33 |
| Damamm | 3.26 | -0.99 | 8.16 | 24.41 | 14.16 | 8.98 | 7.42 | 9.07 |
| Rus | 4.03 | -0.30 | 12.66 | 25.05 | 15.68 | 13.31 | 8.27 | 11.53 |
| Umm Radhuma | 3.18 | -1.17 | 6.47 | 23.69 | 13.78 | 8.17 | 7.42 | 9.21 |
| Tayarat | 3.61 | 0.73 | 9.81 | 24.82 | 15.72 | 10.84 | 7.81 | 10.99 |
| Shiranish | 4.27 | -0.62 | 10.47 | 24.90 | 14.67 | 11.64 | 7.81 | 10.92 |
| Harthe | 3.73 | -0.95 | 8.62 | 25.08 | 15.83 | 9.89 | 7.36 | 9.99 |
| Sa'adi | 3.92 | -0.01 | 7.98 | 25.14 | 15.16 | 10.03 | 9.01 | 12.40 |
| Tanuma | 3.94 | -0.78 | 7.59 | 25.18 | 16.90 | 10.19 | 7.63 | 11.39 |
| Khasib | 3.15 | -1.05 | 7.42 | 24.19 | 15.02 | 8.21 | 7.62 | 10.02 |
| Mishraf 1 | 3.48 | -0.83 | 6.69 | 24.48 | 14.49 | 8.48 | 7.81 | 9.29 |
| Mishraf 2 | 4.03 | -0.90 | 7.87 | 25.09 | 16.23 | 9.99 | 8.44 | 12.70 |
| Mean value | 3.67 | -0.73 | 9.78 | 24.89 | 15.88 | 10.82 | 7.87 | 11.10 |
| Background [17] | 0.20 | 71.00 | 32.00 | 35900.0 | 750.00 | 49.00 | 16.00 | 127.00 |

**Table 7 PLI values for heavy metals for investigating samples**

| Formation Layer | PLI |
|---|---|
| Dibdibba | 1.38 |
| Lower Fars | 1.38 |
| Ghar | 1.24 |
| Damamm | 1.31 |
| Rus | 1.53 |
| Umm Radhuma | 1.29 |
| Tayarat | 1.37 |
| Shiranish | 1.44 |
| Harthe | 1.36 |
| Sa'adi | 1.41 |
| Tanuma | 1.38 |
| Khasib | 1.30 |
| Mishraf 1 | 1.33 |
| Mishraf 2 | 1.40 |

## 4. Conclusion

Oil exploration and production activities lead to increase the amount of heavy metals into the soil and groundwater where such activities are carried out. Thus the concentrations of heavy metals (Cd, Cr, Cu, Fe, Mn, Ni, Pb and Zn) were investigated in fourteen drilling mud samples collected from Az Zubair oil well at different drilling depths (different formations). The results show that

1. The concentrations of the study heavy metals were in the order of Fe> Mn> Ni> Cu> Cr> Zn> Pb> Cd. Concentration Results were compared
2. with some publishrd results, where the discripencies is due to many environmental and geological parameters.
3. The obtained results of EF values are categorized as significant to extremely high enrichment for all the investigated metals.
4. In relation to contamination factors, the results show that the drilling mud samples are highly contaminated with Cd element which is considered as one of the most dangerous components to which man can be uncovered at work or in the environment and low to moderetly

contaminated with the rest of the investigated elements.

5. $I_{geo}$ values in all formations are extremely polluted with Cu, Fe, Ni, Mn, Pb and Zn, strongly polluted with Cd and unpolluted with Cr.
6. The PLI values for the obtained results of the metals are greater than 1 in all types of the investigated Formations.
7. Therefore, the waste that produced with oil exploration should be well treated to prevent the surrounded area for not polluted with heavy metals.

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