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Copper Pollution Parameters in Some Iraqi Soils

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ABSTRACT

This study aims to find out the level of pollution in some agricultural land soils of areas located in central and southern Iraq (Dujail, Abu Ghraib, Hilla, Nasiriyah, Diwaniyah, Kut, Amara, and Qurna). Eight soil sample are collected for the years 2022-2023 to evaluate the degree of copper (Cu) contamination. Soil pollution is evaluated by choosing three indicators; first, is the geochemical accumulation index (Igeo); second, is the enrichment factor (EF); and third, is the contamination factor (CF). The results show that the heavily textured soil contains percentages of clay, silt, and sand ranging between (245-550), (321-500), and (90-299) g kg^{-1} respectively. pH is alkaline, pHS (7.6-7.9), electrical conductivity, ECe (4-56) dS m^{-1}, carbonate minerals (212-375) g kg^{-1}, and low soil organic matter, (SOM) (4-11) g kg^{-1}, and the total copper content ranges from (32.08-45.50) mg kg^{-1}. The contamination factor (CF) ranges between (1.07 and 1.52), and the enrichment factor (EF) ranges from (0.46-0.65) with an average of (0.54). The results of our soil models show a decrease in enrichment factors (EF) and soil pollution. While the values of the geo-accumulation index (Igeo) ranges from (-0.36) to (-0.51). So, it is clear from these results that the soils of the study areas are moderately to highly polluted. Therefore, the diversity of geological and human sources of copper contamination in the soil of the study area is reflected by these factors.

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معايير التلوث بالنحاس في بعض الترب العراقية

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الملخص

تهدف هذه الدراسة الى تقييم مستوى التلوث في ترب بعض المناطق الزراعية الواقعة في وسط وجنوبي العراق (الدجيل وأبو غريب والحلة والناصرية والديوانية والكوت والعمارة والقرنة). تم اختيار ثلاثة نماذج للترب لعامي 2022–2023 لتقييم درجة تلوثها بالنحاس. تم اختيار ثلاثة مؤشرات لتقييم تلوث التربة؛ الأول، هو مؤشر التراكم الجيولوجي (Igeo)؛ والثاني، هو عامل الاثراء (EF)؛ والثالث، هو عامل التلوث (CF). أظهرت النتائج بأن الترب الثقيلة النسجة ذات محتوى من الطين والغرين والرمل يتراوح ما بين 245–550، و321–500، و90– 299 غم كغم$^{-1}$ على التوالي، والأس الهيدروجيني هو قلوي (pHS) 7.9 –7.6، والايصالية الكهربائية (ECe) 4– 56 ديسي سيمنز م$^{-1}$، ومعادن الكربونات 212–375 غم كغم$^{-1}$، ومادة عضوية (SOM) منخفضة للترب 4–11غم كغم$^{-1}$، وأن محتوى النحاس الكلي تراوح 32.08 –45.50 ملغم كغم$^{-1}$. تراوح معامل التلوث (CF) مابين 1.07 –1.52، وعامل الإثراء(EF) مابين 0.650– 0.46 بمتوسط 0.54. وبحسب عينات التربة لعامل الإثراء (EF)، فقد أشارت إلى أن ترب منطقة الدراسة منخفضة التلوث. وتراوحت قيم مؤشر التراكم الجيولوجي (Igeo) ما بين (–0.36) و (–0.51)، مما يدل على أن ترب منطقة الدراسة ملوثة بدرجة متوسطة إلى عالية. وتعكس هذه النتائج المصادر المختلطة (الجيولوجية والبشرية) للتلوث بالنحاس في ترب منطقة الدراسة.

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Introduction

According to Festa and Thiele (2011), soil is the leading natural source of copper (Cu), is a necessary element for all living things. The soil's parent material mainly determines the concentration of Cu in the soil. The movement of copper in the soil is not very fast, so it accumulates in the surface soil as a result of its adsorption on the mineral and organic parts (Kabata-Pendias, 2011; Poggere *et al*., 2023). Cu contamination has been consequently linked to reports of dust fallout, mining, metal scrap, and organic waste deposits, former wood treatment sites, soil accumulation, and crop applications of Cu-based fungicides (Ghazi, 2018; Coelho *et al.*, 2020; Rosas *et al.*; 2023, Poggere *et al.*,2023). Al-Dabbas and Abdullah (2020), Mahmmed *et al*. (2023) and Grafkina *et al*. (2023), all discuss the biological and geographical capacities for heavy metal accumulation as a contributing factor to the problem of increased concentrations in soil. Besides is the movement inside the soil profile (Al-Hassoon *et al*.; 2019; Custodio *et al*., 2021; Al-Hayani *et al*., 2022). Soil minerals govern heavy metals distribution in soil profiles (Sołek-Podwika *et al*., 2016; Al-Dabhas and Abdullh, 2020; Mahmmed *et al*., 2023; Grafkina *et al*., 2023). It is possible to say that the cause of soil contamination with heavy metals is through historical human activity (Al-Sudani, 2021; Rosas *et al*., 2023). Undoubtedly, the sources of anthropogenic pollution currently exist in agriculture, industry, and transportation that impact the accumulation of the heavy metals in soil (Custodio *et al*., 2021; Alsaadoon *et al*., 2023). Because heavy metals bind to dust, they can be extracted from nearby and far-off emission sources and deposited in situ or transported over great distances (Aldaini and Naser, 2020). Most of the pollutants generated by factories are discharged into the atmosphere and onto the soil surface. Most pollutants produced by industries are discharged into the atmosphere and onto the soil surface (Amedi *et al*., 2022; Afonne *et al*., 2022). Natural processes can also lead to an increase in element accumulation. It is shown by Shuguang *et al.* (2015), that the major elements like Si, Al, Fe, Mg, Ca, Na, K and Ti are the essential components of the Earth crust. It is possible that the origin and composition of the parent material in these locations may have caused favorable or perhaps unfavorable conditions that led to the appearance of heavy metals. as some processes that cause natural weathering on the parent material which means it may affect the amount of parent material and heavy metals in the soil (Kierczak *et al*., 2016).

Great attention is currently being paid to serious environmental pollution resulting from high levels of heavy metals, especially in agricultural soils around the world because of their influential role in food production, and thus food security. (Chen and Colleagues, 2015; Al-Hassoon *et al.* 2019; Al-Obaidi and Al-Abadi, 2019). Heavy metals can enter the food chain, affecting human and animal health (Pejman *et al*., 2015 and Othman; Kakey, 2021). Therefore, according to what Therefore, according to Baran *et al.* (2018); Ibrahim *et al*. (2018); Khader *et al*. (2018) ; Khader *et al.* (2021), an appropriate assessment must be made to increase awareness as a result of the continuous expansion of industrial activities as well as environmental risks, and of the significant increase in the use of agricultural land, and thus the impact on the soil content of heavy elements (Al-Khafaji and Jalal, 2020)., as well as environmental risks, as well as the significant increase in the use of agricultural land, and thus the impact on the soil content of heavy elements (Al-Khafaji and Jalal, 2020). Heavy metal contamination can also occur in urban and agricultural areas close to pollution sources (Zhao *et al*., 2022 and Mununga *et al*., 2023). Therefore, we must use precise methods through which we can discover the gradual deterioration and how to stop or control it not to reach the possible maximum extent (Gonge *et al*., 2008).

Therefore, according to Baran *et al.,* (2018) and Ibrahim et al. (2018), Khader *et al.,* (2018) and Khader *et al.,* (2021), an appropriate assessment must be made to increase awareness as a result of the continuous expansion of industrial activities as well as environmental risks, and of the significant increase in the use of agricultural land, and thus the impact on the soil content of heavy elements (Al-Khafaji and Jalal, 2020).

Aim of study

The aim of this study is to determine the amount of pollution in the soils of some agricultural areas located in central and southern Iraq (Dujail, Abu Ghraib, Hilla, Nasiriyah, Diwaniyah, Kut, Amara, and Qurna). In order to accomplish this indicator including the enrichment factor (EF), contamination factor (CF), and geoaccumulation index (Igeo) are used to detect the pollution.

Materials and Methods

Eight samples of surface soil are collected at a depth of (0 - 0.15) m from the Iraqi alluvial plain in central and southern Iraq as shown in Figure (1). This area is characterized by sedimentary rocks mainly composed of carbonates and clastics, with subordinate gypsum, marl and shale (Sissakian and Saeed, 2012). They range in age from Eocene to Holocene. The collected soil samples are then air-dried, crushed, and sieved by a 2 mm sieve to conduct some physical and chemical analyzes as described by Ali and Salem (2012).

Fig. 1. Map of study sites

To measure total heavy metal concentrations, soil subsamples are completely dried at 105°C, ground, and passed through a 63-mesh sieve. Wet acid digestion (1HNO_3:3HCl) is used for a 1 g ground soil sample. Copper pollution is described through pollution indicators as follows (Kapata-Pendias, 2011):

1. The Contamination factor (CF)

One of the criteria expressing soil pollution can be calculated according to the following equation (Savvides *et al*., 1995):

CF= Cn/Cref

Where, Cn: Cu measured concentration (mg kg^{-1}) at the research location: According to Lindsay (2014), Cref: the global average (30 mg kg^{-1}) for the measuring (Cu) concentration in the reference soil.

According to Table (1), four categories of classification analysis of soil pollution were produced by Savvides *et al*. (1995) and Pekey *et al*. (2004).

Table 1: Metal content degree contamination according to the classification of the Contamination Factor (CF).

Class	CF	Designation of sediment quality
1	≤ 1	little contamination
2	1 ≥ - < 3	moderate contamination
3	3 ≥ - < 6	obvious contamination
4	< 6	high contamination

Using this criterion, Nasr *et al.* (2006) evaluated the sediment pollution of twenty-one stations in the ports of Aden, Yemen. The study discovered that the sediments of three stations had significant contamination from websites selling the same goods. In contrast, the findings of the pollution factor values for zinc, copper, and manganese indicated that they were scarce in each site under investigation. According to Al-Wotaify and Saeed's (2017) investigation, the copper contamination coefficient varied from (0.92-1.17), indicating that heavy metal contamination of the Musayyib thermal station's soil is present in Babylon Governorate (Al-khafaji, and Jaafar, 2023).

2. The Enrichment factor (EF)

The purpose of this index is to evaluate sources of elements in the atmosphere, oceans and precipitation. Nowadays, freshwater, marine sediment and soil studies have successfully used this index (Varol, 2011; Goher *et al*., 2014). According to Norouzi and Pourkhbaz (2014), this global index provides a reasonably easy and quick way to calculate the degree of enrichment Table 2. We can compare pollution levels across different environmental media. According to Jahan and Strezov (2018), we can also use this indicator to check if heavy metals and metalloids present in the sediments are the result of human activity. Elsewhere, there are measurable levels of lead and chromium contamination.

Table 2: Mineral enrichment levels per (EF) classification.

Classification of (EF)	Degree of (EF)
< 2	Depletion to enrichment in mineral
2 - 5	Moderate enrichment
5 - 20	Significant
20 - 40	Very high
EF > 40	Extremely high

$$\mathbf{EF= C_n/C_{ref}}$$

Where, Cn: the Cu concentration at the research site measured in mg kg^{-1}, according to Lindsay (2014), Cref: The Cu concentration in the reference environment, which is based on a global average of 70 mg kg^{-1} for the Earth's crust.

3. Geoaccumulation (Igeo)

Muller (1969) created the geo-accumulation index (Igeo), which compares the current concentration of heavy metals and metalloid elements with the pre-industrial level to determine the amount of these elements present in the sediment. Therefore, many researchers from all over the world have used this indicator for the purpose of evaluating the condition of sediments due to its ease in calculation and the possibility of the results being easily understood by public and regulatory bodies (Alves *et al*., 2018; Islam *et al*., 2018; Rajeshkumar *et al*., 2018). We can calculate this indicator using the following formula:

$$\mathbf{Igeo=Log2\ [C_i / (1.5\ C_{ri})]}$$

Were, Cri: the geochemical concentration of copper (70 mg kg^{-1}) in the Earth's crust, as in Lindsay (2014): Ci: the copper concentration in the soil under study (mg kg^{-1}). The factor 1.5 is used to account for variations in the basic value of copper as well as the effects or restricted human intake. To clarify how they are divided, Table (3) shows the divisions into seven categories according to Igeo indicators

Table 3: The degree of geo-accumulation (I_{geo}) classification

I_{geo}	Class	degree of I_{geo}
≤ 0	0	Uncontaminated
0 ≤ - ≤ 1	1	Uncontaminated to moderately contaminated
1 ≤ - ≤ 2	2	Moderately contaminated
2 ≤ - ≤ 3	3	Moderately to strongly contaminated

I_{geo}	Class	degree of I_{geo}
3 ≤ - ≤ 4	4	Strongly contaminated
4 ≤ - ≤ 5	5	Strongly to extremely polluted
> 6	6	Extremely polluted

Fe, Sn, Cu, Mn, Ti, Zr or Al are frequently used for normalization (Habib *et al*., 2018; Jahan and Strezov, 2018). Normalization is crucial to distinguish between the sources of trace elements originating from natural processes and anthropogenic activities. Generally, when the enrichment factor value is near or less than 1, it indicates that natural sources, like marine or crustal environments are the primary sources of trace elements. It turns out that the enrichment factor is the most important, which indicates that human activity is the main source according to studies of Jahan and Strizov (2018), Habib *et al*. (2018) and Kafilat Adebola *et al*. (2018).

Results and Discussion

The results shown in Table (5) indicate that the values of total copper in the soil of the alluvial plain of Mesopotamia range between the lowest value of 32.08 mg kg^{-1} in Hilla soil with a low clay content (245 g kg^{-1}) and a high content of carbonate minerals (375 g kg^{-1}) reaching the highest value of 45.50 mg kg^{-1} in soil of Abu-Ghraib, which is characterized by a high clay content (550 g kg^{-1}) and a low content of carbonate minerals (212 g kg^{-1}).

Table 4: Some physical and chemical properties of the studied soils

Location	pHS	ECe dS m^{-1}	CEC Cmol$_c$Kg^{-1}	O.M	$CaCO_3$	Sand	Silt	Clay	Texture
				g kg^{-1}					
Qurna	7. 6	33	25	5.7	270	153	407	440	Silty Clay
Amara	7.6	22	29	6.5	245	105	395	500	Clay
Kut	7. 8	4	21	9.1	290	98	502	400	Silty Clay
Diwaniyah	7.7	5	20	5	278	90	500	410	Silty Clay
Nasiriyah	7. 5	27	26	11	266	106	444	450	Silty Clay
Hilla	7.9	9	19	4	375	299	456	245	Loam
Abu-Ghraib	7.7	56	32	11	212	129	321	550	Clay
Dujail	7.8	13	27	8	245	135	415	450	Silty Clay

Soil samples are classified as Entisol (Soil Survey Staff, 2022) as shown in Table (4).

Table 5: Total Copper concentration in the study soil (mg Cu kg^{-1} soil)

Location	Total copper (mg Cu kg^{-1} soil)
Qurna	35.20
Amara	41.40
Kut	34.25
Diwaniyah	36.90
Nasiriyah	38.00
Hilla	32.08
Abu-Ghraib	45.50
Dujail	39.20

Based on what was mentioned by (Kabata-Pendias (2011), in some countries of the world and depending on the rates suggested globally for agricultural soils, our results indicate that the total copper in the study soils is less than the maximum permissible and safe (MAC) limits (TAV) of 60-150 and 60-500 mg kg^{-1} respectively, which does not threaten the soil environment, plants, and humans. Upon adoption of the US EPA standard (Train, 1979), which was used by Anderlini *et al.* (1982) and Al-Manssory *et al.* (2004) who have evaluated soil copper contamination based on its concentration in the soil according to the following: uncontaminated soil is less than 25, moderate is 25-50, and severely contaminated soil is more than 50 mg kg^{-1}. respectively. Many countries have taken the initiative to establish standards for evaluating soil pollution, and the standards studied are as follows: -

Contamination factor (CF)

The results in Table (6) show that the contamination factor (CF) range between 1.07 and 1.52 with an average of 1.26, so all the study soils are moderately contaminated with copper according to the contamination factor (CF) classification.

Table 6: The contamination indices (CF, EF and Igeo) for the study soil.

Location	Contamination Factor (CF)	Enrichment Factor (EF)	Geo-accumulation Index (Igeo)
Qurna	1.17	0.50	-0.47
Amara	1.38	0.59	-0.40
Kut	1.14	0.49	-0.49
Diwaniyah	1.23	0.53	-0.45
Nasiriyah	1.27	0.54	-0.44
Hilla	1.07	0.46	-0.51
Abu-Ghraib	1.52	0.65	-0.36
Dujail	1.31	0.56	-0.43
Average	1.26	0.54	-0.44

Enrichment Factor (EF)

The results shown in Table (6) show that the copper enrichment factor (EF) values for the study soils range from 0.46 to 0.65 with an average of 0.54. All the study soils are classified according to the enrichment factor (EF) values shown in Table (3), along with contamination, all the values are less than 1, which gives a clear indication of low contamination for all the study soils.

These results are consistent with what Al-Wotaify and Saeed (2017) found to evaluate soil contamination in the Musayyib thermal station in Babylon Governorate, where the copper enrichment factor range between (0.88 and 1.20).

Geo-accumulation index (Igeo)

It is clear from the results in Table (6) in the current study that the values of (Igeo) are low. The results of the EF values agree with the Igeo values in classifying the soils and the severity of their copper contamination. However, the concept of the Igeo gave wide ranges compared to the enrichment factor. Our results are consistent with Al-Wotaify and Saeed (2017) and Alhello *et al.* (2020). who evaluate the soil contamination of the Musayyib thermal station in Babylon Governorate with heavy metals. It has been found that the Igeo of copper ranges between (0.19 and 0.24).

Statistical analysis

Table (7) indicates a significant negative correlation between the three copper pollution criteria and the soil content of carbonate minerals. The reason for this can be explained by the presence of a high percentage of carbonate minerals in the soil, which corresponds to the soil's copper content, which gave a negative significant relationship, or there is a possibility of it being absorbed or deposited by the carbonate minerals.

Table 7: Simple correlation coefficient (r) between contamination factor (CF) values for copper

Soil property	Correlation coefficient (r)		
	(CF)	EF	(Igeo)
pH	0.50-	0.48-	0.50-
EC	0.65	0.63	0.64
$CaCO_3$	0.21-	0.22-	0.17-
SOM	0.17-	0.20-	0.17-
CEC	0.44	0.42	0.41
Sand	0.43-	0.42-	0.45-
Silt	0.65-	0.63-	0.62-
Clay	0.84	0.83	0.84

Table (7) shows, through the results of the statistical analysis, that there is a significant negative relationship between the three values of EF and soil pH during the study perhaps the reason for this is due to the high pH value of the soil increasing the negative charge of clay minerals and their susceptibility to copper and clay. This was demonstrated by the results of the statistical analysis of the significant correlation coefficient between the values of the enrichment factor and the clay content of the soil, which reached 0.83 during the study. In contrast, statistical analysis showed no significant correlation between the enrichment factor values and the soil content of sand and silt in Table 7. During the study, the role and importance of clay minerals in capturing and exchanging heavy elements becomes clear. The results of the study show that there is a negative significant correlation between the organic matter in the soil and the enrichment factor during the study season, and that these results were consistent with the clay content in the soil, which has mineral importance. Colloids are highlighted in retaining and enriching soils and sediments with heavy metals through negative charges of surfaces or through negative charges of functional groups (carboxylic and phenolic) present in organic materials, which form chelates with heavy metals (Al-Obaidi *et al.*,2012; Olaniran *et al.* 2013; Mawlood and Essa, 2017; Barsova *et al*., 2019).

Conclusion

We conclude from the current study that the contamination factor (CF) values range between (1.07and1.52) and the enrichment factor (EF) values range between (0.46 and 0.65), with an average of (0.54). Moreover, according to soil samples, the enrichment factor (EF) it turns out that the study area has poor soil is low in pollution. The values of the geoacumulation Index (Igeo) ranged from (-0.36) to (-0.51), which indicates that the soil of the study area is moderately to highly polluted. These results reflect the mixed sources (geological and anthropogenic sources of copper in the soils of the study area (like high dose and miss use of fertilizers (organic and nonorganic), oil refinery, petrochemical industry, vehicle emissions and dust.

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