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Evaluation of Bioaccessibility of Metals and Health Risk in Agriculture Soil in Al-Qadisiyah Governorate, Iraq

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***Abstract*---**The agricultural lands in Al-Qadisiyah Governorate are among the most economical sources in which various agricultural crops are grown, such as rice, wheat, and others. Samples were taken from seven agricultural areas in Al-Qadisiyah Governorate, and the heavy elements, including lead, zinc, cadmium, nickel, copper and chromium, were examined by atomic spectrometry. In order to know the extent of the danger of these elements in the soil and their impact on human health, pollution indices and SBET were used for this purpose. The results showed the highest value of relative bioaccessibility of lead (76.14%) in Ghamas, while the lowest value was (32.5%) in Afak. The largest value of the relative bioaccessibility of cadmium was found in Afak (82.22%), and the lowest value (30.24%) in the city of Shamiya. The pollution load indices revealed agricultural soils of Al-Qadisiyah Governorate ranged from light pollution to high pollution so that the lowest pollution values were for Zn to all agricultural soils, and the highest pollution values were for cadmium, especially in three sites (Afak, Albdair and Ghamas). The potential ecological risk index (E_r^i) found that the studied agricultural soils were within the low-risk range for five heavy metals (Cu, Cr, Ni, Pb and Zn), while the soils were suffering from a Considerable risk for Cd.

***Keywords*---**Heavy metals, Bioaccessibility, Soil, Al-Qadisiyah

Introduction

Al-Qadisiyah Governorate is the agricultural capital of Iraq, and one of the most important agricultural areas for the cultivation of rice and wheat in Iraq. As a result of climatic changes such as high temperatures, salinity and water pollution in the city, agricultural soils have become exposed to pollution in recent years. Therefore, pollution with heavy metals threatens agriculture and other human

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food sources, in addition to its impact on the growth of vegetation cover and weakening Plant resistance to various agricultural pests and consequently the deterioration of the ecosystem (Adelekan & Abegunde, 2011). The presence and continuity of heavy metals in the environment can lead to bioaccumulation, causing severe dangers to some living organisms and more than what is present in the environment. The type and chemical form or form in which heavy metals are present in an ecosystem may make it highly bioavailable, because of its biological toxicity and bioaccumulation, heavy metal contamination in soil remains a popular study area (Jia et al., 2020; Wang et al., 2020). Heavy metals are enriched in food via agricultural roots, and subsequently reach the human body through food consumption (Lu et al., 2015). The majority of the heavy metals found in food come from the heavy metals that are present in agricultural soils. It is critical to do research on the pollution of agricultural soil if one wishes to guarantee the food produced by agriculture is free of harmful substances. (Wang et al., 2020). The soil acts as a primary terrestrial reservoir and a terminal sink for a wide variety of environmental pollutants, including both organic and inorganic substances (Marchand et al., 2011). Moreover, soil content of heavy metals has reached levels that are orders of magnitude higher than their levels in the natural background over the course of the last several decades as a direct result of anthropogenic activity, particularly in soils found in industrial areas. (Shokunbi et al., 2020). The primary sources of heavy metals in soil are naturally occurring soil native materials such as weathering and things that come from the outside, like the use of chemicals in farming, the wrong way to get rid of trash, industrial particulate emissions, dust, aerosols, and smoke from burning coal Some examples of these activities include: Other causes, such as volcanic eruptions and emissions from nuclear power plants, can also contribute to the presence of heavy metals in soils(Quan et al., 2015; Romic & Romic, 2003; Zhao et al., 2008). Due to the harmful features of these minerals, such as their inability to biodegrade and their persistence, the presence of trace metals in soils can have long-term effects on both the environment and human health (Huang et al., 2007). The accumulation of heavy metals in the soil over a period of time can lead to concentrations of these minerals that are higher than the threshold limit. This can have a negative impact on the organisms that live in the soil, as well as on the yield of the crop, the health of farm products and, in the end, the health of consumers, both animals and people (Malandrino et al., 2011). Heavy metals, after increasing their concentration in the soil, can through root activities concentrate in plants, and as a result, heavy metals can migrate up the food chain to humans and cause them major health problems. (Chang et al., 2014; Mohamed et al., 2010; Nadgórska-Socha et al., 2013). Among the health problems that may be caused by some of these chemical pollutants, Individuals' neurological systems, kidney function, immunological systems, reproductive and developmental systems, and cardiovascular systems can all be harmed by long-term exposure to Pb (Cui et al., 2020). Frequent exposure to Cr has been shown to cause diseases such as bronchitis, diarrhea, and tuberculosis, and a high dose of Zn has been shown to damage islets,disrupt protein metabolism, and cause arteriosclerosis (Wei et al., 2020). Also Ni poisoning can result in nausea, dizziness, headaches, weakness, and rashes (Hernández et al., 2020). Cu can also cause health problems for humans when exposed to it in quantities through its effect on the liver and kidneys (Yang et al., 2019). As a result, investigating heavy metal contamination is important not just for reducing environmental stress, but also for human health. The SBET method is applied to mimic the gastric phase bioaccessibility, but lately the SBET was performed to set bioaccessibility together the gastric and intestinal phases (Kabir et al., 2022; Poggio et al., 2009). Many studies that established heavy metals in agricultural soils in Iraq calculated total metals where bioaccessibility represented by SBET was unknown and not done before in Iraq soil. In the current study, bioaccessible simulations of agricultural soil were carried out in gastric phases only. The objectives of this study were (1) to assess heavy metals concentration in agricultural soil and (2) to evaluate the bioaccessibility of heavy metal in agricultural soil and (3) to estimate the health risk of heavy metals.

Method

Materials and methods

Study area

Al-Qadisiyah Governorate is one of the cities located in the near central part of Iraq and is famous for its many diverse crops. Iraq's climate is characterized by a dry and very hot summer, with temperatures reaching 50 degrees during the months of July and August, which are mostly in Al-Qadisiyah Governorate. Winter in Iraq is cold with a temperature of 4 degrees (Kadhum et al., 2020; Kadhum, 2020). The source of water in agricultural lands in the city of Qadisiyah in the Euphrates River and some springs and wells, which in turn suffer from salinity and water pollution. Samples were collected from the following sites in Al-Qadisiyah Governorate: Sumer (S1), Hamza (S2), Afak (S3), Al-Budair (S4), Sania (S5), Ghammas (S6), Al-Shamiya (S7) Figure 1.

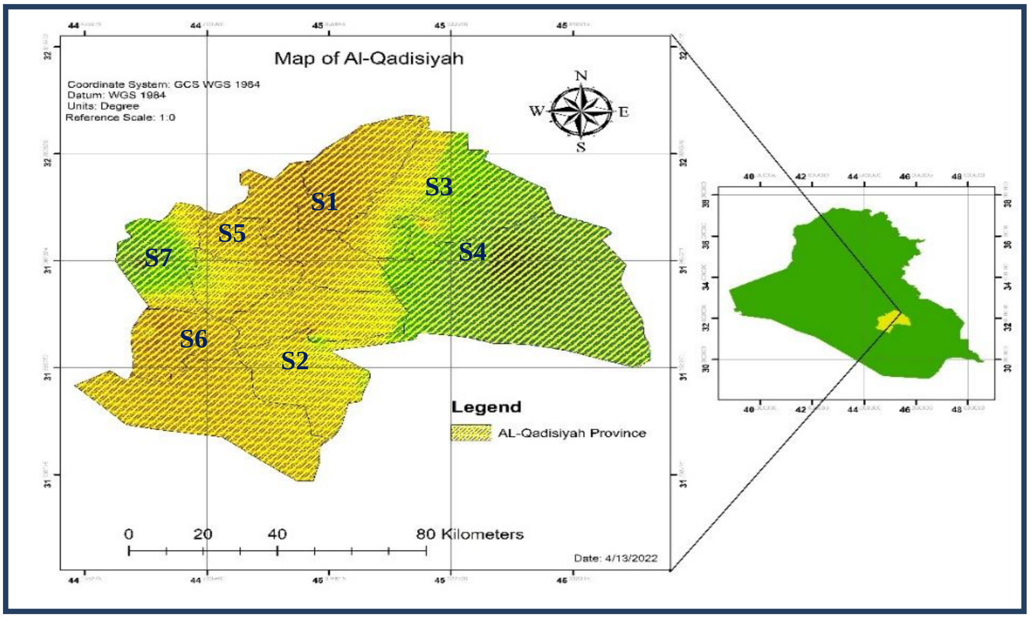

Fig 1. Iraq map and Al-Qadisiyah Governorate (Source map: Kazim and Kadhum, 2022)

Soil Samples collection and analysis

Thirty-five soil (10 cm) samples were collected at seven sites in Al-Qadisiyah Governorate between November and December 2021.Sampling analysis were conducted based on (Karimi et al. 2009; Sparks et al. 1996) to measure the total of heavy metals while the bioaccessbility of heavy metals were measured according to SBET is a one-step in vitro digestion test (Oomen et al., 2002). The samples were calculated for metals levels using Atomic Absorption Spectrophotometer (AAS) (SHIMADZU AA-7000)

Pollution indices

Geoaccumulation index(*Igeo*)

It is used to assess heavy element contamination in agriculture soil. The method requires the total content of the heavy element in the soil, taking into account human activities and the geochemical environmental conditions of the site, as well as taking into account the natural decomposition that could cause a change in the original value (Wang et al., 2010). This indicator was used by (Muller, 1979). As it relied on the concentrations of elements in the earth's crust as a reference concentration and according to the following equation and Table 1:

$$Igeo = \log_2 (Cn/(1.5Bn)$$

Where:
Cn: The soil's level of the metal being tested.
Bn: The abundance of the metal in the earth's crust.
Igeo: A scale consisting of a scale from (0-6).

Table 1:Classification of soil according to Geoaccumulation index(*Igeo*) (Muller, 1979).

Igeo Category	Igeo value	Defining the quality of the soil
0	Igeo≤0	Unpolluted
1	0< Igeo <1	Unpolluted to moderately polluted
2	1< Igeo <2	Having a moderate amount of contamination
3	2< Igeo <3	Polluted from moderate to severe
4	3< Igeo <4	Highly polluted
5	4< Igeo <5	Heavily polluted to very heavily polluted
6	Igeo≥5	Excessively polluted

Contamination factor (CF)

The contamination factor was calculated for the studied samples in soil, where in order to quantify the extent of contamination, the contamination factor (CF) is used to compare the metal's average crustal composition or the measured background values from uncontaminated locations(Tijani et al., 2004). It is expressed as and Table 2:

CF = Cm / Bm   Where:
Cm: The average amount of heavy metals found in the soil.
Bm: The average concentration of heavy metals in the earth's crust.

Table 2: Classification of Soils by contamination factor (Hakanson, 1980)

The factor of contamination	Description
$CF<1$	Slightly contaminated
$1\leq CF<3$	Moderately contaminated
$3\leq CF<6$	Highly contaminated
$CF\geq 6$	Extremely contaminated

Pollution load index (PLI)

for each sample, the pollutant load index was determined. An easy statistical technique known as the pollution load index (PLI) is used to evaluate soil elements that exceed the standard concentration. PLI provides clear information about the toxicity of chemicals in individual samples (Tomlinson et al., 1980). The pollutant load index can be calculated using the following formulas:

$$PLI=\sqrt[N]{(CF1 \times CF2 \times CF3 \times \ldots \times CFN)}$$

Where:

PLI: pollutant load index.
CF: is the contaminant factor.
N: How many elements are there.

There is pollution if the PLI is greater than 1, and there is none if it is less than 1.

3.6.4 Ecological risk factor(E_r^i)

The Ecological risk factor(E_r^i)was calculated, which represents one of the most important techniques for assessing environmental risks in the soils whose degree of contamination is to be studied based on the toxicity of heavy metals and environmental response factors. Depending on the study of Hakanson, (1980), Ecological risk factor was calculated using the following equation and Table 3:

$E_r^i = T_r \times C_f$

Where:

E_r^i : is the Ecological risk factor.
T_r : It represents the toxic response factor for each heavy metal. C_f : is the contamination factor.

Table 3: Classification of Soils by Ecological risk factor(E_r^i))(Jiang et al., 2021)

Category	Description
$E_r^i < 40$	Low risk
$40 \leq E_r^i < 80$	Moderate risk
$80 \leq E_r^i < 160$	Considerable risk
$160 \leq E_r^i < 320$	High risk
$E_r^i \geq 320$	Very high risk

Potential Ecological Risk Index (RI)

Potential Ecological Risk Index (RI)of the studied samples was calculated due to its importance, as it is possible to estimate dangers to the environment from soil using the potential ecological risk index (RI). To determine the potential ecological danger associated with a polluted site, a detailed assessment must be performed(Tisha et al., 2020). RI was determined according to the findings of Hakanson, (1980),study using the following equation :

$RI = \sum E_r^i$ Where:
RI: is Potential Ecological Risk Index.
E_r^i : is the ecological risk factor.

Table 4: Classification of Soils by Potential Ecological Risk Index (RI)(Kang et al., 2020).

Category	Description
RI < 150	Low risk
150 ≤ RI < 300	Moderate risk
300 ≤ RI < 600	Considerable risk
RI ≥ 600	High risk

Results and Discussion

Total and bioacccessbility of Heavy metals

The mean concentrations of total and bioaccessibility of heavy metals in the agricultural land of the Qadisiyah Governorate from all the sites are presented in Table (6, 7). It is notified that some metals such as nickel (Ni) and chromium (Cr) were the high pollution levels in the soil followed by Zn, Cu, Pb and Cd, it has shown that agricultural soil in the Qadisiyah Governorate was significantly contaminated as compared with average shale (Turekian & Wedepohl, 1961).

The results of relative bioaccessibility of heavy metals in agricultural soils in the current study showed that the values ranged from (10.79%) to (67.52%) for chromium (Table 2). The results of relative bioaccessibility for Cd and Pb (67.33%, 47.74%) respectviely have showed a high in the soil, while the rest of the metals, such as zinc, chromium. copper and nickel showed the results of the relative bioaccessibility to have a low value (27.98%; and 7.74%, 10.79%, 18.68% and 19.3%) respectively in the different sites of agriculture soil. Becuase the concept of bioaccessibility has not been studied in the soils of Iraq in general and the soils of the city of Al-Qadisiayh in particular, the results of the current study for the metals that had critical results (cadmium and lead) which are compared with the results of international studies such as bioaccessibility of cadmium is close to the extent of bioaccessibility Cadmium (53.3 to 76.9%) reported by Juhasz et al. (2010) in some Chinese soils as well as the bioaccessibility of cadmium for the study of Kadhum et al.(2017),which was conducted on the sediments of Langat River, Malaysia (17.9 to 55.3%), and the bioaccessibility of lead (47.36%) was close to bioaccessibility range (37.8–66.4%) for lead reported by Juhasz et al.(2009). The largest value of the relative bioaccessibility of cadmium was found in Afak (82.22%), and the lowest value (30.24%) in the city of Shamiya. As for lead, it reached the highest value of relative bioaccessibility (76.14%) in Ghamas, while the lowest value wase (32.5%) in Afak, while the rest of the elements (Zn, Ni, Cr and Cu) showed the results of bioaccessibility to close proportions in all study area. The results of the bioaccessibility of heavy metals in agricultural soils for the current study showed the following order: Cd > Pb > Zn > Ni > Cu > Cr.

Table 6: Total heavy metals concentrations in agriculture soil of Qadisiyah Governorate (Kazim and Kadhum, 2022).

Metals	Units	Min	Max	Mean	SD	Var	A.V[a]
Cd	Mg/kg	0.61	1.57	1.17	0.39	0.18	0.30
Cr	Mg/kg	108.98	140.50	124.50	13.08	171.1	90
Ni	Mg/kg	170.51	233.96	189.99	21.37	533.02	68
Zn	Mg/kg	44.40	58.36	50.18	5.45	34.67	95
Cu	Mg/kg	32.64	46.81	36.90	5.14	30.82	45
Pb	Mg/kg	20.58	52.30	35.25	11.21	146.76	20

Table 7: The relative bioaccessbility (%) and bioaccessbility (mg/kg) of the heavy metals for the study samples.

Sites	Bioaccessible (mg/kg)						Relative bioaccessible (%)					
	Cu	Cd	Cr	Ni	Pb	Zn	Cu	Cd	Cr	Ni	Pb	Zn
Shamiya	6.71	0.23	11.36	35.12	23.03	12.76	18.18	30.24	10.1	19.7	51	26.33
Sania	6.65	0.75	10.95	34.98	15.45	11.65	18.09	77.4	9.9	19.8	39.98	26.24
Hamza	8.91	0.94	13.47	40.54	18.48	14.19	20.92	78.82	10.7	21	45.97	25.84
Albdair	5.33	1.1	14.11	29.65	12.19	9.63	16.33	69.83	10.9	17.2	42.49	21.2
Afak	5.71	1.49	10.15	28.27	6.69	12.55	16.12	82.22	9.31	16.6	32.5	28.26
Sumer	9.25	0.42	16.38	43.73	9.77	18.79	20.05	68.83	11.7	21.3	46.07	33.98
Ghamas	9.86	0.82	18.61	45.66	39.83	19.87	21.06	63.99	13	19.5	76.14	34.04
Mean	7.489	0.82	13.58	36.85	17.92	14.21	18.68	67.33	10.8	19.3	47.74	27.98

Pollution Indices

In order to assess the level of pollution in agricultural soils for some areas of Al-Qadisiyah Governorate, pollution indicators were used to serve this purpose.

Contamination Factor (CF)

The results of the pollution factor for agricultural soils in Al-Qadisiyah Governorate, according to classification of (Hakanson, 1980) Table 2, ranged from light pollution to strong pollution, where CF of Zn (0.82) and Cu (0.52) showed light pollution in all study areas. The results of the study also showed that all studied areas were moderately polluted for Pb (1.7627) and Cr (1.3834). Moreover, The result of Ni in agricultural soils found the moderate degree of pollution in some sites such as Shamiya , Sania , Hamza , Albdair, and Afak ,while it was highly polluted in the Sumer and Ghamas regions. For Cadmium, the results were showed a variation in the level of pollution in the soil, as it ranged from moderate pollution, as in sites of Shamiya and Sumer, to high pollution, as in some sites, such as Sania, Hamza, Albdair and Sumer, the highest value of Cd (6.041) pollution according to CF was in Afak city which indicates that it is extremely contaminated soils. The reason for the contamination of these soils with Cd and Pb may be attributed to agricultural practices such as the use of chemical fertilizers represented by basic fertilizers such as (NPK), and these fertilizers are usually accompanied by heavy metals such as Cd and Pb as impurities, and with the repeated use of these compounds, may accumulate Cd and Pb in the soil. In addition to the entry of Cd and Pb into the composition of phosphate fertilizers, which accumulates in the soil during repeated use (Sumner, 2000). Also vehicle exhaust and fuel combustion emissions, as well as random waste dumping sites near polluted agricultural lands, all factors observed during sample collection helped to increase the concentration of heavy metals in agricultural soils such as (Cd, Ni, Pb, Cu, Cr and Zn).

Table 8: the contamination factor, as well as the pollution load index of heavy metals contamination in sampling locations.

Sity	CF Cu	Cd	Cr	Ni	Pb	Zn	PLI
Shamiya	0.7689	2.535	1.2531	2.6182	2.2577	0.5102	1.3949
Sania	0.766	3.2301	1.2289	2.5947	1.9323	0.4674	1.3872
Hamza	0.8875	3.9751	1.3997	2.8372	2.0099	0.5781	1.592
Albdair	0.6801	5.2508	1.4415	2.5363	1.4345	0.478	1.441
Afak	0.7378	6.041	1.2109	2.5076	1.0291	0.4675	1.3665

Sumer	0.9611	2.0339	1.5611	3.0234	1.0603	0.582	1.3363
Ghamas	0.9753	4.2712	1.5886	3.4406	2.6154	0.6144	1.822
Mean	0.8252	3.9053	1.3834	2.794	1.7627	0.5282	1.4771

Pollution load index (PLI)

The results of the pollution load index in the agricultural soils of the study area were more than one, which considered as baseline pollution in all sites where the largest value of PLI appeared in Ghamas sity and its lowest value was in Sumer sity. Classification of (Tomlinson et al., 1980), places these areas within the scope of the polluted areas. Therefore, these areas need more attention and awareness to reduce pollutants, being agricultural areas that are considered a source of food for the human being living in these areas and even neighboring areas.

Geo-accumulation index (Igeo)

The results of the index of the Geo-accumulation of heavy metals in the study area, based on the classification of Muller,(1979) (Table 1), showed that the agricultural soils of Al-Qadisiyah Governorate graded from unpolluted areas to medium to highly polluted areas where, as shown in the Table 9, that all study areas appeared to be unpolluted with Zn and Cu, which fell within category (0), while Pb and Cr fell between two categories (0,1) as some areas such as Shamiya ,Sania, Albdair and Afak were unpolluted(class 0) with Cr, while Sumer and Ghamas were unpolluted to moderately polluted (class1), for Pb was areas such as Albdair, Afak and Sumer not contaminated (class 0), and other areas such as Shamiya, Sania, Hamza and Ghamas belong to class (1), which indicates that they are not polluted to moderately polluted, while Cd results showed that it fell within classes (1,2, 3) as the areas of Shamiya and Sumer fall into class (1), which indicates that they are unpolluted to moderately polluted, while the areas of Sania, Hamza and Albdair fall into class (2), which indicates that they are moderately polluted, while Afak area fell within Classification (3) which indicates it is a moderate to strong pollution area. The evidence of gathering for the element cadmium is an affirmation that the human sources that polluted most of the agricultural soils in Al-Qadisiyah Governorate with this metals as a result of excessive agricultural practices such as the use of fertilizers and pesticides in addition to irrigation with contaminated water, and that the contamination of land helped not to adopt any sample as a reference sample because of Humanitarian intervention that leads to a change in the quality of the soil, so it relied on the concentration of heavy elements in the earth's crust as reference values Turekian & Wedepohl, (1961), as the result of the geochemical pool coefficient for the current study took the following order: Cd > Ni > Pb > Cr > Cu > Zn.

Table 9: Geo-accumulation index (Igeo) with its classes to samples of study area.

Sity	Igeo						Igeo Class					
	Cu	Cd	Cr	Ni	Pb	Zn	Cu	Cd	Cr	Ni	Pb	Zn
Shamiya	-0.96	0.757	-0.259	0.804	0.59	-1.5	0	1	0	1	1	0
Sania	-0.97	1.107	-0.288	0.791	0.365	-1.7	0	2	0	1	1	0
Hamza	-0.75	1.406	-0.1	0.92	0.422	-1.4	0	2	0	1	1	0
Albdair	-1.14	1.808	-0.057	0.758	-0.06	-1.6	0	2	0	1	0	0
Afak	-1.02	2.01	-0.309	0.741	-0.54	-1.7	0	3	0	1	0	0
Sumer	-0.64	0.439	0.0576	1.011	-0.5	-1.4	0	1	1	2	0	0
Ghamas	-0.62	1.51	0.0828	1.198	0.802	-1.3	0	2	1	2	1	0

Ecological risk factor (E_r^i) and Potential Ecological Risk Index (RI)

The results of the study showed that the index of potential environmental risks (E_r^i) for heavy metals for agricultural soils were presented in Table 10, which ranged from low to moderate risks based on classification (Hakanson, 1980; Jiang et al., 2021) Table 3. It was found that all elements except for Cd fall within the category E_r^i < 40, which indicates that these elements are of low risk in all areas of the study, while the potential ecological risk of cadmium falls within the category (40−80) in the regions of Shamiya and Sumer, which refers to the Moderate potential ecological risk and for the rest of the regions, such as Sania, Hamza, Albdair and Afak E_r^i for Cd fell into the category (80−160), which indicates a Considerable potential ecological risk. Thus, Cadmium, which is considered one of the elements dangerous to human health, and which causes many health problems, ending with cancerous diseases, and which reaches humans through the food chain, therefore, the use of sources of this element must be reduced. As for the ecological risk index (RI) for the study areas (Table 4-6), it was found that some areas such as Shamiya, Sania and Sumer fall within the category of low ecological risk (RI<80) according to the classification shown by (Kang et al., 2020). (Table 3-7), as for the RI for the rest of the regions, which are Hamza, Albdair, Afak and Ghamas, they fell within the category (150−300), which indicates Moderate potential ecological risk. According to the classification Kang et al. (2020), Table 4, the RI of heavy metals for the seven studied areas are graded as follows:

RI (Afak)>RI (Albdair) >RI (Ghamas) >RI (Hamza) >RI (Sania) >RI (Shamiya) >RI (Sumer)

Table 10: Ecological risk factor (E_r^i), and Potential Ecological Risk Index (RI) of heavy metals of samples collected from the study area.

				E_r^i			
Sites	Cu	Cd	Cr		Ni	Pb	RI
	Zn						
Shamiya	3.84	76.05	2.51	13.09	11.29	0.51	107.3
Sania	3.83	96.9	2.46	12.97	9.662	0.47	126.3
Hamza	4.44	119.3	2.8	14.19	10.05	0.58	151.3
Albdair	3.4	157.5	2.88	12.68	7.172	0.48	184.1
Afak	3.69	181.2	2.42	12.54	5.145	0.47	205.5
Sumer	4.81	61.02	3.12	15.12	5.301	0.58	89.94
Ghamas	4.88	128.1	3.18	17.2	13.08	0.61	167.1
Maen	4.13	117.2	2.77	13.97	8.814	0.53	147.4

Conclusion

The objective of this study was to assess the total and bioaccessibility of six metal concentrations in agricultural soils. The results found those mean concentrations of Ni and Cr were higher than average shale. The results showed the highest value of relative bioaccessibility of Pb in Ghamas, while the largest value of the relative bioaccessibility of Cd was found in Afak. These Elements (Pb and Cd) may impact the integrity of agricultural production in the soil of Qadisiyah Governorate as well as human health. The pollution load indices found in agricultural soils of Al-Qadisiyah Governorate ranged from light pollution to high pollution so the highest pollution values were for cadmium, especially in three sites (Afak, Albdair and Ghamas). The potential ecological risk index (E_r^i) found that the studied agricultural soils were within the low-risk range for five heavy metals (Cu, Cr, Ni, Pb and Zn), while the soils were suffering from a Considerable risk for Cd. Thus, it is necessary to pay attention to these elements in the future. These results will be useful to develop appropriate solutions in order to reduce the increase of heavy elements in Iraqi soils, especially Al-Qadisiyah Governorate

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