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Assessment of Potential Environmental Risks of Some Heavy Metals in Agricultural Soils within Dubz District, Lower Zab River Basin, Northeastern Iraq

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Abstract

Fifty-three agricultural soil samples have been collected within the boundary of Dubz District, Lower Zab River Basin, Northeastern Iraq, between latitudes 35°30'0''–35°50'0'' N and longitudes 43°48'41''–44°16'6'' E. This study focuses on determining the concentration values and distributions of Co, Cu, Ni, Cr, Zn, Cd, Pb, As and Mn using the ICP-MS analytical technique to assess the environmental influences of these metals in soil samples by several pointers including the contamination factor (Cf), degree of contamination (Cdeg), potential ecological risk (Er), risk index (RI), toxic units (TUs) and the adverse effect index (AEI). The findings indicate that the values of these metals are arranged in descending order as follows: Mn> Ni> Cr> Zn> Cu> Co> Pb> As> Cd > Co > Cu > Zn > Pb > Cd > Ni > Cr > Mn > As. Except for As and Cd, the majority of the elements have values lower than the Earth's crust average. The level of Co, Cr, Ni, Cu, Zn, Pb, and Mn contamination is low, whereas the contamination level of Cd is moderate, and As is considerably contaminated. Based on the results of ecological risk and potential risk index (RI), heavy metals indicate a low ecological risk of these metals in all collected soil samples. Depending on the values of the Adverse Effect Index (AEI) for Ni, Cr, Cu, and Mn, most of the studied agricultural soil samples indicate a probable effect on biota due to the concentration of these metals being high enough to affect the organisms negatively. Whereas the total toxic units (∑TUs) for all the sites indicate that the depositional and behavioral forms in the studied soils indicate a moderate toxicity of heavy metals to the ecosystem.

Keywords:

Heavy element, Pollution, Environmental Risk, Agricultural Soil, Kirkuk.

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1. Introduction

Agricultural soil is a vital natural resource that directly contributes to food security and environmental sustainability. However, these soils are exposed to a range of environmental challenges, most notably heavy metal pollution due to its negative impacts on soil quality, human health, and surrounding ecosystems. Soil is the basic component of urban and agricultural environments as well as human activities that take place on it. Therefore, agricultural activity and other human activities such as manufacturing, mining, and urban expansion are factors that contribute to the leaching of heavy metals into the soil. These elements include cadmium (Cd), lead (Pb), mercury (Hg), chromium (Cr), and nickel (Ni) (Ali et al., 2021; Rifat et al., 2024). These elements can accumulate in soil from various sources such as contaminated irrigation water, the use of chemical fertilizers and pesticides, and industrial waste. The accumulation of these elements in soil changes its physical and chemical properties, affecting the productivity and growth of crops. These pollutants also move through the food chain, posing a risk to human and animal health. Therefore, understanding the level of pollution, its causes, and its effects is an essential step in developing sustainable soil management strategies (Al-Jubοury, 2009; Kozlov et al., 2022; Rifat et al., 2024).

Heavy elements are one of the environmental pollutants that spread in the environmental parts (air-water-soil). Through these parts, heavy elements are linked directly and indirectly to human and animal health through their effect on the growth of plants that living organisms feed on. The importance of pollution with heavy elements in nature results from the inability to decompose their nuclei, unlike other chemical pollutants. Their decomposition due to a number of environmental factors such as heat, humidity, sunlight, or biological factors often leads to a reduction in their toxicity. The increased accumulation of elements in the soil is toxic to humans, plants, and animals. Also, long-term exposure to heavy elements leads to many health problems depending on the type of metal and the amount to which the person was exposed (Rifat et al., 2024). Where, heavy metals are among the largest environmental pollutants, as their continued emission leads to an increase in their concentrations in the soil. They include a large group of them, some of which are important to humans, such as iron and copper, and some of which are toxic to living things. Heavy metals are characterized by their high specific gravity (Kruus et al., 1991; Al-Hawi et al., 2024).

The problem of environmental pollution is one of the most serious problems of the era as a result of human exposure to many new environmental pollutants that emerged due to the tremendous development in technology, which led to the emergence of many previously unknown industrial pollutants. Natural events resulting from the parent substances or from human, agricultural, and industrial activities are among the most significant sources of heavy metal contamination in soil. These activities are related to anthropogenic inputs like the use of fertilizers, dumping, urban effluents, traffic emissions, and the long-term use of wastewater in agricultural land (Rinklebe and Shaheen, 2017; Kafle et al., 2022). Recently, many private oil and gas refineries have spread in the areas adjacent to the study area. The discharges, waste, and particulates of gases resulting from them may cause pollution of the agricultural land near them, in addition to the pollution resulting from the population expansion of the district of {on the map Dubz???} and the area of Altun Kopri and other human activities and the effect of fertilizers used in agriculture, which may add some chemical elements to the soil and change the chemical and qualitative content of these soils. Whereas the contamination by heavy metals alters some of the soil's physical and chemical properties, upsetting the essential elemental balance (Aydinalp and Marinova, 2003; Al-Sheraefy et al., 2023).

Dubz District is one of the most significant agricultural land areas of the lower part of the Lower Zab River Basin in northeastern Iraq and is characterized by vast areas of arable land along the river. Therefore, this study aims to clarify the distribution of concentration values of some heavy elements represented by Co, Cr, Ni, Cu, Zn, Cd, Pb, As, and Mn. Also, the extent of the ecological impact of heavy metals is estimated by estimating their pollution in the Dubz agricultural soil by utilizing the contamination factor, degree of contamination (Cdeg), potential ecological risk (Er), in addition to the risk index (RI), toxic units (TUs), and the adverse effect index (AEI).

2. Location and Geological Setting

The study region is represented by the agricultural lands within the boundaries of Dubz District, the lower part of the Lesser Zab River (LZR) Basin, which is situated in the northeastern part of Iraq between latitudes 35°30'0"–35°50'0" N and longitudes 43°48'41"–44°16'6" E (Fig. 1). The study region is situated between 230 and 631 meters above sea level. The LZR's catchment area is 22,250 km², and it flows 400 km till it meets the Tigris River 35 km southwest of Sharqat City (Fig. 2) (Ali, 2012). The LZR in the study area flows through numerous villages, towns, and agricultural lands where potential anthropogenic sources could impact the water quality, in addition to the natural pollution causes such as spring waters, erosion, and weathering of outcrops (Qadir et al., 2024).

The area under study is situated within the unstable shelf in the Foothill Zone of the foreland basin and related basin in Iraq; this situation is reflected in the formation of the stratigraphic characteristics of the area. The foothill zone is primarily composed of coarse detrital sediments from the upper Miocene and Pliocene, which are softly folded parallel to the structural trend of the Zagros Mountains along the NW-SE plane axis (Berry et al., 1970). The study area includes geological formations consisting of sedimentary rocks, mostly carbonate in the middle part and detritus in the lower part (Fig. 2) (Ma’ala, 2007; Sissakian, 1998). The rocks are characterized by their porosity and permeability, which allow water to penetrate through them and form water reservoirs inside those rocks. By relying on this water as a source of irrigation, the quality of the soil and its chemical content can be affected (Ali, 2012; Ali and Al-Talabani, 2018; Al-Saady et al., 2022).

3. Materials and Methods

A total of 53 agricultural soil samples were collected during November-December 2024 at 0-20 cm depth from the land cover within the boundaries of Dubz District, Lower Zab River Basin, northeastern Iraq (Table 1 and Fig. 1). In the study area, rock outcrops of Bai Hassan, Mukdadiyah, Injana, and Fatha formations that are restricted to thin soil are observed (Fig. 2) (Sissakian and Fouad, 2015). The locations of samples are determined using GPS. According to Carver (1971), after 48 hours of air drying, the soil samples were crushed in a ceramic mortar and sieved through a 63-mesh sieve. Heavy metal (Co, Cr, Ni, Cu, Zn, Cd, Pb, As, and Mn) content values were determined by powdering ten grams of soil samples using Inductively Coupled Plasma Mass Spectrometry (ICP-Mass Spectrometer) to analyze these samples in the laboratory of the Application Centre for Earth Science Research (YEBIM), Ankara, Turkey.

There are a variety of techniques and indicators utilized to thoroughly evaluate the extent of heavy metal contamination and ecological hazards in soil and sediment, which are considered significant in determining the grade of soil or sediment pollution with these substances (Al-Manssory et al., 2004) such as the contamination factor, contamination degree, potential ecological risk index (RI), toxic units (TUs) and the adverse effect index (AEI), with a view to differentiating the natural and anthropogenic provenance of ecological pollution as well as estimating the heavy elements richness and the contamination level of the soils.

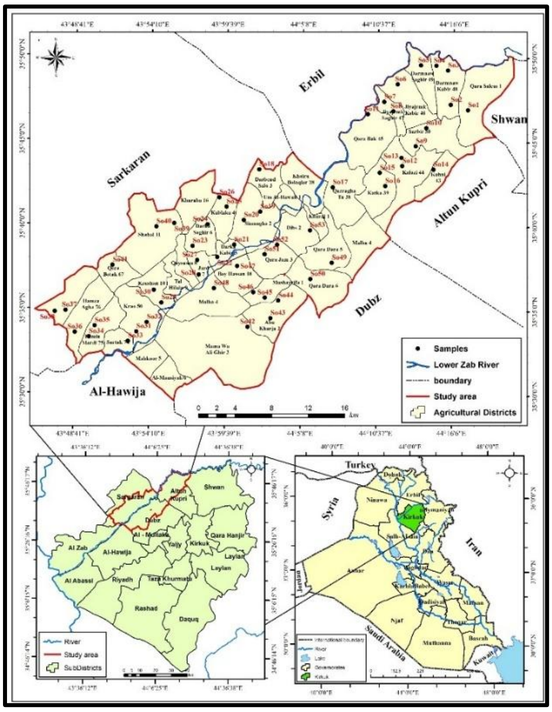

Fig. 1: Sampling sites on the location map.

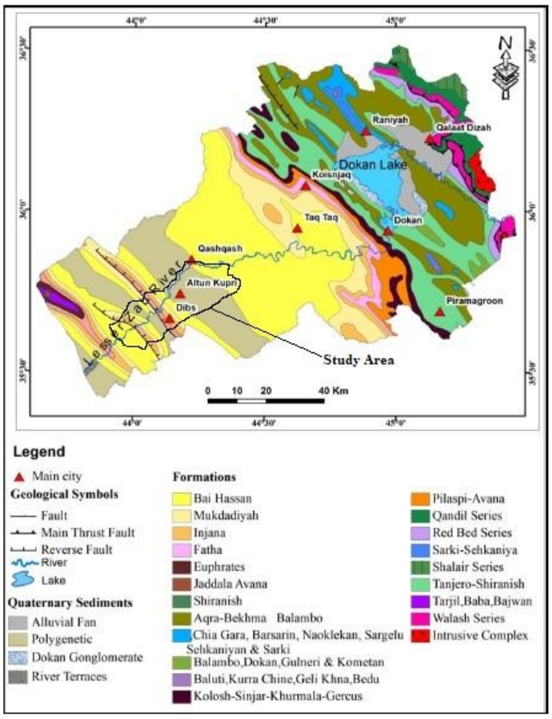

Fig. 2: Geological map showing the study area (Sissakian and Fouad, 2015).

Table 1: Coordinates of studied agricultural soil samples.

Sample No	Longitude	Latitude	Description A sample has been collected from:
SO1	44°14'51.447"E	35°46'17.107"N	Agricultural land
SO2	44°16'21.384"E	35°45'57.276"N	Agricultural land
SO3	44°15'22.897"E	35°49'31.729"N	Agricultural land
SO4	44°14'9.862"E	35°49'51.509"N	Agricultural land
SO5	44°13'37.906"E	35°49'32.335"N	Agricultural land near a sand washing plant.
SO6	44°12'2.038"E	35°48'31.619"N	Agricultural land
SO7	44°10'48.539"E	35°48'6.054"N	Agricultural land
SO8	44°11'10.908"E	35°46'58.946"N	Agricultural land
SO9	44°13'28.639"E	35°44'33.652"N	Agricultural land near traffic roads.
SO10	44°14'8.628"E	35°45'50.486"N	Agricultural land near traffic roads and residential areas.
SO11	44°9'48.568"E	35°46'40.163"N	Agricultural land
SO12	44°12'24.649"E	35°43'35.764"N	Agricultural land near residential areas.
SO13	44°12'20.794"E	35°44'5.028"N	A sample was taken from agricultural land
SO14	44°14'41.777"E	35°43'23.851"N	Agricultural land near a livestock barn
SO15	44°11'44.293"E	35°43'12.824"N	Agricultural land
SO16	44°11'27.758"E	35°42'48.64"N	Agricultural land near traffic roads.
SO17	44°7'22.483"E	35°42'17.91"N	Agricultural land near residential areas.
SO18	44°1'48.547"E	35°43'42.863"N	Agricultural land near an oil refinery.
SO19	44°2'26.592"E	35°41'8.513"N	Agricultural land near traffic roads.
SO20	44°1'45.75"E	35°40'25.5"N	Agricultural land
SO21	44°0'15.692"E	35°38'51.5"N	Agricultural land near which there are oil pipelines.
SO22	43°59'2.602"E	35°38'6.857"N	Agricultural land
SO23	43°59'26.916"E	35°41'17.419"N	Agricultural land near residential areas.
SO24	43°58'19.445"E	35°40'2.824"N	Agricultural land near an oil refinery.
SO25	43°57'29.383"E	35°42'10.84"N	Agricultural land near traffic roads.
SO26	43°59'29.688"E	35°42'26.204"N	Agricultural land
SO27	43°57'35.086"E	35°37'55.639"N	Agricultural land near traffic roads.
SO28	43°56'53.545"E	35°37'34.561"N	Agricultural land
SO29	43°54'43.283"E	35°35'6.911"N	Agricultural land
SO30	43°54'29.851"E	35°34'36.304"N	Agricultural land near traffic roads.
SO31	43°53'13.474"E	35°33'39.856"N	Agricultural land
SO32	43°53'58.499"E	35°34'13.544"N	Agricultural land
SO33	43°46'12.792"E	35°33'5.836"N	Agricultural land near traffic roads.
SO34	43°49'31.177"E	35°33'35.838"N	Agricultural land
SO35	43°49'31.523"E	35°33'36.4"N	Agricultural land
SO36	43°48'46.098"E	35°33'36.011"N	Agricultural land near residential areas.
SO37	43°48'4.9"E	35°34'53.645"N	Agricultural land
SO38	43°47'18.107"E	35°34'48.958"N	Agricultural land
SO39	43°55'54.116"E	35°40'6.082"N	Agricultural land near residential areas.
SO40	43°54'36.274"E	35°39'53.611"N	Agricultural land near which there are oil pipelines.
SO41	43°53'40.535"E	35°39'4.813"N	Agricultural land
SO42	44°1'17.285"E	35°33'59.749"N	Agricultural land located near military bases.
SO43	44°2'48.106"E	35°35'0.193"N	Agricultural land
SO44	44°2'26.106"E	35°35'34.091"N	Agricultural land near traffic roads.
SO45	44°1'54.926"E	35°36'9.367"N	Agricultural land near a livestock barn and residential areas.
SO46	44°14'20.076"E	35°36'19.289"N	Agricultural land near which there are oil pipelines.
SO47	44°0'22.507"E	35°37'47.294"N	Agricultural land near a traffic road and a waste dump, and an oil refinery station is located nearby.
SO48	43°59'29.119"E	35°36'58.889"N	Agricultural land near traffic roads.
SO49	44°7'21.209"E	35°37'50.25"N	Agricultural land
SO50	44°7'16.244"E	35°37'49.926"N	Agricultural land
SO51	44°2'42.137"E	35°38'56.339"N	Agricultural land near residential areas close to the river bank.
SO52	44°3'32.432"E	35°39'10.876"N	Agricultural land near the river bank.
SO53	44°5'45.208"E	35°39'44.629"N	Agricultural land near residential areas.

4. Results and Discussion

A. Distribution of heavy metals

Understanding the mobility and distribution of heavy elements in various ecosystems requires an understanding of statistics. Therefore, the values are descriptive for the analyzed heavy metals, including the standard deviation, coefficient of variation (C.V.), arithmetic mean, and maximum and minimum values. They are calculated in order to determine the overall variability of heavy metal distribution in the agricultural soil of the studied sites in the Dubz district (Table 2).

The spatial distribution of heavy elements in soil and sediments is a significant subject for a variety of environmental, climatic, and public health reasons (Aghababaeian et al., 2021), where the upward dispersion and transport of elements are affected by the organic components and clay mineral content in soil (Ali et al., 2021; Al-Sheraefy et al., 2023; Rifat et al., 2024).

The heavy metal concentration values, in general, diverge by 19 to 50% for soil samples and are arranged in descending order: Co > Cu > Zn > Pb > Cd > Ni > Cr > Mn > As> Mn> Ni> Cr> Zn> Cu> Co> Pb> As> Cd. The coefficient of variation (C.V.) is significantly (40 < C.V. < 50%) for Cu and Co, (30 < C.V. < 40%) for Cr, Ni, Cd, Pb, and Zn, and is within 20% for As and Mn (Table 2). These results indicate that the values of the coefficient could have been influenced by external parameters like anthropogenic activities (Al-Dulaimi and Al-Mallah 2024; Kareem et al., 2024).

Hence above, the findings show that the mean concentration values of Co, Cr, Ni, Cu, Zn, Pb, and Mn are 16.81, 72.33, 73.89, 23.56, 44.07, 10.56 and 565.65 ppm respectively throughout each of the soil samples, which are lower than their rate values recorded for the earth's crust, except for Cd (0.30 ppm), and As (5.66 ppm) is greater in all present study samples than the earth crust rate values (Table 2) (Mason, 1982). The majority of naturally occurring soils have low levels of arsenic, but industrial effluents, pesticides, phosphate fertilizers, and atmospheric deposition can contribute significant amounts of arsenic to the soil (Dehghani et al., 2017; Al-Sheraefy et al., 2023; Rifat et al., 2024).

The existence of cadmium is related to several factors, including the accumulation of waste piles that are primarily burned on-site for disposal, the combustion of fuel derivatives containing some heavy elements like cadmium, the frequent spread of generators, batteries, and electronic panels, and increased traffic density as well, which increases the friction of automobile tires with the ground (Saeedi et al., 2013). High values of cadmium concentrations may be attributed to the combustion of products derived from petroleum containing cadmium, such as kerosene, welding materials, and diesel oil (Boutron and Wolff, 1989). During the most recent war (2014–2017), the deposition of air pollutants and the large usage of weapons and ammunition that went along with it both contributed to a rise in the content of arsenic and cadmium in the soil (Vandana et al., 2011; Lidija et al., 2018; Al-Sheraefy et al., 2023). In addition to phosphate fertilizers, detergents, and sewage sludge, cadmium is emitted from nickel/cadmium (Ni/Cd) batteries and polymers that include pigments and stabilizers for cadmium compounds.

According to Mason (1982), the high levels of concentration of Co, Cr, Ni, Zn, and Pb in a portion of the soils are greater than those in the earth's crust, as shown in Table 2. The increased concentration values of these elements in agricultural soil samples within the study area are caused by improper use of chemical fertilizers, use of inappropriate methods of wastewater disposal, as well as the effect of wind in transporting pollutants and increasing their value in the surface soil (Vandana et al., 2011). Lead pollution is on the rise due to industrial processes like burning lead-containing fuel, making lead-acid batteries, and degrading paint, which can contaminate nearby groundwater used for irrigation, resulting in elevated lead (Pb) levels found in some of the soil samples under study (Table 2) (Rawat and Katiyar, 2015; Kumar et al., 2020).

Table 2: Heavy metal concentrations in the studied agricultural soils.

Element	Co	Cr	Ni	Cu	Zn	Cd	Pb	As	Mn
SO1	11.68	51.98	35.62	10.14	45.85	0.12	9.08	4.6	505.33
SO2	7.35	52.36	52.94	10.55	26.49	0.11	4.57	4.7	426.38
SO3	16.61	107.35	104.29	21.28	55.17	0.35	12.09	5.3	502.39
SO4	19.33	118.29	128.37	25.19	85.66	0.42	14.08	7.4	519.33
SO5	9.45	92.38	78.14	14.19	32.18	0.19	7.26	4.6	324.19
SO6	11.29	72.88	80.08	16.55	33.21	0.11	5.26	5.8	630.19
SO7	21.08	92.58	89.25	22.29	49.81	0.33	10.13	7.4	721.11
SO8	26.62	107.08	134.58	31.14	56.29	0.41	17.58	7.4	736.29
SO9	10.36	56.39	78.29	15.66	35.69	0.37	15.22	4.8	699.34
SO10	10.28	52.39	75.44	13.99	32.58	0.35	13.74	4.6	578.19
SO11	9.28	48.25	62.38	12.47	30.22	0.32	12.78	4.6	488.74
SO12	20.69	50.33	66.78	13.28	34.59	0.37	14.08	5.1	508.39

Element	Co	Cr	Ni	Cu	Zn	Cd	Pb	As	Mn
SO13	18.92	50.14	66.56	13.08	34.08	0.37	13.88	4.9	500.17
SO14	14.72	49.28	53.19	12.77	52.39	0.41	15.07	5.2	510.39
SO15	9.88	39.67	34.19	10.52	27.88	0.34	10.33	4.9	708.19
SO16	10.66	55.98	35.62	15.14	45.39	0.12	7.08	4.7	505.33
SO17	13.58	48.69	32.59	13.29	38.91	0.28	9.24	5.3	512.39
SO18	9.54	64.28	60.71	11.63	36.24	0.15	4.98	4.6	350.71
SO19	10.95	96.11	75.12	14.12	34.63	0.24	5.49	5.8	515.16
SO20	16.32	112.25	60.89	15.32	39.37	0.35	4.76	7.5	614.24
SO21	15.22	98.33	55.37	15.12	27.97	0.35	3.87	7.2	578.55
SO22	13.28	87.25	35.95	13.27	25.63	0.22	3.55	5.7	592.37
SO23	11.49	92.62	76.89	18.14	40.22	0.34	6.16	5.6	514.47
SO24	35.77	105.55	123.28	38.17	55.36	0.54	18.22	5.2	775.33
SO25	10.95	96.11	75.04	13.99	34.62	0.21	5.66	4.7	321.72
SO26	11.05	88.75	72.89	14.23	35.52	0.32	8.21	4.7	422.89
SO27	21.92	96.74	120.54	37.71	41.51	0.42	9.47	4.6	762.19
SO28	10.11	82.45	91.45	22.39	36.23	0.32	9.27	6.9	802.14
SO29	11.25	85.66	91.98	25.74	38.41	0.35	10.37	5.8	642.36
SO30	25.62	75.52	54.18	34.99	40.11	0.37	12.33	7.4	647.11
SO31	18.16	63.18	53.24	30.24	36.27	0.33	10.08	7.4	635.69
SO32	22.44	70.02	55.11	40.22	38.74	0.35	11.39	4.8	598.63
SO33	26.77	71.28	62.47	42.19	39.99	0.32	14.38	4.6	556.49
SO34	23.44	68.11	60.74	33.87	28.47	0.22	11.12	4.6	552.39
SO35	16.57	50.36	57.81	28.97	28.11	0.12	10.39	5.1	438.19
SO36	10.52	50.24	54.21	25.47	25.22	0.12	10.09	7.6	782.31
SO37	7.33	48.78	53.8	10.52	23.17	0.13	8.93	6.8	270.01
SO38	9.52	49.77	51.22	10.23	20.74	0.12	5.61	7.4	321.32
SO39	10.49	85.62	79.89	16.14	39.22	0.34	5.96	5.6	508.47
SO40	32.17	95.66	95.58	36.18	40.31	0.31	6.18	4.5	728.39
SO41	16.55	49.23	62.19	28.19	35.11	0.28	5.69	7.2	625.28
SO42	28.14	50.55	88.29	32.72	65.48	0.38	14.38	5.2	745.19
SO43	8.29	16.28	70.22	25.15	55.19	0.32	14.95	6.7	774.19
SO44	10.58	38.29	83.19	30.14	55.14	0.12	15.87	4.9	805.65
SO45	23.19	66.75	98.29	34.19	62.12	0.35	16.22	6.5	642.18
SO46	35.26	97.43	102.44	40.19	79.74	0.42	15.66	4.7	788.29
SO47	42.09	105.25	153.29	42.88	82.19	0.42	17.72	5.2	755.87
SO48	36.19	47.39	77.49	35.11	77.19	0.37	13.47	4.8	557.12
SO49	14.29	59.29	80.19	40.55	80.24	0.41	14.44	4.7	589.44
SO50	10.52	73.29	79.19	37.66	79.82	0.4	12.27	5.8	433.42
SO51	20.14	75.39	66.79	37.18	68.79	0.32	10.99	7.6	327.18
SO52	8.23	91.29	52.78	21.14	33.19	0.28	10.35	6.5	307.87
SO53	14.56	82.39	75.29	23.17	38.95	0.27	9.75	4.7	320.19
Minimum	7.33	16.28	32.59	10.14	20.74	0.11	3.55	4.5	270.01
Maximum	42.09	118.29	153.29	42.88	85.66	0.54	18.22	7.6	805.65
Average	16.81	72.33	73.89	23.56	44.07	0.30	10.56	5.66	565.65
SD	8.47	23.35	25.90	10.60	16.98	0.11	4.02	1.09	149.89
CV	50.37	32.28	35.05	44.98	38.54	35.18	38.05	19.25	26.50
Average Crust	25	100	75	55	70	0.2	13	1.8	950

B. Evaluation of Soil Pollution

Contamination Factor and contamination degree

Assessing soil pollution is pivotal to understanding the extent of environmental contamination and its possible impact on ecosystems and human health (Rifat et al., 2024). Widely used indicators to evaluate contamination levels in soil sediments are the contamination factor and the contamination degree.

The contamination factor is a quantitative measure that expresses the proportion of the value of a specific contaminant in the soil to its baseline or background value. It offers evidence on the degree of pollution or enrichment brought on by particular pollutants. The cumulative contamination effect of several contaminants within soil and sediments is assessed by the Degree of Contamination (Cdeg), an aggregated metric. According to Hakanson (1980), the following formulas (equations 1 and 2) are used to determine the contamination factor and the degree of contamination:

$$Cf = \frac{(Csm)sample}{(Cbg)background} \qquad (1)$$

$$Cdeg = \sum_{i=1}^{n} Cf \qquad (2)$$

Where: *Csm* refers to the values of metal concentrations in the study soils, and *Cbg* refers to these elements' background value, which is the mean value for the upper earth crust (Mason, 1982); *n* refers to the number of elements analyzed in the study area.

Depending on Hakanson (1980) and Mekky et al. (2019), the contamination factor and the degree of contamination are classified into four categories as explained in Tables 3 and 4, respectively.

Table 3: Values of contamination factor levels.

Contamination Factor level	Value of Contamination
Low contamination	< 1
Moderate contamination	1≤3
Considerable contamination	3≤6
Very high contamination	>6

Table 4: Classification of contamination degree index (Cdeg) (Hakanson, 1980).

Contamination level	Contamination index value
Low pollution factor	$C_{deg} < 8$
Medium pollution factor	$16 \leq C_{deg} < 8$
High pollution factor	$16 \leq C_{deg} < 32$
Very high pollution factor	$C_{deg} \geq 32$

Table (5) and Figure (3) exhibit the measurements of the heavy metal contamination factor in the research area, which is located within Dubz district, Lower Zab River Basin, northeastern Iraq. In the studied sites, the findings indicate that the detected heavy metal contamination factor falls in the following order: As > Cd > Ni > Pb > Cr > Co > Zn > Mn > Cu. The level of Co, Cr, Ni, Cu, Zn, Pb, and Mn contamination is low, while the level of Cd contamination is moderate. However, the findings also refer to the fact that the studied samples are considerably contaminated with arsenic. The contamination degree values are between 6.06 and 13.88, with a rate of 9.49. Generally, this means that the agricultural soil samples had low to medium levels of pollution, as shown in Tables 4 and 5.

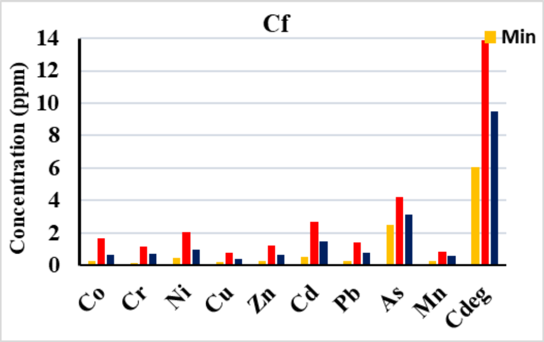

Fig. 3: Contamination factor and contamination degree evaluation of heavy elements in the study area.

Table 5: Calculated values of (Cf) and (Er) of heavy elements in the soil samples.

Elements	Contamination Factor		Elements	Ecological Risk (Er)	
	Range	Average		Range	Average
Co	0.29 - 1.68	0.67	Co	1.47 -8.44	3.36
Cr	0.16 - 1.18	0.72	Cr	0.33-2.37	1.45
Ni	0.43 - 2.04	0.99	Ni	2.17-10.22	4.93
Cu	0.18 - 0.78	0.43	Cu	0.92--3.90	2.14
Zn	0.31 - 1.22	0.63	Zn	0.31-1.22	0.63
Cd	0.55 - 2.71	1.51	Cd	16.5-81.00	44.86
Pb	0.27 - 1.41	0.81	Pb	1.37-7.01	4.06
As	2.51 - 4.22	3.14	As	25.00-42.22	31.44
Mn	0.28 - 0.85	0.61	Mn	0.28-0.85	0.61
Contamination Degree (Cdeg)	6.06 - 13.88	9.49	Ecological Risk Index (RI)	52.21-139.46	93.46

C. Potential Ecological Risk Index (RI)

The Ecological Risk Index (RI) is an extensively used tool for estimating and measuring the potential risks affected by heavy element content values to ecosystems. The (RI) is proposed by Hakanson (1980) and originally intended to evaluate the environmental hazards of heavy metals in sediments, especially in aquatic ecosystems. The (RI) has become a foundational framework to comprehend the impact of heavy metal pollution on ecosystems, environmental scientists, and policymakers. The ecological risk index is determined by the following equations (3 and 4):

$$Er = Cf * Ti \qquad (3)$$

$$RI = \sum Er \qquad (4)$$

Where: *Er* represents the ecological risk factor for heavy metal; *Cf* is the contamination factor; *Ti* represents the toxicity response factor related with a specific substance with values assigned as follows: As = 10, Zn = 1, Co = Ni = Pb = Cu = 5, Cd = 30, Cr = 2, Mn = 1 (Kabata-Pendias, 2011; Hakanson, 1980; Wang et al., 2019; Sojka et al., 2022).

The Ecological Risk and Potential Ecological Risk Index of heavy metals in the area under study are illustrated in Tables 4 and 10, respectively. For all studied heavy metals, the (Er) is lower than 40, and the (RI) < 150, indicating a low ecological risk of these metals in all collected soil samples under study (Tables 5, 6, and Fig. 4).

Table 6: Ecological Risk Factor (Er) and Potential Ecological Risk Index (RI) Classifications.

Potential Ecological Risk Category	Er	Risk Index Category	RI
Low potential ecological risk	Er<40	Low ecological risk	RI<150
Moderate potential ecological risk	40≤Er<80	Moderate ecological risk	150≤RI <300
Considerable potential ecological risk	80≤Er<160	Considerable ecological risk	300≤RI<600
High potential ecological risk	160≤Er<320	Very high ecological risk	RI≥600
Very high ecological Risk	Er≥320		

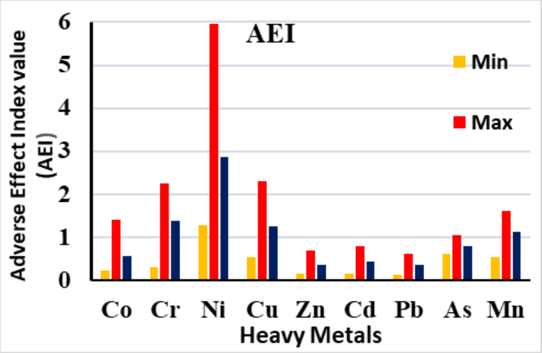

Fig. 4. Ecological risk value of heavy elements in the study area.

D. Adverse Effect Index (AEI) Assessment

The Adverse Effect Index (AEI) is a quantitative measure used in the current study to determine whether these metals can generate negative biological impacts on this soil ecosystem. By consolidating the concentrations and toxic effects of numerous heavy metals, the AEI provides a thorough indication of soil health and potential ecological risks. Thus, the AEI is measured by the following equation (5):

$$AEI = \frac{Cn}{TEl} \qquad (5)$$

Where: *Cn* is the heavy metal content in agricultural soil samples, whereas the *TEL* represents the threshold effect level (Chromium, Cr = 52.3 ppm; Arsenic, As = 7.24 ppm; Copper, Cu = 18.7 ppm; Zinc, Zn = 124 ppm; Cadmium, Cd = 0.68 ppm; Lead, Pb = 30.24 ppm; Nickel, Ni = 15.9 ppm; Cobalt, Co = 30 ppm; Manganese, Mn = 500 ppm) (CCME. 2001; Muñoz-Barbosa et al., 2012; Baraud et al., 2017; Yan et al., 2020).

According to Koukina and Lobus (2020) and Yan et al. (2020), these elements are insufficient to make a detrimental biological impact (or moderate influence is suspected) if their present values are less than 1. On the other hand, when the AEI values are more than 1, negative impacts on biota are likely to happen.

Depending on the values of the Adverse Effect Index (AEI) for Ni, Cr, Cu, and Mn, most of the studied agricultural soil samples refer to a probable influence on biota because the concentration of these metals is high enough to negatively affect the organisms (Fig. 5).

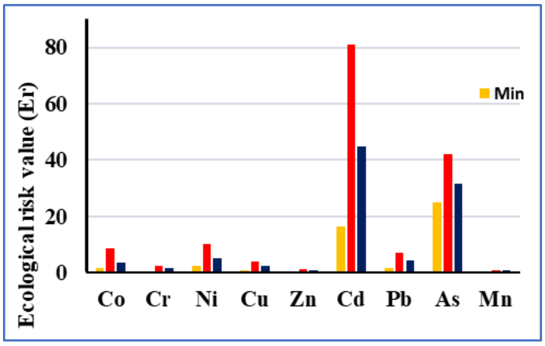

Fig. 5: Values of the Adverse Effect Index (AEI) of heavy elements in the study area.

E. Toxic Units (TUs)

The toxic units (TUs) are a very important concept in environmental science, particularly when assessing soil pollution and its possible environmental effects. The toxic units of a standardized scale for assessing the toxicity of different contaminants in soil allow for a clearer comparison of their effects on organisms and ecosystems (Landis and Yu, 2003).

The toxic units (TUs) for heavy element concentrations are measured in soil samples and determined using Equation (6):

$$TUs = \frac{Cn}{PEL} \qquad (6)$$

Where: the heavy metal value in the soil samples is denoted by *Cn*, whereas *PEL* indicates to the probable effect level for metals (Chromium, Cr = 160 ppm; Arsenic, As = 41.6 ppm; Copper, Cu = 108 ppm; Zinc, Zn = 271 ppm; Cadmium, Cd = 4.21 ppm; Lead, Pb = 112 ppm; Nickel, Ni = 42.8 ppm; Cobalt, Co = 20 ppm; Manganese, Mn= 1500 ppm) (Yan et al., 2022).

As stated by Yan et al. (2020), if the total value of toxic units (ΣTUs) is less than 4, the ecosystem toxicity is low. On the other hand, if the total value of toxic units (ΣTUs) is greater than 4, the ecosystem toxicity is moderate.

After toxic unit analysis is described, the application of the findings is implemented. The evaluation of toxic units (TUs) for the heavy metals in the Lesser Zab River basin agricultural soil based on the findings of the present study shows a decreasing trend in the order Ni > Co > Cr > Mn > Cu > Zn > As > Pb > Cd in the present study (Fig. 6). Toxic units for Ni in the studied soils are significantly higher than the toxic units of the other heavy metals at sampling points, exceeding the cumulative toxic units of Cd, Pb, and Cr. Although Ni is not harmful in general, it can have a toxic effect if it is present in excess of the safe amount (Das et al., 2023). Generally, the individual values of the calculated toxicity units for each heavy element are less than 4. Whereas the total value of toxic units (∑TUs) for all the sites is more than four (∑TUs > 4), indicating that the depositional and behavioral forms of the studied soils were exposed to moderate heavy metal toxicity and suggesting a moderate toxicity to an ecosystem (Fig. 6) (Xiao et al., 2012).

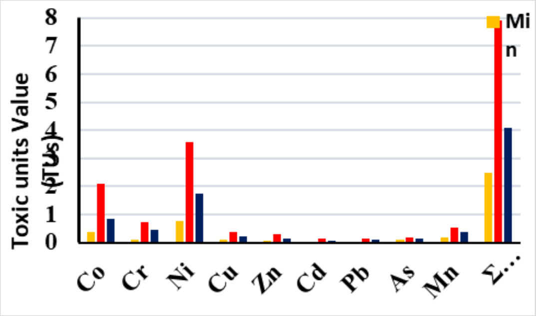

Fig. 6. Toxic units (TUs) values of heavy elements in study area.

5. Conclusion

The findings of the chemical analysis indicate that the heavy metal concentration values in agricultural soil samples are arranged as follows: Mn > Ni > Cr > Zn > Cu > Co > Pb > As > Cd, and they reveal, except for As and Cd, that the majority of the elements have values lower than the reference values representing the Earth's crust average. The evaluation of contamination by utilizing the contamination factor and degree of contamination reveals that the agricultural soils are moderate to considerably contaminated with Cd and As, respectively, and these metals have a low environmental risk in all the studied sites.

The majority of the agricultural soil samples have Adverse Effect Index (AEI) values for Ni, Cr, Cu, and Mn, which indicate a likely impact on biota because the concentrations of these metals are high enough to have an adverse effect on the organisms. Whereas the behavioral and depositional forms in the soils show a moderate toxicity of heavy metals to the ecosystem, as indicated by the total values of the toxic units (∑TUs) for all the sites.

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تقييم المخاطر البيئية المحتملة لبعض العناصر الثقيلة في الترب الزراعية ضمن قضاء دبس، حوض نهر الزاب الأسفل، شمال شرقي العراق

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الملخص

تم أخذ ثلاثة وخمسين نموذجا للترب الزراعية ضمن حدود قضاء الدبس، حوض نهر الزاب الأسفل، شمال شرقي العراق بين خطي العرض "0'35°50–"0'35°30 شمالاً وخطي الطول "6'44°16–"41'43°48 شرقاً. ركزت هذه الدراسة على تحديد قيم تركيز بعض العناصر الثقيلة (Co، Cr، Ni، Cu، Zn، Cd، Pb، As، و Mn) باستخدام تقنية التحليل ICP-MS)) البلازمي لتحديد توزيع هذه العناصر ضمن حدود منطقة الدراسة وتقييم آثارها البيئية باستخدام العديد من المؤشرات مثل عامل التلوث (Cf) ودرجة التلوث (Cdeg) والمخاطر البيئية المحتملة(Er) ومؤشر المخاطر (RI) والوحدات السامة (TUs) ومؤشر التأثير الضار (AEI) . اظهرت النتائج بأن قيم تركيز العناصر الثقيلة مرتبة تنازليا على النحو التالي: $Mn < Ni < Cr < Cr < Zn < Cu < Co < Pb < As < Cd$. وكشفت النتائج باستثناء الزرنيخ والكادميوم، بان قيم غالبية العناصر أقل من متوسط قيمها في القشرة الارضية. وتشير النتائج إلى أن مستوى التلوث بالكوبالت والكروم والنيكل والنحاس والزنك والرصاص والمنغنيز كان منخفضًا، في حين كان مستوى التلوث بالكادميوم متوسطًا، وملوثًا بشكل كبير بالزرنيخ. ووفقًا لنتائج المخاطر البيئية (Er) ومؤشر المخاطر المحتملة (RI)، فإن النتائج تشير إلى انخفاض المخاطر البيئية لهذه العناصر في منطقة الدراسة. ووفقًا لقيم مؤشر التأثير الضار (AEI) للنيكل والكروم والنحاس والمنغنيز في معظم عينات التربة الزراعية المدروسة، فانها تشير إلى التأثير المحتمل لهذه العناصر على الكائنات الحية نظرًا لكون تركيزها مرتفعًا بما يكفي للتأثير سلبًا على الكائنات الحية. في حين أن القيمة الإجمالية للوحدات السامة (∑TUs) لجميع المواقع تشير إلى أن الأشكال الترسيبية والسلوكية في الترب الزراعية للعناصر الثقيلة هي معتدلة التاثير في النظام البيئي.

الكلمات المفتاحية:

العناصر الثقيلة، التلوث، الخطر البيئي، التربة الزراعية، كركوك،

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