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QUALITATIVE ASSESSMENT OF SOIL AND SEDIMENT POLLUTION WITH SOME HEAVY METALS: A CASE STUDY OF DUHOK VALLEY IN THE KURDISTAN REGION OF IRAQ

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ABSTRACT:

The current study was conducted on the valley of Duhok and the agricultural lands irrigated from it, where three sites were identified for collecting samples quarterly from soil and sediment using clean plastic bags for the purpose of measuring lead, nickel, cobalt and copper. Pollution load index (PLI), Nemerow pollution index (PIN), Potential Ecological Risk (PER) and Geo-accumulation Index (Igeo) were also calculated according to the internationally approved methods. The results indicated that most of lead, nickel and copper concentrations in soils and sediments exceeded the limits allowed by WHO, reaching annual rates (96.758, 168.746 and 29.88) , (111.25, 219.65 and 48.162) mg.kg^{-1}, respectively. This fluctuation in concentrations was reflected in the values of the studied indicators for both soil and sediment, where 50% and 58% of the studied specimen are of the polluted grade and the remnant are of the non-polluted grade according to the PLI values. So is the case with PIN where 58% of the soil specimen and 41.6% of the sediment samples were of the severe pollution grade, while 25% and 33.3% of the specimen were of the heavy pollution grade and the remnant were slightly pollution grade. The same applies to the results of the PER index values, where 50% and 41.67% of the specimen were from the Medium ecological risk category, and the rest were from the low ecological risk category, likewise for the (Igeo) values, 100% and 96% of the soil and sediment samples were from the Weakly polluted category.

KEYWORDS: Duhok Valley., Soil and Sediment Pollution, Heavy Metal, PLI, PIN, Igeo.

1. INTRODUCTION

Heavy metals include all metallic and semi-metallic elements that have a relatively high density (five times the density of water), and are characterized by their high toxicity and lack of decomposition or damage, as well as the possibility of their entry into the human body through vegetables, meat, drinking water and air such as As, Hg, Cd, Pb, Cr, Co, Ni, Mn and Zn. Etc. Its danger comes as a result of its tendency to accumulate and biomagnify within the bodies of living organisms, which represents the increase in the concentration of chemicals (including heavy metals) in the bodies of living organisms over time compared to their concentrations in the environment in which they live (Vetrimurugan et al, 2017; El-Saadani et al, 2022; Qaseem et al, 2022a). Some of these minerals (Microelements such as Zn, Cu, Co, Mn and Fe etc.) have a necessary role in the vital processes of plants and animals when they are present in low concentrations in the environment, but it becomes toxic at high concentrations (Suresh et al. 2015; Xu et al. 2016; Billah et al. 2017). Heavy metals arise to pollute soils and bottom sediments of rivers, streams, and valleys, either naturally as a result of the processes of decomposition and erosion of rocks in the ground or through human activities (Wuana et al, 2020), such as chemical and petrochemical industries, fossil fuel combustion, agricultural activities, vehicle exhaust products, waste disposal, etc. The differences in the concentrations of heavy metals in soil and sediments depended on the size of the particles and the amount of organic matter in them, because the abundance of organic materials works to bind and deposit them. (Samy and El-Bady, 2014; Pereira et al, 2022). As for the distribution and spread of heavy metals within ecosystems, they are subject to many complex processes for the exchange of such pollutants (El-Sorogy etal, 2017). Heavy metals may also be released into the soil solution or the water that rises, bottom sediments as a result of microbial activities in the oxidation and reduction processes that lead to a decrease in the pH, except for cobalt, it is amphoteric complexes (Abdo, 2004), to be absorbed by plants and microorganisms to enter the food chain (Al-Khashman, 2012; ElSorogy etal, 2012). Which negatively affects ecosystems as a result of their ability to accumulate and bio-magnify within ecosystems (Ragi et al, 2017; Billah et al, 2017; Rakib et al, 2021).As for Duhok valley, the pollution of the bottom sediments of the valley may be caused because it is a waterway that collects most of the wastewater (civil, agricultural and industrial) through estuaries spread on its sides and municipal solid waste, as it is removed in an unscientific method and placed in open places, which causes a serious danger to the surrounding environment (Hassan and Al-barware, 2016; Hammash and Abed, 2022; Qaseem et al, 2022b). These minerals are also transferred to the agricultural soils near it as a result of irrigation operations with the water of the valley, in addition to the use of agricultural fertilizers and particles falling on them due to the burning of fossil fuels and plastic materials, and as a result of the importance of heavy metal pollution for their negative effects on plants and humans, and the lack

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of such studies in Iraq the current study investigates the heavy metal elements in the bottom sediments of the valley and agricultural soils that uses the water of the valley for irrigation with the application of some mathematical indicators to assess the quality of the soils and sediments, to take appropriate actions when needed**.**

When the concentrations of these mineral elements rise in the soil or from the bottom sediments that will be released to the surrounding environment at a low pH, which confuses the ecosystem and negatively affects the crustaceans and aquatic organisms that will accumulate in them with the possibility of their transmission to humans through the food chain, causing serious health damage at high concentrations. Such as cancerous diseases, prostate, kidney dysfunction, nervous system and heart diseases, etc. (Biswas et al, 2017; Rakib et al, 2021).

2. MATERIALS AND METHOD

2.1 Characterization of the study area

The current study was conducted on Duhok valley (which is locally called Hishkaro valley) and the adjacent lands in the Duhok Governorate in northern Iraq. This valley is one of the natural valleys to drain rainwater during the winter season, as well as sulfur springs located in the northern part of the city, also, part of the water of Duhok Dam, located north of the study area, is drained into the valley. As well as the discharge of all domestic, agricultural and industrial wastewater through many estuaries scattered on both sides of the valley to be transferred outside the city through its 25 km course to pour into the Mosul Dam lake, causing negative effects on the quality of its water. which may affect the productivity of plants and soils irrigated with valley water (Qaseem et al, 2022c). The region is characterized by a hot, dry climate in summer and cold, rainy winter with little rainfall in recent years and extreme temperatures to rise more than 53˚C in summer while dropping below zero ˚C in winter.

2.2 Methodology

All used glass and tools must be washed with 10% nitric acid solution and then rinsed with distilled water several times, and all the reagents used in the study are of high purity (Kouassi et al, 2015). After conducting a field survey, three sites were selected to collect sediment samples from the valley and the soils of farms irrigated from its water during the four seasons (at the rate of three repetitions per season for each site) starting from February 2021 until January 2022. Table (1) and Figure (1) show some characteristics of the study area.

Table (1): Characteristics of the studied sites for the collection of sediments and soil samples of Duhok valley, northern Iraq.

Sites		Altitude	Longitudes (E)	Latitudes (N)
N1	Duhok dam	607 m	40°00'09"	36°87'74"
N2	Khashman Spring[1]	523 m	42°99'38"	36.85'39"
N3	Bakhotmy	364 m	42°85'38"	36°80'86"

[1]*Near Duhok Stadium*

Where the samples are placed in polyethene bags, and then kept in a cooler box until taken to the laboratory for the purpose of air drying the samples at atmospheric temperature, then air drying them in an oven at 75° C for an hour (Chandrasekaran et al, 2014; APHA, 2017). Fine pebbles and foreign bodies are removed and the dried sediment and soil samples are smoothed using a ceramic mortar and passed through a 2 mm sieve with manual stirring for several minutes. After that, the samples are transferred to a polyethylene bag until the digestion operations are performed.

A gram of samples was weighed and transferred quantitatively to a glass beaker, in which small ceramic pieces were added to avoid cracking and losing part of the sample, then (10) ml of the digestion solution was added (acid mixture of H_2SO_4, HNO_3 and H_2ClO_4) (Balakrishnan et al, 2015), the baker was covered with a glass watch to heat the samples by placing them in a sand bath on a hotplate(in the hood), until the white and

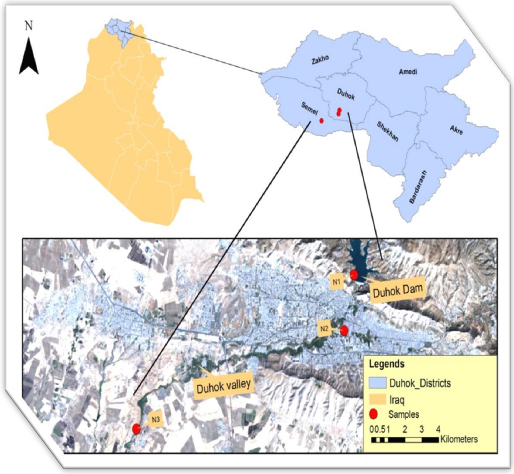

Figure (1): shows the study area and sample collection sites.

brown fumes disappear and the solution becomes clear (an appropriate amount of digestion solution is added if necessary), The samples are cooled to complete the volume to 50 ml with solution 2 % HNO_3. The concentration of metallic elements (Pb, Cu, Co and Ni) in the digested were measured using the Atomic Absorption Spectrophotometer (AAS Perkin Elmer analysis) with the use of the Blank coefficient as the samples, then the concentrations of the elements are found compared to the standard curves prepared previously and the results are expressed in $mg.km^{-1}$ dry weight. according to (APHA, 1998; 2017; Zhang et al, 2021)

2.3 Assessment status of heavy metal contamination

The state of pollution in sediments and soil for the current study determined four indices (Najamuddin et al, 2016; Hu et al, 2013):

2.3.1 The pollution load index (PLI): The pollution load index for soil and sediment is calculated for each site according to (Manea et al, 2019), as follows:

$$PLI = \sqrt[n]{\Pi\ CFn}$$

$$PLI = \sqrt[n]{CF1 \times CF2 \times \ldots\ldots\ldots\ldots \times CFn}$$

Where: n = the number of mineral elements, CF = Contamination factor which represents the proportion of the metallic element measured over the background concentration (Cf = Ci/ Bn), if the PLI value is higher than 1 it means that the samples are contaminated, and if less than

1 it means that there is no contamination in the sample, according to (Manea et al, 2019; Kouakoui et al,2021)

2.3.2 Nemerow pollution index (PIN): The general pollution of the soil represents the sedimentation with heavy metals and is calculated through the following equation (Hu et al, 2013):

$$\text{PIN} = \sqrt{\frac{(\text{PI})\text{R}^2 + (\text{PI})\text{Max}^2}{2}}$$

Where: (PI)R: is the average value of a single pollution index., (PI)Max: is the maximum value of a single pollution index, which is calculated from the ratio between the concentration of the metallic element (Ci) in the soil or sediment sample and the reference value (Si), (PIi = Ci/ Si). Therefore, soil and sediment quality are classified into five categories (Kour et al, 2022): $PI_N < 0.7$: un polluted, $0.7 < PI_N \leq 1.0$: Slightly polluted., $1.0 < PI_N \leq 2.0$ moderately polluted., $2.0 < PI_N \leq 3.0$: Severely polluted., $PI_N > 3.0$: Heavily polluted.

2.3.3Geo-accumulation Index (Igeo): The geographical accumulation index (Igeo) is calculated to assess the risks of heavy metals according to the Müller equation referred to (Najamuddin et al, 2016; Wong et al, 2017; El-Saadani et al, 2022):

$$\text{Igeo} = \text{Log}_2 \times \left[\frac{Cn}{1.5\, Bn}\right]$$

where Cn: is the measured concentration of mineral n in soils and benthic sediments, and Bn: is the value of the geochemical background of mineral n. The factor 1.5 compensates for possible fluctuations in background values of a given substance in the environment, as well as very small human influences. Müller identified seven categories for theGeo-accumulation Index (Igeo) (Chen et al, 2022):

Igeo ≤ 0 is class 1 (unpolluted)., 0 < Igeo ≤ 1 is class 2 (weakly polluted)., 1 < Igeo ≤ 2 is class 3 (moderately polluted)., 2 < Igeo ≤ 3 is class 4 (moderately to strongly polluted) ., 3 < Igeo ≤ 4 is class 5 (strongly polluted)., 4 < Igeo ≤ 5 is class 6 (strongly to extremely polluted)., Igeo > 5 is class 7 and extremely polluted.

2.3.4Potential Ecological Risk index (PERI): This index is widely used to assess the environmental parameters of heavy metals in soils and sediments (Kaue et al, 2022) and is calculated from the equations he mentioned (Kormoker et al, 2019; Wana et al, 2020):

$$\text{PERI} = \sum \text{ERf}$$

$$\text{ERf} = \text{CF}_i \times \text{Tri}$$

$$ERf = \frac{Ci}{Bn} \times Tri$$

Where, ERf: Ecological Risk factor, CFi: contamination factor of heavy metal, Ci: concentration of metal, Bn: Background Value of soil, Tri: toxicity response factor of heavy metal the toxic response factors for lead: 5, copper: 5.5, cobalt: 23 and nickel: 5 (Izah et al., 2018). The Potential Ecological Risk index (PERI) values are categorized into five classes as follows: PERI < 30: Slight risk., 30 ≤ PERI < 60: Medium risk., 60 ≤ PERI < 120: Strong risk., 120 ≤ PERI < 240 Very strong risk., 240 ≥ PERI ≥ 240: Extremely strong risk (Wuana et al, 2020).

3 RESULTS AND DISCUSSION

3.1 Heavy metals concentration in soil and sediment:

The seasonal, annual averages and the standard deviation of the four heavy metal ions concentrations in the soils of fields and farms irrigated from the waters of Duhok valley indicate that the seasonal average of lead concentration for the three sites (N1, N2, N3) were (35.76 to 122.12), (44.40 to 131.35 and (61.03 to 155.15) mg. kg $^{-1}$ respectively, while the annual rate of lead fluctuated between (32.645 ± 87.048 to 32.472 ± 97,375) mg. kg-1, as for copper, cobalt and nickel, the annual rates of the studied sites ranged between (29.88 ±5.6392 to 27.09 ±9.3635), (29.115 ±5.3607 to 32.088 ±19.119) and (111.43 ±6.8508 to 168.74 ±47.013) successively, as in table 2.

Table (2): The seasonal and annual average of heavy metal concentrations ions in the soils in the study area (mg. kg^{-1} dry weight).

Elements	Sites	Winter	Spring	Summer	Autumn	Mean	± Sd
Pb	N1	83.520	122.12	106.79	35.760	87.048	32.645
	N2	131.35	44.400	113.06	100.69	97.375	32.472
	N3	155.15	65.390	105.46	61.030	96.758	37.901
Cu	N1	35.600	35.230	25.860	22.830	29.880	5.6392
	N2	28.800	34.200	25.960	24.900	28.465	3.6051
	N3	38.930	13.770	23.830	31.830	27.090	9.3635
Co	N1	30.360	27.830	33.560	27.200	29.738	2.5038
	N2	33.930	20.100	32.130	30.300	29.115	5.3607
	N3	64.690	16.370	25.830	21.460	32.088	19.119
Ni	N1	156.82	97.020	205.25	215.88	168.74	47.013
	N2	133.42	110.59	98.620	136.12	119.69	15.694
	N3	111.32	105.92	105.82	122.65	111.43	6.8508

The presence of heavy metal elements in the soil is due to natural causes or human activities (Salem and Alwaleed, 2019), where the descending order of the elements was: Ni > Pb > Co > Cu. In general, most of the concentration rates of Ni, Pb, and Cu ions were exceeding the standard permissible limits for soils according to the WHO and US-EPA, which was referred to by Ahmed (2019). The concentration of heavy elements in the bottom sediments, depended on many factors including: the amount of organic matter, the size of the sediment particles, pH, electrical conductivity and ionic strength, as well as the discharge of various wastewater into the valley. It is noted from Table (3) that the relative high concentrations of heavy metals in the bottom sediments of the valley is a result of the high concentration of organic matter in the sediments that chelate with mineral ions, which facilitates their sedimentation (Ghrefat and Yusuf, 2006). In addition to this, the reduction processes under anaerobic conditions for some

Table (3): The seasonal and annual average of heavy metal concentrations ions in the sediments in the study area (mg. kg^{-1}).

Elements	Sites	Winter	Spring	Summer	Autumn	Mean	± Sd
pb	N1	43.362	69.226	56.994	63.994	58.394	9.7032
	N2	77.959	132.82	67.893	91.536	92.508	24.718
	N3	113.36	101.86	94.991	134.79	111.25	15.092
Cu	N1	20.898	29.697	24.598	31.364	26.639	4.1473
	N2	17.498	71.526	43.296	60.327	48.162	20.358
	N3	26.597	29.830	45.895	12.665	28.747	11.816
Co	N1	22.998	27.797	17.232	40.329	27.089	8.5102
	N2	18.831	26.064	29.664	33.997	27.139	5.5584
	N3	34.497	24.764	35.196	37.096	32.889	4.7859
Ni	N1	176.02	281.14	190.98	230.44	219.65	40.690
	N2	60.794	84.192	65.427	77.159	71.893	9.2735
	N3	142.85	104.79	203.33	116.66	141.91	38.050

ions that precipitate mineral elements, so that the seasonal average concentration of Pb, Cu, Co and Ni ions in the valley deposits reaches (134.79, 71.526, 37.096 and 281.14) mg. kg^{1}, and for the annual rate, it reached (111.25 ± 15.092, 48.162 ±20.358, 32.889 ±4.7859 and 219.65 ±40.69) mg. kg^{-1} respectively. It is noted that most of the concentration rates of lead, nickel and copper exceed the threshold effect levels (TEL) according to (Rahman et al, 2017), as for the descending order of the annual rates for the elements in the sediments as follows: Ni > Pb > Co > Cu. The presence of nickel, lead, copper and cobalt elements in the soils and sediments may be due to their presence naturally as a result of the weathering processes of the rocks, as well as human activities such as atmospheric deposits, civil, agricultural and industrial technical wastewater from car repair shops, repair of brakes and car tires, electric storage batteries, Welding and paint shops, emissions from burning fossil fuels and burning civil waste, especially plastics and gasoline containing high concentrations of tetraethyl or methyl lead, which are still used in Iraq to raise the octane number of fuel and prevent cracking in vehicle engines (Bakan and Ozkoc, 2007; Yahya et al, 2012; Salem and Alwalayed, 2019; Islam, 2021).

Pollution Load Index (PLI)

The importance of the Pollution Load Index **(PLI)** comes to know the extent of contamination with heavy metals in soils and sediments to take the essential actions to reduce their pollution and preserve the environment from deterioration (Abou Elnwar et al, 2018; Kormoker et al, 2019; Perumal et al, 2021). The results of the heavy metal pollution load index (PLI) values Table (4) indicate the fluctuation of values in agricultural soils between (0.617 to 1.418), where 42% of the soil samples irrigated from the valley water were contaminated with heavy metals, because the PLI values are greater than 1.0 (Perumal et al, 2021) due to the relative high concentration of the studied metal elements, especially lead and nickel, which exceeded the baseline. As for the valley sediments, the studied samples were between polluted to non-polluted sediments. The values of the metal pollution load index (PLI) ranged between (1.305 to 0.617) Table (4), where 50% of the sediments were polluted to exceed the safe limits, while the rest were uncontaminated.

Table (4): Results of the values and status of the pollution loads index (PLI) of heavy metal in soil and sediments in the Duhok valley region.

Season / Sites		Winter		Spring		Summer		Autumn		Annual rate	
		Value	Status	Value	Status	Value	Status	Value	Status	Value	Status
Soil	N 1	1.071	P. E.	1.012	P. E.	1.153	P. E.	0.817	N. P.	1.015	P. E.
	N 2	1.123	P. E.	0.749	N. P.	0.964	N. P.	0.990	N. P.	0.957	N. P.
	N 3	1.418	P. E.	0.617	N. P.	0.894	N. P.	0.830	N. P.	0.934	N. P.
Sedimen	N 1	0.764	N. P.	1.106	P. E.	0.809	N. P.	1.148	P. E.	0.957	N. P.
	N 2	0.617	N. P.	1.180	P. E.	0.853	N. P.	1.077	P. E.	0.932	N. P.
	N 3	1.084	P. E.	0.925	N. P.	1.305	P. E.	0.910	N. P.	1.056	P. E.

P. E.: Pollution Exist, N. P.: No Pollution

Generally, 33% of the annual rate of soil and sediment samples are considered polluted. This rise in pollution loads index values in agricultural soils and sediments may be due to the relative high concentrations of lead and nickel elements compared to the rest of the studied heavy metals, as it was characterized by high values of contamination factor (CF) in the soil and due to the impact of human activities such as the discharge of civil, agricultural and industrial waste into the valley (Mekky et al, 2019).

Nemerow pollution index (PIN)

The Nemerow Pollution Index (PIN) is used for the environmental assessment of the quality of soil and bottom sediments on a global scale to know the levels of total pollution resulting from the continuous presence of a group of heavy metals instead of pollution resulting from a single mineral element (Yang et al, 2014; Hu et al, 2013).Table (5) summarize the values and condition of the soil and the studied sediments for the Nemerow index of heavy metals pollution (Pb, Cu, Co and Ni**)**, where the quality of the studied agricultural soil was between slight pollution to severe pollution, the PIN values fluctuated between (1.47 to 3.42). This deterioration in soil quality is caused by the high concentrations of lead and nickel ions, which was negatively reflected in the high PI values of lead and nickel concentrations to reach (1.84 and 3.67) respectively, where 58%

Table (5): Results of the quarterly averages of the (PIN) values and the status of the soils and sediments for the studied sites.

Sites \ Season		Winter		Spring		Summer		Autumn	
		Value	Status	Value	Status	Value	Status	Value	Status
Soil	N 1	2.85	Se. P.	2.29	Se. P	3.07	H.P.	3.42	H.P.
	N 2	2.67	Se. P.	2.20	Se. P	1.47	Sl. P.	1.84	Sl.P.
	N 3	2.77	Se .P.	2.16	Se. P	3.29	H.P.	2.47	Se. P.
Sediment	N 1	2.93	Se. P.	3.72	H.P.	3.07	H.P.	3.42	H.P.
	N 2	1.48	Sl.P.	2.42	Se. P	1.47	Sl.P.	1.84	Sl.P.
	N 3	2.75	Se. P.	2.24	Se. P	3.29	H.P.	2.47	Se. P

Se. P.; Severely Polluted, Sl.P.: Slightly Pollution., H.P.: Heavy Pollution

of the samples were severely polluted and 25% were heavy polluted and the rest were slightly polluted. As for bottom sediments, their quality was between slight pollution to heavy pollution, with PIN values ranging between (3.72 to 1.47), where 33.33% of the sediment samples were Heavy Pollution, 41.67% Severely Pollution and the rest were Slightly Pollution. This deterioration in quality is due to the high concentrations of lead and cobalt in the sediments, which was reflected in the high PI values and the negative impact on the quality of the sediments.

Geo-accumulation Index (Igeo)

The results of the assessment of the pollution of agricultural soil irrigated from the waters of Duhok valley according to the calculation of the Igeo values, Table (6) indicates that the values for lead, copper, cobalt and nickel for the three sites studied

Table (6): Seasonal results of (Igeo) values and status of soils for different sites in the studied area.

Elem.	Sites \ Seas.	Winter		Spring		Summer		Autumn	
		Value	Status	Value	Status	Value	Status	Value	Status
Pb	N1	0.316	Weakly polluted	0.462	Weakly polluted	0.404	Weakly polluted	0.135	Weakly polluted
	N2	0.497	Weakly polluted	0.168	Weakly polluted	0.428	Weakly polluted	0.381	Weakly polluted
	N3	0.587	Weakly polluted	0.248	Weakly polluted	0.399	Weakly polluted	0.231	Weakly polluted
Cu	N1	0.079	Weakly polluted	0.079	Weakly polluted	0.058	Weakly polluted	0.051	Weakly polluted
	N2	0.064	Weakly polluted	0.076	Weakly polluted	0.058	Weakly polluted	0.056	Weakly polluted
	N3	0.087	Weakly polluted	0.031	Weakly polluted	0.053	Weakly polluted	0.071	Weakly polluted
Co	N1	0.124	Weakly polluted	0.114	Weakly polluted	0.137	Weakly polluted	0.111	Weakly polluted
	N2	0.139	Weakly polluted	0.082	Weakly polluted	0.132	Weakly polluted	0.124	Weakly polluted
	N3	0.265	Weakly polluted	0.067	Weakly polluted	0.106	Weakly polluted	0.088	Weakly polluted
Ni	N1	0.684	Weakly polluted	0.423	Weakly polluted	0.895	Weakly polluted	0.942	Weakly polluted
	N2	0.582	Weakly polluted	0.482	Weakly polluted	0.430	Weakly polluted	0.594	Weakly polluted
	N3	0.486	Weakly polluted	0.462	Weakly polluted	0.462	Weakly polluted	0.535	Weakly polluted

throughout the study period were weakly polluted, where the values fluctuated between (0.135 to 0.587), (0.031 to 0.087, (0.067 to 0.265) and (0.423 to 0.942) respectively.

The same applies to the Igeo values Table (7) for the bottom sediments of the valley and for all the studied sites during the seasons of the year were weakly contaminated with the exception of nickel at site N1 due to the deterioration of the quality of the sediments relatively to medium pollution during the spring and autumn seasons to reach the value of the index to (1.226 and 1.005), respectively. It is also noted from the table that the seasonal rates of values for nickel increased compared to the rest of the heavy metals studied, bringing the annual average values for (*Igeo*, Ni) five times the annual average values of (*Igeo*, Co) and eight times the values for (*Igeo.* Cu). This relative rise in the values is due to the high concentrations of heavy elements in the sediments, and in general, the rates of values for soils and sediments are consistent with the studied index's, so that the ascending order of the rates is as follows: Igeo (Ni) > Igeo (Pb) > Igeo (Co) > Igeo (Cu).

Table (7): Seasonal results of (Igeo) values and status of sediments for different sites in the studied area.

Elem.	Seas. / Sites	Winter		Spring		Summer		Autumn	
		Value	Status	Value	Status	Value	Status	Value	Status
Pb	N1	0.164	W. Poll.	0.262	W. Poll.	0.216	W. Poll.	0.242	W. Poll.
	N2	0.295	W. Poll.	0.503	W. Poll.	0.257	W. Poll.	0.346	W. Poll.
	N3	0.429	W. Poll.	0.386	W. Poll.	0.360	W. Poll.	0.510	W. Poll.
Cu	N1	0.047	W. Poll.	0.066	W. Poll.	0.055	W. Poll.	0.070	W. Poll.
	N2	0.039	W. Poll.	0.159	W. Poll.	0.097	W. Poll.	0.135	W. Poll.
	N3	0.059	W. Poll.	0.067	W. Poll.	0.102	W. Poll.	0.028	W. Poll.
Co	N1	0.094	W. Poll.	0.114	W. Poll.	0.071	W. Poll.	0.165	W. Poll.
	N2	0.077	W. Poll.	0.107	W. Poll.	0.121	W. Poll.	0.139	W. Poll.
	N3	0.141	W. Poll.	0.101	W. Poll.	0.144	W. Poll.	0.152	W. Poll.
Ni	N1	0.768	W. Poll.	1.226	M. Poll.	0.833	W. Poll.	1.005	M. Poll.
	N2	0.265	W. Poll.	0.367	W. Poll.	0.285	W. Poll.	0.337	W. Poll.
	N3	0.623	W. Poll.	0.457	W. Poll.	0.887	W. Poll.	0.509	W. Poll.

W. Poll.: Weakly polluted., M. Poll.: Moderately polluted

Potential Ecological Risk index (PERI)

The Potential Ecological Risk Index (PERI) is one of the necessary indicators to monitor the degree of the risk of heavy metal contamination of soils and bottom sediments (Wuana et al, 2020). Table (8) indicates an increase in the PERI values, where the quality of the studied soils and sediments were between slight ecological risk to medium ecological risk, and the values ranged between (26.207 to 59.481) and (23.871 to 51,952) respectively. This relative deterioration in the quality of soils and sediments is due to the relative high values of ecological risk factor (ERf) for lead, cobalt and nickel to reach (14.637, 15.926, and 17.046) and (12.716, 17.413 and 30.559) respectively.

Table (8): Quarterly Results of (ERf), (PERI) and Condition of Soils and Sediments of the Study Area.

Results	Site	Season	Ecological Risk factors (ERf)				PERI	Status
			Pb	Cu	CO	Ni		
Soil	N 1	Winter	7.879	2.176	14.251	17.046	41.351	M. Eco. Risk
		Spring	11.521	2.153	13.063	10.546	37.282	M. Eco. Risk
		Summer	10.075	1.580	15.753	22.310	49.717	M. Eco. Risk
		Autumn	3.374	1.395	12.767	23.465	41.001	M. Eco. Risk
	N 2	Winter	12.392	1.760	15.926	14.502	44.580	M. Eco. Risk
		Spring	4.189	2.090	9.435	12.021	27.734	S. Eco. Risk
		Summer	10.666	1.586	15.081	10.720	38.053	M. Eco. Risk
		Autumn	9.499	1.522	14.222	14.796	40.039	M. Eco. Risk
	N 3	Winter	14.637	2.379	30.365	12.100	59.481	M. Eco. Risk
		Spring	6.169	0.842	7.684	11.513	26.207	S. Eco. Risk
		Summer	9.949	1.456	12.124	11.502	35.032	M. Eco. Risk
		Autumn	5.758	1.945	10.073	13.332	31.107	M. Eco. Risk
Sediment	N 1	Winter	4.091	1.277	10.795	19.132	35.295	M. Eco. Risk
		Spring	6.531	1.815	13.048	30.559	51.952	M. Eco. Risk
		Summer	5.377	1.503	8.088	20.759	35.727	M. Eco. Risk
		Autumn	6.037	1.917	18.930	25.048	51.932	M. Eco. Risk
	N 2	Winter	7.355	1.069	8.839	6.608	23.871	S. Eco. Risk
		Spring	12.530	4.371	12.234	9.151	38.287	M. Eco. Risk
		Summer	6.405	2.646	13.924	7.112	30.086	M. Eco. Risk
		Autumn	8.619	3.687	15.958	8.387	36.650	M. Eco. Risk
	N 3	Winter	10.694	1.625	16.192	15.527	44.039	M. Eco. Risk
		Spring	9.609	1.823	11.624	11.390	34.446	M. Eco. Risk
		Summer	8.961	2.805	16.521	22.103	50.390	M. Eco. Risk
		Autumn	12.716	0.774	17.413	12.680	43.582	M. Eco. Risk

S. Eco. Risk: Slight Ecological Risk, class A., M. Eco. Risk: Medium Ecological Risk, class B.

It is noted that the results of (ERI) values agree with the results of (PLI) and (PLN) ones. In general, the descending order of Erf rates for soils and sediments is as follows:

Erf(Ni) > Erf(Co) > Erf(Pb) > Erf(Cu).

Finally, the movement of heavy metals, whether in soil and sediment into the soil solution or aquatic environment, is affected by pH values. The occurrence of decomposition processes of organic matter leads to the production of organic acids and in anaerobic conditions leads to the formation of hydrogen sulfide, which oxidizes when exposed to dissolved oxygen to sulfuric acid. In these cases, heavy metals is released into the aquatic environment, causing damage to the aquatic ecosystem through their entry and accumulation in microorganisms and then their transfer to crustaceans, fish, etc. The Biomagnification of these metals may occur in aquatic organisms. Hence, the impact on the human being, the final consumer of the food chain (Al-Saffawi, 2018).

4 RECOMMENDATIONS AND CONCLUSIONS

The study recommended periodic follow-up of the concentration of pollutants and heavy metals in agricultural soils and bottom sediments to reduce pollution problems.

1. The current study indicated that most of the concentrations of Ni, Pb, and Cu ions were exceeding the permissible standard limits for soil and sedimentation according to WHO.
2. 42% of the soil samples and 50% of the sediment samples are considered polluted according to the PLI values, while the percentage was 50% and 41.7%, respectively, of medium ecological risk (Class B) according to potential ecological risk index.

The results of Nemerow pollution index (PIN) values indicated that 58% of the soil samples were severely polluted and 25% of them were heavy polluted, while 41.7% of the sediment samples were severely polluted and 33.33% were heavy polluted. Finally, most of the studied soil and sediment samples according to the concentrations of lead, copper, cobalt and nickel were from the weakly polluted class according to the Igeo index.

Therefore, the study recommends periodic follow-up of the concentrations of heavy metals in the region, while activating environmental laws to prevent violators by dumping wastewater contaminated with toxic metal compounds and treating it before dumping it into the valley.

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