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An Assessment of Heavy Metals Soil Pollution and Health Risk Around Industrial District in Qayarah Area, Northern Iraq

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ABSTRACT

Industrial district as well as human and natural activity are the main sources of pollution in Al-Qayarah City area. These sources release pollutants into nearby areas. Twenty-six soil samples were collected at a depth range of (0-30) centimeters. The heavy metals (As, Cd, Co, Cr, Ni, Pb) are analyzed using ICP-MS technique; in addition to measuring some physicochemical properties of the soil such as pH, EC, OM. Contamination factor, enrichment factor, pollution loading index, and long-term carcinogenic risk estimation are calculated based on exposure through ingestion, dermal contact, and inhalation. The average values of pH, EC, and OM% are 7.7, 3.37 dS/m, and 2.35% respectively. The average concentrations of As, Cd, Co, Cr, Ni, and Pb are (6.40, 0.205, 18.68, 101.46, 159.06, and 9.93) ppm respectively.The significance of the contamination and enrichment factors, as well as the pollution loading index, for heavy elements range from low to medium values. The pollution loading index for the contaminated samples follows the following order:
AB6>QR1>AB5>AB4>QF8>AB3>AB2>GS4>QF7>QR2>QF9.
Whereas, the enrichment and pollution factors for heavy elements follow the following order: As>Ni>Cd>Cr>Pb>Co. The values of the total carcinogenicity factor through ingestion, dermal contact, and inhalation are (1.2x10-4), (6.91x10-4), and (7.85x10-3) respectively. All exposure pathways to studied pollutants are in the following order: Carcinogenic inhalation hazard > Carcinogenic skin hazard > Carcinogenic oral hazard. Site AB6 is considered the most polluted due to the impact of most influential factors and a high probability of cancer risk.

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تقييم التلوث بالعناصر الثقيلة والخطر الصحي حول المنطقة الصناعية في منطقة القيارة، شمالي العراق

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الملخص

تعد فعاليات القاطع الصناعي فضلاً عن الفعاليات الطبيعية من المصادر الرئيسة للتلوث في مدينة القيارة، اذ تطلق العديد من الملوثات الى المناطق القريبة منها. تم جمع ست و عشرين عينة من تربة المنطقة وبعمق (0–30 سم). ولغرض التعرف على قياس تراكيز العناصر الثقيلة (As, Cd, Co, Cr, Ni, Pb) تم تحليلها باستخدام تقنية ICP-MS، فضلاً عن قياس الخواص الفيزيوكيميائية للتربة التي هي (pH , EC, OM). تم حساب معامل التلوث وعامل الاثراء وعامل حمل التلوث اضافة الى حساب تخمين الخطر المسرطن طويل الامد بالاعتماد على التعرض عن طريق الفم والجلد والاستنشاق. كانت قيم كل من pH، EC، OM بمعدل 7.7 ، 3.37 ds/m، 2.35 % على التوالي. و كانت قيم As، Cd، Co، Cr، Ni، Pb بمعدل (6.40 ، 0.205 ، 18.68 ، 101.46 ، 159.06 ، 9.93) جزء بالمليون على التوالي. قيم معاملات التلوث والاثراء فضلاً عن معامل حمل التلوث للعناصر الثقيلة هي واطئة الى متوسطة الاهمية، بينما اظهر مؤشر حمل التلوث (PLI) الترتيب التالي:
AB6> QR1>AB5> AB4> QF8> AB3> AB2> GS4> QF7> QR2> QF9 بينما اظهرت معدلات عامل الاثراء (EF) ومعامل التلوث (CF) للعناصر الثقيلة الترتيب التالي: As> Ni> Cd> Cr> Pb> Co. وتمثل جميع قيم معاملات التلوث بكونها واطئة الى متوسطة الاهمية، اما قيم معدل مجموع العامل المسرطن عن طريق الفم والجلد والاستنشاق فقد كانت x10-41.2 و x10-46.91 وx10-37.85 على التوالي، وجميعها تدل على احتمالية عالية في خطر الاصابة بالسرطان، وتشير نتائج البحث ان طرق التعرض للملوثات كانت بالترتيب التالي: الخطر المسرطن بوساطة الاستنشاق > الخطر المسرطن بوساطة الجلد > الخطر المسرطن بوساطة الفم، ويمكن اعتبار الموقع AB6 الاكثر تلوثاً بواسطة العوامل اعلاه والاكثر احتمالية ليكون سبباً للسرطان.

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Introduction

In industrial areas, pollution is considered one of the most challenging issues (Rahman *et al*., 2022). Soil is a vital element for human life to survive on planet Earth and is supposed to be the primary recipient of persistent pollutants such as toxic metals (Karim *et al*., 2014). Soil pollution with toxic elements is a major environmental problem worldwide due to its extensive sources, its toxicity, and its non-biodegradable nature. According to the United States Environmental Protection Agency (EPA), toxic elements such as chromium, nickel, copper, arsenic, cadmium, and lead are among the most toxic elements in the environment (Proshad *et al*., 2017). The natural content of heavy elements can vary greatly depending on the material from which the soil was formed. The difference between background values and baseline values is very important. Baseline values are the natural content of the material in the soil depending entirely on the compositional and mineralogical characteristics of the parent geological material/source.

Baseline levels are the actual range typically observed for the concentration of a specific element in a particular area depending on the nature of the geological material/original source and on the historical spread in the environment of pollutants from human sources. Various indicators are generally used to determine Mineral concentrations of environmental importance that include Metal Enrichment Factor (EF) (Barbieri *et al.*, 2015).

Heavy elements can persist in nature for a long time. Heavy elements can't be decomposed even with biological treatment, and they are dangerous due to their toxicity even at low concentrations (1.0-10.0 mg/liter) (Rahman et al., 2022). Over the past two decades, the term "heavy metals" has been widely used and is associated with chemical hazards. It is often used as a collective name for metals and semi-metals (metalloids) that have been linked to potential pollution and environmental toxicity (Kabata-Pendias, 2011). On the other hand, any heavy metal or semi-metal may have toxicity towards living organisms depending on the dose and duration of exposure. The most common pollutants of heavy metals in the environment are Cr, Mn, Ni, Cu, Zn, Cd, and Pb (Khan *et al.*, 2011). There are numerous acute and chronic toxic effects of heavy metals on various organs of the body, such as gastrointestinal and renal impairments, and nervous system disorders, skin diseases, damage to blood vessels, immune system disorders, birth defects, and cancer are examples of complications from the toxic effects of heavy metals. The simultaneous exposure to two or more elements may have cumulative effects (Mood *et al.*, 2021). The weathering and erosion processes lead to the natural presence of heavy elements in the soil. Additionally, human activities can release quantities of heavy elements into the soil, turning it into a basin or reservoir for pollutants that pose a significant threat to the natural environment and human health. Heavy elements, besides being major pollutants, have the characteristic of remaining stable and difficult to be absorbed by plants. They are also insoluble and have high density more than five gm/cm^3, which increases their impact on inhalation, ingestion, and skin contact. This also leads to their entry into the food chain and their bioaccumulation in the bodies of humans and animals. Heavy elements such as nickel (Ni), lead (Pb), cadmium (Cd), zinc (Zn), copper (Cu), and cobalt (Co) increase the chances of developing lung, nasal, and skin cancer. It can also cause damage to the liver and kidneys due to excessive levels. For example, nickel is considered an essential element for plant growth, but excessive amounts can accumulate in the human and animal body, leading to the development of nasal, skin, and lung cancer (Kareem *et al.*, 2022). Environmental Risk Assessment (ERA) is a method for assessing the risks associated with the presence, fate, and transport of chemicals in the environment.

Environmental Risk Assessment (ERA) can be considered as an analysis of the potential harmful effects of chemicals at a specific site to find appropriate remedial actions. The risks may result from floods, extreme weather phenomena, processes technology practices, chemical factors products, radiation procedures, and industrial activities that can pose threats to ecosystems, animals, and humans (Kareem *et al.*, 2022).

Multiple sources (natural and human) and uncontrolled events that occurred in the past decade have led to a lack of control over many sources of pollution in the study area (the city of Qayarah). Qayarah is one of the important cities in the south of Nineveh province, northern Iraq. It contains many industrial facilities (an oil fields, an oil refinery, and a gas power station) in addition to many natural sources (sulfur springs and oil leakage), as well as human activities and agricultural activities. All these human and natural sources of pollutants cause biological damage to the surrounding ecosystem and pose multiple risks to human health, necessitating the need to study and evaluate the area from an environmental perspective and assess environmental and health risks.

Materials and Methods

Study area and sampling

The current study includes Qayarah sub-district, which is located about 60 km to the south of Mosul City. It lies in between northern (336820 - 348491) to the eastern (3971498 - 3959035) in UTM units as shown in Figure (1). The study area contains many sources of natural and industrial pollution. As for the natural sources, they include sulfur springs (Mishraq plant near it to produce acid raining) and tar oil spills, which are distributed in the southeastern part of the city of Qayarah, adjacent to the Tigris River, which passes through the city at the southern plunge of the Qayarah fold forming a floodplain with a width of up to four kilometers on both sides of the river (Al-Khafaji, 2019) and (Alfaris, 2022). The study area is also characterized by the presence of structural phenomena such as the Qayarah fold plunge and the faults associated with it. As for the industrial areas, it includes the Qayarah oil field, the Qayarah refinery, and the gas power station, in addition to many other sources such as fuel stations, the city of Qayarah, the main roads, as well as sewage water and agriculture areas. The study area is located tectonically in a transformed belt and within the range of low folded zone. The formation of the Fat'ha (middle Miocene) is revealed in most areas of the current study area, which consists of successive cycles of clay, gypsum, anhydrite and calcareous rocks with layers of marl.

Twenty-six different sites are selected for sampling in this study in the Qayarah area. The study area covers approximately 100 square kilometers (Fig. 1). Soil samples were collected during March-April 2022. Auger is used to collect samples at a depth of 0-30 cm, and the cone and square method is used to select representative samples. The samples are kept in nylon bags in a cool place and air-dried at room temperature for two weeks, then they have ground and homogenized for analysis and determination dangerous heavy metals. A ceramic mortar is used to break up the soil, and a 63 mm sieve is used to sift the soil and store it in clean airtight bags for chemical analysis.

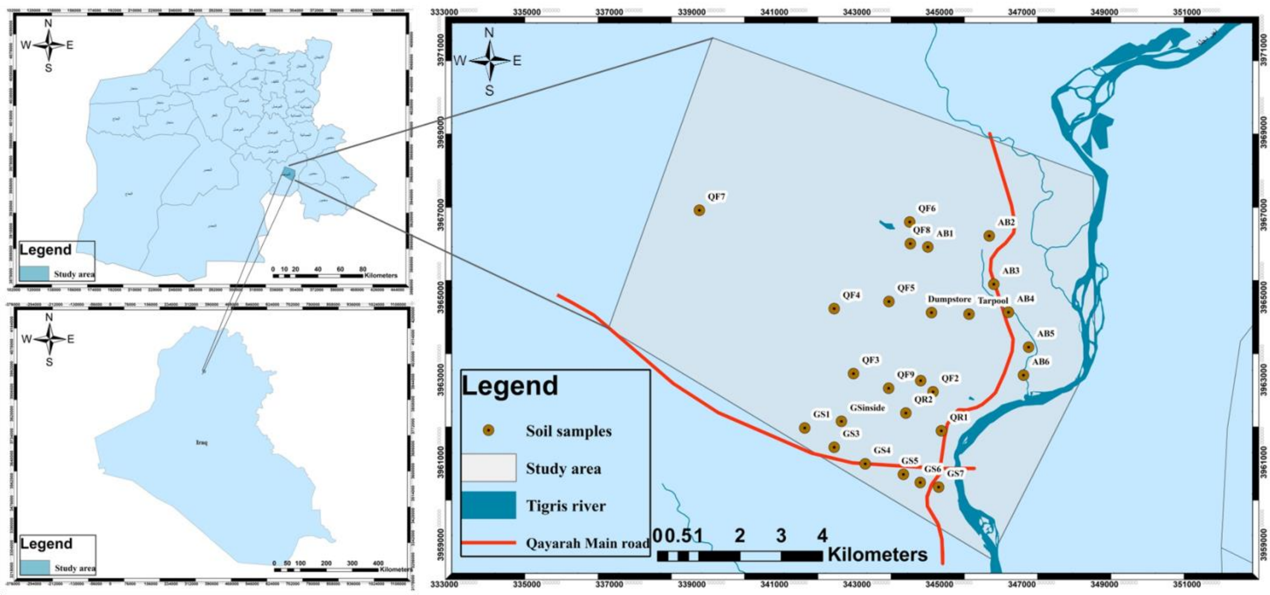

Fig. 1. map of study area and sample's location.

Instrumental analysis

The Aqua Regia Super Trace method is used to digest the samples (Hutchison,1974), and then used inductively coupled plasma mass spectrometry (ICP-MS) for heavy element analysis at the ALS company group in Seville, Spain. The pH and direct conductivity are measured using (1:1) soil to water ratio, while the organic matter is measured by titration with potassium dichromate solution (Estefan *et al*. 2013). The applications used for mapping and statistical analysis are ArcGIS v10.8 and SPSS v.26 respectively.

Quality control

Enrichment factor (EF)

To assess the volume of hazardous elements in the environment, the use of a fortification agent is good to determine the anthropogenic effects of hazardous elements in the soil, the enrichment factor is calculated using the following formula (1):

$$\boldsymbol{EF} = \frac{\left(\frac{C_M}{C_{Al}}\right)_{sample}}{\left(\frac{C_M}{C_{Al}}\right)_{background}} \ldots\ldots..(\mathbf{1})$$

Where, $\left(\frac{C_M}{C_{Al}}\right)$ is assumed to be the ratio of the heavy element ($\boldsymbol{C_M}$) to aluminum ($\boldsymbol{C_{Al}}$) concentrations in the soil sample, and $\left(\frac{C_M}{C_{Al}}\right)_{background}$ is the same as the reference ratio in the background sample. Aluminum is used because it is stable and immobile in weathering condition, and we use average background of crustal concentrations of published elements by (Kabata-Pendias, 2011). If the EF value of a heavy element is 1, it means that the element may be entirely from crustal material or natural weathering processes. (EF < 2) deficient to minimal enrichment, (2 < EF < 5) moderate enrichment, (5 < EF < 20) high enrichment, (20 < EF < 40) very high enrichment, (EF > 40) extremely high enrichment.

Contamination factor

The pollution level is evaluated using the contamination factor (CF) recognized in Hakanson (1980) based on the following equation (2):

$$\boldsymbol{CF} = \frac{C_s}{C_b} \ldots\ldots..(\mathbf{2})$$

Where, $\boldsymbol{C_s}$ is the heavy metal concentration in the study samples, and $\boldsymbol{C_b}$ is the baseline concentration. Baseline concentrations are as reported in the background sample (Background means the background concentrations for elements published by Kabata-Pendias, (2011). Hakanson (1980) classified pollution factor as follows: CF (<1) is low, CF (1 to <3) is moderate, CF (3 to <6) is significant, CF > 6 is high pollutions.

Pollution load index (PLI)

The pollution load index works as an integrated method for assessing soil quality from the six calculated heavy metals (Cr, Ni, Cu, As, Cd, Pb). PLI can be calculated using the following equation (3):

$$PLI = \sqrt[n]{CF_1 * CF_2 * CF_3 * \dots * CF_n} \dots\dots (3)$$

Where (*CF*) is contamination factor; the total toxicity status of soil heavy metals can be assessed from the pollution load index (PLI) with the following classification: PLI > 1 is contaminated, and PLI < 1 is uncontaminated.

Cancer risk

The lifetime average daily dose (LADD) used in the cancer risk assessment of the heavy elements is calculated for each exposure method as shown in equation (4):

$$LADD = \frac{C * EF}{AT} * \left(\frac{CR_{child} * ED_{child}}{BW_{child}} + \frac{CR_{adult} * ED_{adult}}{BW_{adult}}\right) \dots\dots (4)$$

Where the variables C, EF, AT, ED and BW are mentioned in Table (1) except CR is the contact rate; i.e., ingestion [CR = IngR], inhalation [CR = InhR], and dermal absorption rates. [CR = SA x SAF x DA]. CR for children is generally greater than that of adults due to their lack of awareness. The risk from carcinogenic effects is determined by multiplying the mean life time to daily dose (LADD) with the regression factor corresponding to the exposure pathway, then the risks of each exposure pathway are summed to get the total cancer risk equation (5):

$$Cancer\ risk = LADD * SF \dots\dots\dots\dots (5)$$

Where, SF is the cancer slope factor of the pollutants mentioned in Table (2). Cancer risk between (10^{-6}) and (10^{-4}) indicates potential health risks according to (USEPA, 1993), while greater than (10^{-4}) indicates potentially higher health risks (Yu, *et al*., 2014).

Table 1. Exposure parameters used for the health risk assessment through different exposure pathways for soil.

Adult			
Symbol and unit	Description	value	reference
C (ppm)	Heavy metal concentration		
EF (day/year)	Exposure frequency	350	(USEPA, 2001)
AT (day)	Averaging time for carcinogenic effects	25550	(USEPA, 2001)
CR (mg/day)	Contact rate	100	
ED Adult (year)	Exposure duration	30	(USEPA, 2001)
BW Adult (kg)	Average body weight	70	USEPA, 1989
SA(cm^2)	Exposed skin area	5700	(USEPA, 2001)
SAF(gm/cm^2)	Skin adherence factor	0.07	(USEPA, 2001)
DA (without unity)	Dermal absorption factor	As=0.03 Other elements=0.001	(USEPA, 2002)
Child			
Symbol and unit	Description	value	reference
C (ppm)	Heavy metal concentration		
EF(day/year)	Exposure frequency	350	(USEPA, 2001)
AT(day)	Averaging time for carcinogenic effects	25550	(USEPA, 2001)
CR (mg/day)	Contact rate	200	
ED Child (year)	Exposure duration	6	(USEPA, 2001)
BW Child (kg)	Average body weight	15	USEPA, 1989
SA (cm^2)	Exposed skin area	2800	(USEPA, 2001)
SAF (gm/cm^2)	Skin adherence factor	0.2	(USEPA, 2001)
DA (without unity)	Dermal absorption factor	As=0.03 Other elements=0.001	(USEPA, 2002)

Table 2: Cancer slope factor for heavy metals

Elements	Slope factor (mg/ kg/day)		
	Ingestion	Dermal	inhalation
As	1.5(1,2)	1.5(2)	15.1(1,2)
Cd	0.38(3)	25.6(4)	6.3(1,2)
Co	N/A	N/A	9.8(2)
Cr	0.5(2)	38.5(4)	42(1)
Ni	0.084(4)	2.1(4)	0.84(1)
Pb	0.0085(1,2)	N/A	0.042(2)
V	N/A	N/A	N/A
Zn	N/A	N/A	N/A

(1) Abed, (2015), (2) Kamunda, *et al*. (2016), (3) Nduka, *et al*. (2019) (4) Caceres, *et al*. (2021).

Results and Discussion

The range of soil pH values is (7.1-8.2), and the average value of pH is 7.4 as mentioned in Table (3). The studied soil is slightly alkaline according to the classification of Islam *et al*., (2020), which could be due to the decomposition of carbonates exposed in study area. This criterion has limited importance on the distribution of heavy elements, which largely determines their mobility due to the neutral alkaline environment (Al Shurafi, *et al*, 2023).

High pH values are not favourable for the availability of heavy metal cations in the soil as mentioned in Table (4). Many mineral complexes are insoluble in alkaline conditions and may lead to a low fix of heavy metals in soil and decrease in the availability of it (Kabata-Pendias, 2011).

The range of EC values is (0.6-13.1) dS/m, while the average soil EC value of electrical conductivity is 3.37 dS/m as mentioned in Table (3). The average value of electrical conductivity indicates a very slight salinity of soil according to USDA, (2017). The low value of EC in QF4 is due to the abundance of limestone, marl and carbonate soils that agrees with Abate *et al*., (2014), while the maximum value of EC in (GS1, AB4, AB6, Tar pool) due to the high content of sodium salts (field observations) from the groundwater, are raised by capillary action to the surface of the soil.

Table 3. Concentrations of heavy metals and some physiochemical properties of soil.

Elements	Elements concentration						Physiochemical properties		
Samples	As ppm	Cd ppm	Co ppm	Cr ppm	Ni ppm	Pb ppm	pH unity	EC (dS/m)	organic matter %
QF1	6.26	0.091	25.7	137	262	5.78	7.5	1.8	0.89
QF2	3.57	0.065	7.68	38.6	63.3	3.68	7.4	1.8	4.07
QF3	4.56	0.096	13.15	66.3	106	6.1	7.3	1.8	2.75
QF4	6.62	0.205	15.75	76.5	121.5	6.52	7.5	0.6	1.58
QF5	9.02	0.264	18.2	90.3	140.5	7.99	7.3	1.9	1.93
QF6	5.16	0.127	13.75	79.8	120.5	5.71	7.5	1.7	0.72
QF7	6.78	0.241	19.45	101	161.5	13.15	7.1	2	3.31
QF8	7.09	0.275	20.8	119.5	185	15.7	7.6	2.9	1.55
QF9	6.22	0.211	21.2	117.5	211	8.32	7.4	1.7	2
GS1	6.2	0.208	18.3	103	153.5	8.04	8.2	10.1	1.86
GS3	5.61	0.196	17.15	100	147.5	8.21	7.4	3.3	3.2
GS4	6.9	0.255	20	103	172	10.1	7.4	2.1	2.69
GS5	6.03	0.221	15.7	99.8	130	12.4	7.4	1.7	0.72
GS6	6.07	0.207	16.95	101	140.5	8.7	7.3	1.9	1.75
GS7	6.22	0.19	18.3	152	144.5	7.44	7.8	0.9	2.62
AB1	5.32	0.177	14.15	78.6	126.5	6.13	7.5	1.6	0.72
AB2	6.67	0.239	22	114	190.5	9.3	7.6	1	0.55
AB3	6.87	0.246	22.8	117	192.5	9.97	7.3	3.2	1.31
AB4	7.38	0.276	23.3	116.5	195	11.05	7.2	10.4	0.37
AB5	7.62	0.258	26.3	133	225	11.05	7.4	1.9	3.58
AB6	8.03	0.209	29.5	148.5	262	10.7	7.2	12.5	2.27
QR1	7.11	0.348	17.25	94.2	139.5	38	7.5	1.8	4.17
QR2	7.44	0.252	17.5	119	152	11.6	7.4	2.6	4.96
GS inside	6.37	0.201	16.7	92	134.5	6.83	7.4	1.8	4.41
Tar pool	5.02	0.137	15.25	65.9	122.5	7.65	7.4	13.1	2.79
Dump store	6.29	0.135	19	74.1	136.5	8.22	7.4	1.6	4.51
Mean	6.40	0.205	18.68	101.46	159.07	9.93	7.44	3.37	2.35
Minimum	3.57	0.065	7.68	38.60	63.30	3.68	7.10	0.60	0.37
Maximum	9.02	0.348	29.50	152.00	262.00	38.00	8.20	13.10	4.96
WHO (*)	20	3	50	100	50	100	-	-	-
Average Soil	6.83	0.4	11.3	59.5	29	27	-	-	-
Average crust	1.8	0.2	25	100	75	13	-	-	-

(*) Maximum permissible level of heavy metals in soils (mg/kg) in WHO (1996) as [Chiroma (2014)]

Table 4. Correlation matrix between concentrations and physiochemical properties.

	As	Cd	Co	Cr	Ni	Pb	pH	EC	OM%
As	1								
Cd	0.761**	1							
Co	0.706**	0.409*	1						
Cr	0.619**	0.439*	0.834**	1					
Ni	0.589**	0.303	0.964**	0.831**	1				
Pb	0.364	0.696**	0.153	0.161	0.100	1			
pH	-0.156	-0.045	-0.125	0.102	-0.100	-0.027	1		
EC	0.101	0.019	0.293	0.118	0.252	-0.017	0.028	1	
OM%	-0.029	-0.001	-0.203	-0.197	-0.273	0.230	-0.125	-0.110	1
**	Correlation is significant at the 0.01 level (2-tailed).								
*	Correlation is significant at the 0.05 level (2-tailed).								

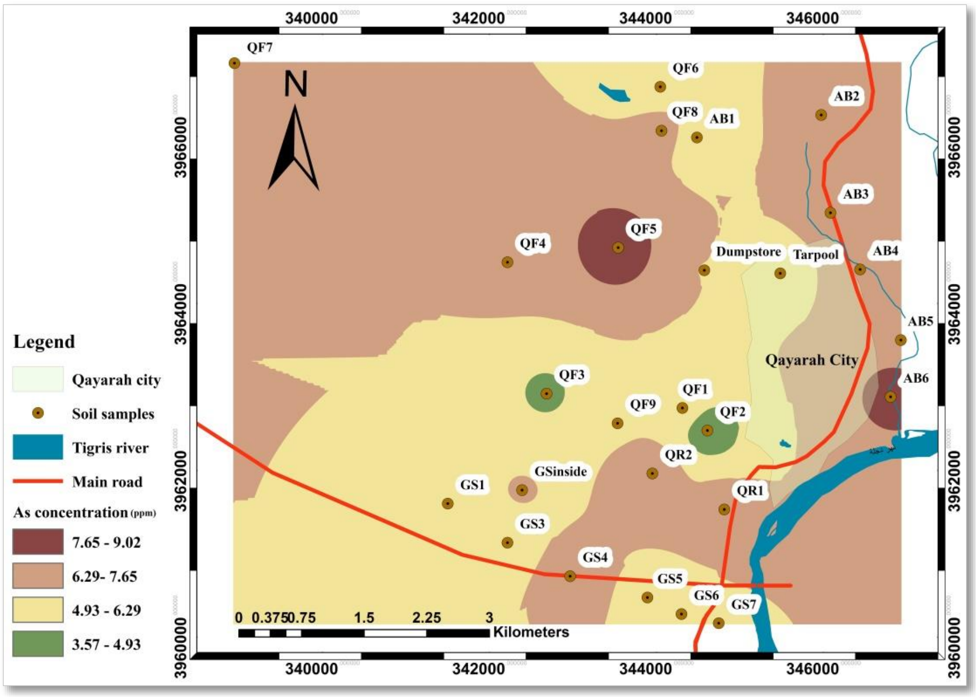

Fig. 2. Spatial distribution of Arsenic (As) in study area.

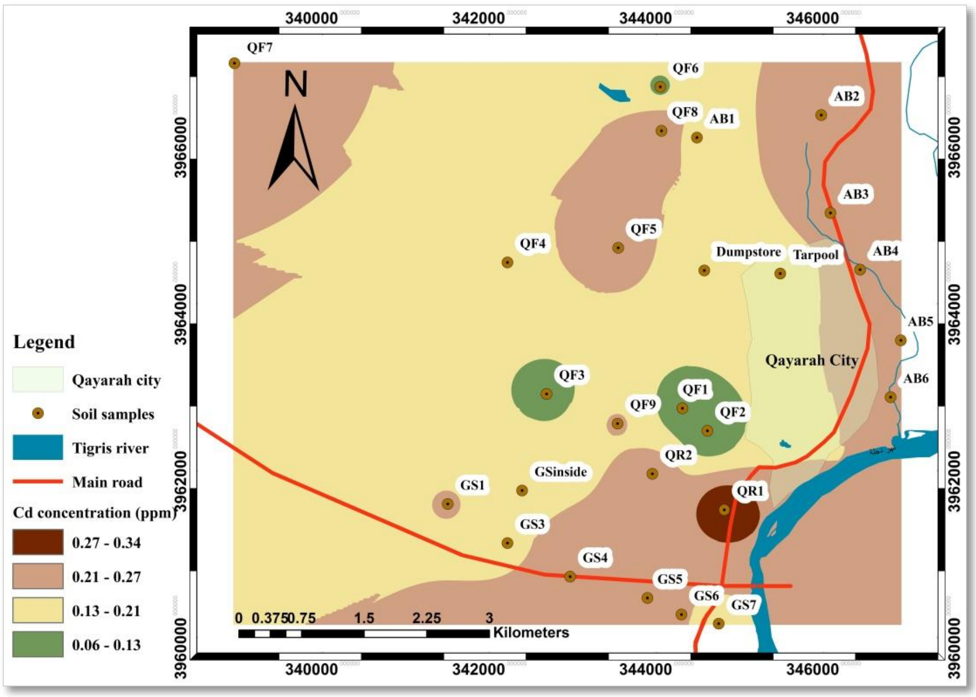

Fig. 3. Spatial distribution Cadmium (Cd) in study area.

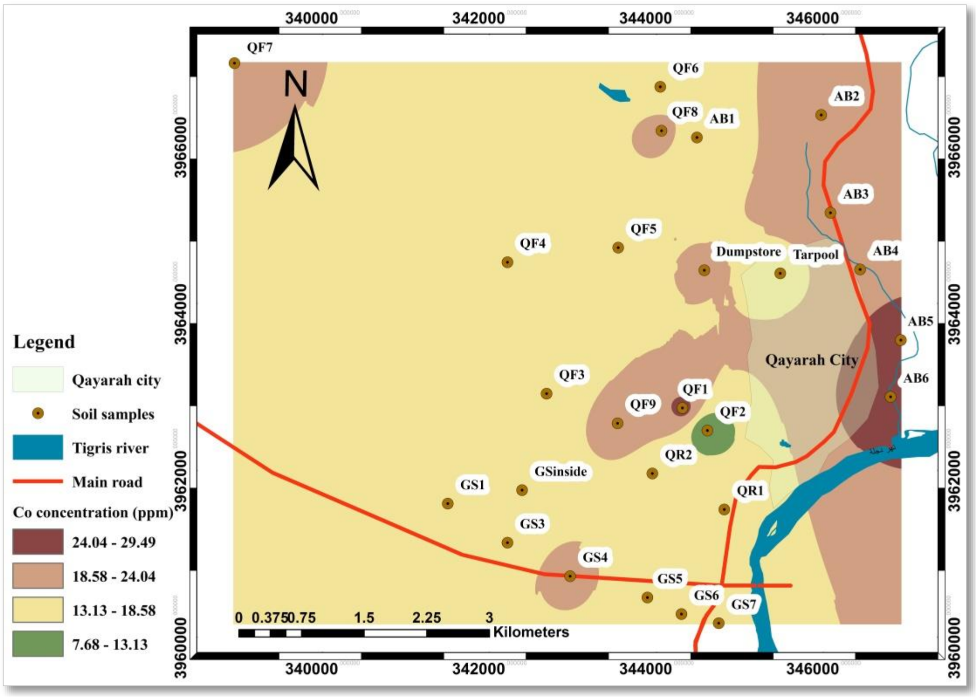

Fig. 4. Spatial distribution of Cobalt (Co) in study area.

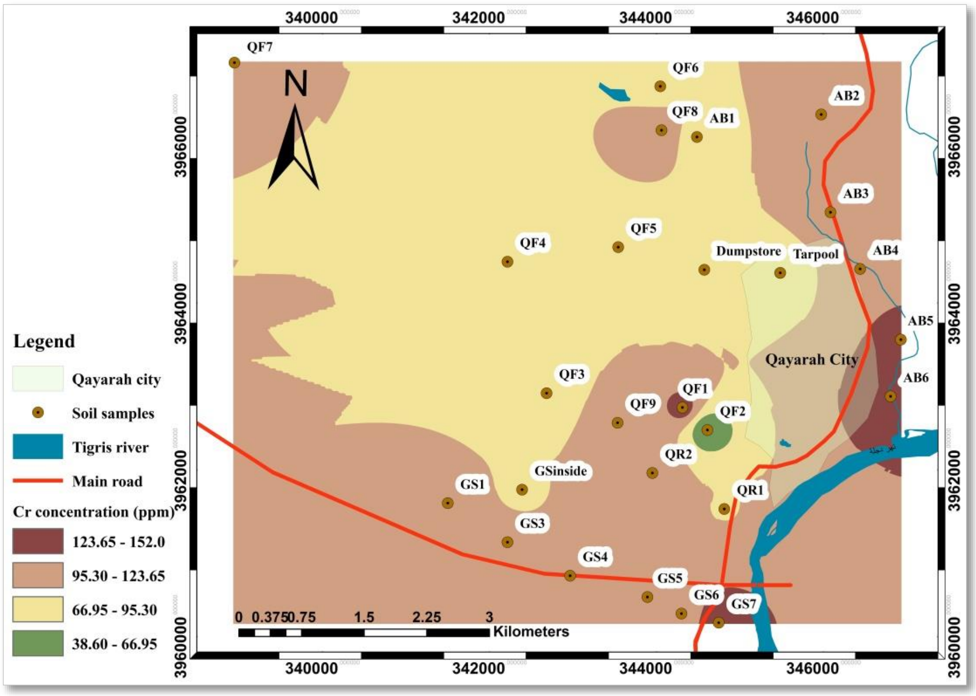

Fig. 5. Spatial distribution of Chromium (Cr) in study area.

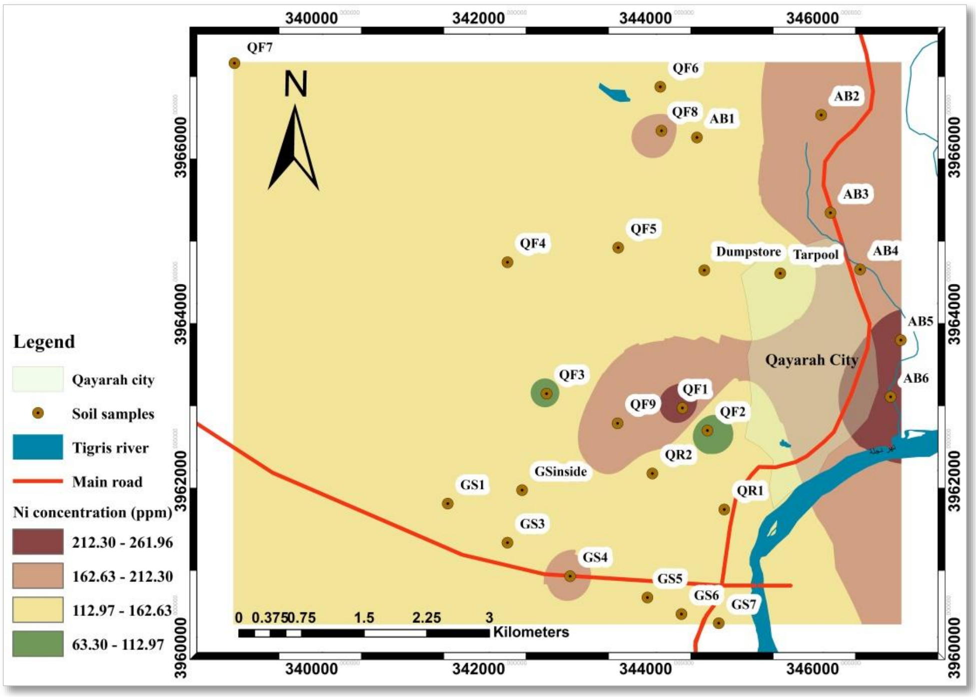

Fig. 6. Spatial distribution of Nickel (Ni) in study area.

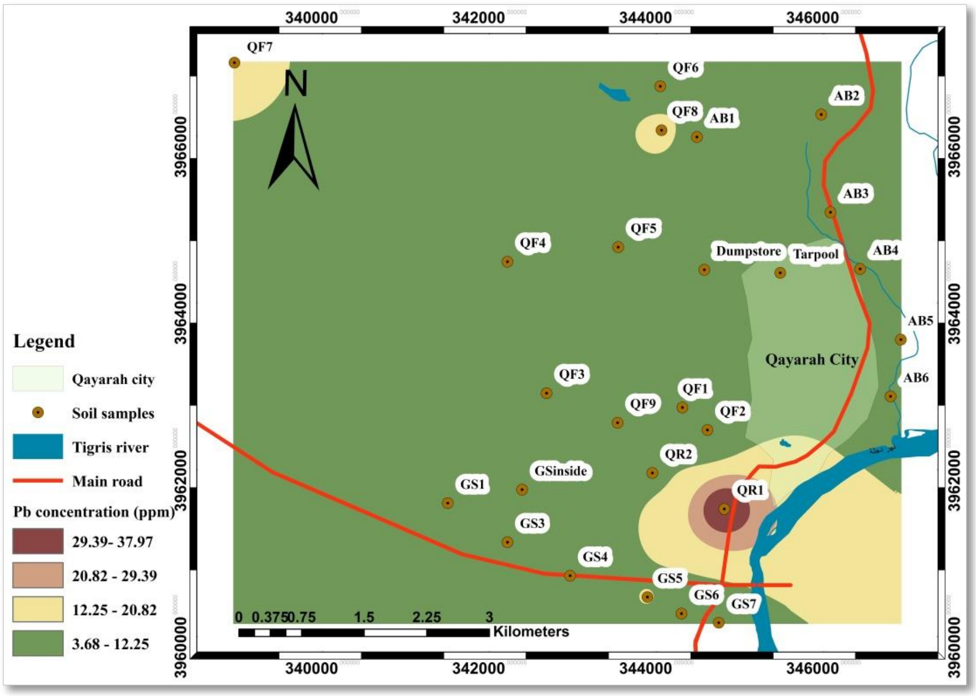

Fig. 7. Spatial distribution of lead (Pb) in study area.

Table 5. Enrichment factor, contamination factor and pollution load index.

Samples	Elements												
	Enrichment factor						Contamination factor						Pollution load index (PLI)
	As	Cd	Co	Cr	Ni	Pb	As	Cd	Co	Cr	Ni	Pb	
QF1	12.03	1.57	3.56	4.74	12.09	1.54	3.48	0.46	1.03	1.37	3.49	0.44	0.942
QF2	20.41	3.34	3.16	3.97	8.69	2.91	1.98	0.33	0.31	0.39	0.84	0.28	0.383
QF3	14.50	2.75	3.01	3.80	8.09	2.69	2.53	0.48	0.53	0.66	1.41	0.47	0.620
QF4	17.09	4.76	2.93	3.55	7.53	2.33	3.68	1.03	0.63	0.77	1.62	0.50	0.779
QF5	19.40	5.11	2.82	3.50	7.25	2.38	5.01	1.32	0.73	0.90	1.87	0.61	0.945
QF6	15.96	3.54	3.06	4.44	8.95	2.45	2.87	0.64	0.55	0.80	1.61	0.44	0.672
QF7	15.16	4.85	3.13	4.07	8.67	4.07	3.77	1.21	0.78	1.01	2.15	1.01	1.021
QF8	15.25	5.32	3.22	4.63	9.55	4.68	3.94	1.38	0.83	1.20	2.47	1.21	1.111
QF9	13.07	3.99	3.21	4.44	10.64	2.42	3.46	1.06	0.85	1.18	2.81	0.64	0.997
GS1	14.36	4.34	3.05	4.29	8.53	2.58	3.44	1.04	0.73	1.03	2.05	0.62	0.910
GS3	14.48	4.55	3.19	4.65	9.14	2.93	3.12	0.98	0.69	1.00	1.97	0.63	0.861
GS4	15.20	5.06	3.17	4.08	9.10	3.08	3.83	1.28	0.80	1.03	2.29	0.78	1.022
GS5	16.61	5.48	3.11	4.95	8.59	4.73	3.35	1.11	0.63	1.00	1.73	0.95	0.886
GS6	16.32	5.01	3.28	4.89	9.07	3.24	3.37	1.04	0.68	1.01	1.87	0.67	0.905
GS7	17.03	4.68	3.61	7.49	9.49	2.82	3.46	0.95	0.73	1.52	1.93	0.57	0.897
AB1	15.71	4.70	3.01	4.18	8.96	2.51	2.96	0.89	0.57	0.79	1.69	0.47	0.710
AB2	13.76	4.44	3.27	4.23	9.43	2.66	3.71	1.20	0.88	1.14	2.54	0.72	1.047
AB3	13.26	4.27	3.17	4.07	8.92	2.66	3.82	1.23	0.91	1.17	2.57	0.77	1.078
AB4	12.97	4.37	2.95	3.69	8.22	2.69	4.10	1.38	0.93	1.17	2.60	0.85	1.119
AB5	13.93	4.25	3.46	4.38	9.87	2.80	4.23	1.29	1.05	1.33	3.00	0.85	1.208
AB6	14.00	3.28	3.70	4.66	10.97	2.58	4.46	1.05	1.18	1.49	3.49	0.82	1.258
QR1	17.27	7.61	3.02	4.12	8.13	12.78	3.95	1.74	0.69	0.94	1.86	2.92	1.214
QR2	18.99	5.79	3.22	5.47	9.31	4.10	4.13	1.26	0.70	1.19	2.03	0.89	0.998
GS inside	16.73	4.75	3.16	4.35	8.48	2.48	3.54	1.01	0.67	0.92	1.79	0.53	0.836
Tar pool	17.31	4.25	3.79	4.09	10.14	3.65	2.79	0.69	0.61	0.66	1.63	0.59	0.679
Dump store	14.64	2.83	3.18	3.11	7.63	2.65	3.49	0.68	0.76	0.74	1.82	0.63	0.825
Mean	15.59	4.42	3.21	4.38	9.05	3.32	3.56	1.03	0.75	1.01	2.12	0.76	0.92

Table 6. Oral, dermal and inhalation cancer risk.

Samples	Elements														
	Cancer Risk(oral)					Cancer Risk(dermal)				Cancer Risk(inhalation)					
	As	Cd	Cr	Ni	Pb	As	Cd	Cr	Ni	As	Cd	Co	Cr	Ni	Pb
QF1	1.6E-05	5.8E-08	1.2E-04	3.7E-05	1.5E-05	1.5E-06	3.8E-07	8.6E-04	8.9E-05	1.6E-04	9.6E-07	3.9E-04	9.7E-03	3.7E-04	4.1E-07
QF2	9.0E-06	4.2E-08	3.2E-05	8.9E-06	5.3E-08	8.7E-07	2.7E-07	2.4E-04	2.2E-05	9.1E-05	6.9E-07	1.2E-04	2.7E-03	8.9E-05	2.6E-07
QF3	1.2E-05	6.1E-08	5.6E-05	1.5E-05	8.7E-08	1.1E-06	4.0E-07	4.1E-04	3.6E-05	1.2E-04	1.0E-06	2.0E-04	4.7E-03	1.5E-04	4.3E-07
QF4	1.7E-05	1.3E-07	6.4E-05	1.7E-05	9.3E-08	1.6E-06	8.5E-07	4.8E-04	4.1E-05	1.7E-04	2.2E-06	2.4E-04	5.4E-03	1.7E-04	4.6E-07
QF5	2.3E-05	1.7E-07	7.6E-05	2.0E-05	1.1E-07	2.2E-06	1.1E-06	5.6E-04	4.8E-05	2.3E-04	2.8E-06	2.8E-04	6.4E-03	2.0E-04	5.6E-07
QF6	1.3E-05	8.1E-08	6.7E-05	1.7E-05	8.2E-08	1.3E-06	5.3E-07	5.0E-04	4.1E-05	1.3E-04	1.3E-06	2.1E-04	5.6E-03	1.7E-04	4.0E-07
QF7	1.7E-05	1.5E-07	8.5E-05	2.3E-05	1.9E-07	1.7E-06	1.0E-06	6.3E-04	5.5E-05	1.7E-04	2.6E-06	3.0E-04	7.1E-03	2.3E-04	9.3E-07
QF8	1.8E-05	1.8E-07	1.0E-04	2.6E-05	2.2E-07	1.7E-06	1.1E-06	7.5E-04	6.3E-05	1.8E-04	2.9E-06	3.2E-04	8.4E-03	2.6E-04	1.1E-06
QF9	1.6E-05	1.3E-07	9.9E-05	3.0E-05	1.2E-07	1.5E-06	8.8E-07	7.3E-04	7.2E-05	1.6E-04	2.2E-06	3.2E-04	8.3E-03	3.0E-04	5.9E-07
GS1	1.6E-05	1.3E-07	8.7E-05	2.2E-05	1.2E-07	1.5E-06	8.6E-07	6.4E-04	5.2E-05	1.6E-04	2.2E-06	2.8E-04	7.3E-03	2.2E-04	5.7E-07
GS inside	1.6E-05	1.3E-07	7.7E-05	1.9E-05	9.8E-08	1.6E-06	8.4E-07	5.7E-04	4.6E-05	1.6E-04	2.1E-06	2.6E-04	6.5E-03	1.9E-04	4.8E-07
GS3	1.4E-05	1.3E-07	8.4E-05	2.1E-05	1.2E-07	1.4E-06	8.1E-07	6.2E-04	5.0E-05	1.4E-04	2.1E-06	2.6E-04	7.1E-03	2.1E-04	5.8E-07
GS4	1.7E-05	1.6E-07	8.7E-05	2.4E-05	1.4E-07	1.7E-06	1.1E-06	6.4E-04	5.9E-05	1.8E-04	2.7E-06	3.1E-04	7.3E-03	2.4E-04	7.1E-07
GS5	1.5E-05	1.4E-07	8.4E-05	1.8E-05	1.8E-07	1.5E-06	9.2E-07	6.2E-04	4.4E-05	1.5E-04	2.3E-06	2.4E-04	7.1E-03	1.8E-04	8.8E-07
GS6	1.5E-05	1.3E-07	8.5E-05	2.0E-05	1.2E-07	1.5E-06	8.6E-07	6.3E-04	4.8E-05	1.5E-04	2.2E-06	2.6E-04	7.1E-03	2.0E-04	6.1E-07
GS7	1.6E-05	1.2E-07	1.3E-04	2.0E-05	1.1E-07	1.5E-06	7.9E-07	9.5E-04	4.9E-05	1.6E-04	2.0E-06	2.8E-04	1.1E-02	2.0E-04	5.3E-07
AB1	1.3E-05	1.1E-07	6.6E-05	1.8E-05	8.8E-08	1.3E-06	7.4E-07	4.9E-04	4.3E-05	1.4E-04	1.9E-06	2.2E-04	5.6E-03	1.8E-04	4.3E-07
AB2	1.7E-05	1.5E-07	9.6E-05	2.7E-05	1.3E-07	1.6E-06	9.9E-07	7.1E-04	6.5E-05	1.7E-04	2.5E-06	3.4E-04	8.1E-03	2.7E-04	6.6E-07
AB3	1.7E-05	1.6E-07	9.8E-05	2.7E-05	1.4E-07	1.7E-06	1.0E-06	7.3E-04	6.6E-05	1.7E-04	2.6E-06	3.5E-04	8.3E-03	2.7E-04	7.0E-07
AB4	1.9E-05	1.8E-07	9.8E-05	2.8E-05	1.6E-07	1.8E-06	1.1E-06	7.3E-04	6.6E-05	1.9E-04	2.9E-06	3.6E-04	8.2E-03	2.8E-04	7.8E-07
AB5	1.9E-05	1.6E-07	1.1E-04	3.2E-05	1.6E-07	1.9E-06	1.1E-06	8.3E-04	7.7E-05	1.9E-04	2.7E-06	4.0E-04	9.4E-03	3.2E-04	7.8E-07
AB6	2.0E-05	1.3E-07	1.2E-04	3.7E-05	1.5E-07	2.0E-06	8.7E-07	9.3E-04	8.9E-05	2.0E-04	2.2E-06	4.5E-04	1.0E-02	3.7E-04	7.6E-07
QR1	1.8E-05	2.2E-07	7.9E-05	2.0E-05	5.4E-07	1.7E-06	1.4E-06	5.9E-04	4.8E-05	1.8E-04	3.7E-06	2.6E-04	6.7E-03	2.0E-04	2.7E-06
QR2	1.9E-05	1.6E-07	1.0E-04	2.1E-05	1.7E-07	1.8E-06	1.0E-06	7.4E-04	5.2E-05	1.9E-04	2.7E-06	2.7E-04	8.4E-03	2.1E-04	8.2E-07
Tar pool	1.3E-05	8.8E-08	5.5E-05	1.7E-05	1.1E-07	1.2E-06	5.7E-07	4.1E-04	4.2E-05	1.3E-04	1.5E-06	2.3E-04	4.7E-03	1.7E-04	5.4E-07
Dump store	1.6E-05	8.6E-08	6.2E-05	1.9E-05	1.2E-07	1.5E-06	5.6E-07	4.6E-04	4.7E-05	1.6E-04	1.4E-06	2.9E-04	5.2E-03	1.9E-04	5.8E-07
Mean	1.6E-05	1.3E-07	8.5E-05	2.2E-05	7.0E-07	1.6E-06	8.5E-07	6.3E-04	5.4E-05	1.6E-04	2.2E-06	2.9E-04	7.2E-03	2.2E-04	7.0E-07

The range of organic matter concentration (OM%) is within (0.37%-4.96%) from very low to high, and the average value is 2.35%, as mentioned in Table (3). These are average values according to the classification Islam et al., (2020). Organic matter plays a role in the mobility of heavy elements, the decomposition of organic matter and the subsequent formation of carbonic acid. Higher soil acidity (lower pH values) favours the availability of cations in the soil (Proshad et al., 2019). Also, there is a non-significant relationship between OM and heavy elements as mentioned in Table (4) due to the slight alkalinity in the soil of the study area.

The range of (As) in soil is (3.57-9.02) ppm. The average value is (6.40) ppm as mentioned in Table (3). The largest is as in QF5 sample, because of the closest location of this sample to the EPF gas isolation station and it is located in the direction of the wind as shown in figure (1), while the lowest value is detected in sample QF2 because of the gypsious soil type as heavy elements do not prefer the gypsum phase This is consistent with Taqi (2021). Because of the concentration of (As) in the average crust is (1.8 ppm), arsenic has a large contamination factor and a large enrichment factor as listed in Table (4). The kinetics of arsenic (As+5) is slow due to strong adsorption by clays, hydroxides, and SOM in pH (7-9) (Kabata-Pendias, 2011). Arsenic has been called a "slow poison" or death metal because it slowly kills people every time it enters the human body (Proshad et al., 2019). Arsenic concentrations are associated with industrial activities (mineral processing, chemical works based on S and P metals, coal combustion) (Kabata-Pendias, 2011).

Cadmium is one of the most environmentally toxic metals that have harmful effects on all biological processes of humans, animals and plants (Kabata-Pendias, 2011). The range of cadmium in the soil is from (0.065 - 0.348) ppm, and the average is (0.205) ppm. The highest value of cadmium is in the QR1 sample near Qayarah refinery, and the lowest value is in the QF2 samples (gypsious soil) as shown in figure (2). The cadmium concentration in the average crust is (0.2 ppm). Cadmium in the study area is of low-to-moderate contamination factor and of minimal-to-moderate enrichment factor.

The higher cadmium concentration in the soil may be related to industrial activity, metal processing, atmospheric emissions, and cadmium-coated materials (Proshad et al., 2019).

The range of cobalt concentration in the soil is (7.68 - 29.5) ppm with an average of (18.68) ppm. Its greatest value is found in sample AB6, where the meeting point of Al-Ain Al-Bayda valley with the main sewage valley of Qayarah City. The lowest cobalt value is found in the sample QF2 (gypsious soil) as shown in figure (3). The average value of cobalt in the average crust is (28) ppm, as it has a moderate enrichment factor and a low contamination factor. A higher cobalt value content is found at the top of soils in arid and semi-arid regions, and the combustion of coal and other fuels is much less significant. Roadside soils and street dust are usually fortified with cobalt (Kabata-Pendias , 2011).

The range of chromium in the soil is about (38.6-152) ppm with an average of (101.46) ppm. The largest content of chromium is found in sample GS7, which is probably the last point of decline near the Tigris River, where the point of impact of the slope and the direction of the wind coming from the Qayarah power plant and the Qayarah refinery meet. The lowest Cr is found in the QF2 due to gypsious soil distribution as shown in figure (5). The average crust content of chromium is about (100) ppm, and it has a moderate to large enrichment factor and a low to medium contamination factor. When pH reaches 5.5 or more, chromium precipitates almost completely, and its compounds are very stable in soil. On the other hand, chromium (VI) is very unstable in the soil and its transmission is more easily in both acidic and alkaline media. Soil uptake of Cr is primarily associated with clay contents, and to a lesser extent with Fe (OH)2 and organic rich soil (Kabata-Pendias, 2011).

Nickel is considered a dangerous pollutant as it emanates from mineral processing plants and from the increased combustion of coal and oil (Kabata-Pendias, 2011). The range of nickel in the soil is (63.3-262) ppm with the average of (159.07) ppm. The highest value of nickel is in the AB6 sample, where the meeting point of Al-Ain Al-Bayda valley with the main sewage valley within Al-Qayarah City, and the lowest value is (63.3) ppm in the QF2 sample (gypsious soil) as shown in figure (6).

The average presence of nickel in the average crust is (75) ppm. Nickel has a significant enrichment factor and a moderate to large contamination factor. Nickel is abundant in all soil groups, with greater accumulation observed in oil stained, carbonaceous, and clay soils (Kabata-Pendias, 2011).

The soil is contaminated with lead (Pb) from the products and residues of the mining process and industrial activities. The extent of lead presence in the soil ranges from (3.68-38) ppm with an average of (9.93) ppm. The highest value is found in sample QR1 closest to the Qayarah refinery, while the lowest value is recorded in sample QF2 (gypsum soil) as shown in figure (7). Increasing acidity leads to an increase in the solubility of lead and its accumulation near the soil surface, mainly due to its uptake by soils rich in organic matter. The average concentration of lead in the average earth's crust is 15 ppm (Kabata-Pendias, 2011). Lead has a low to medium enrichment factor and a low to medium contamination factor. The difference in the content of lead values between one site and another within the study area is due to several reasons, including the difference in the acidity value of the soil that restricts the release of the element according to its degree and the extent of the spread of gypsious soil, as well as the proximity of the sampling site to oil processing foundation and sewage sites. The average concentrations of studied heavy metals lower than maximum permissible level in (WHO) as mentioned in table (3) except chromium's concentration higher than maximum permissible level in (WHO).

Pollution load Index (PLI) for samples (QF1, QF2, QF3, QF4, QF5, QF6, GS1, GS3, GS5, GS6, GS7, AB1, GS inside, Tar pool and dump store) indicates that they are uncontaminated, while the other samples are polluted and can be classified in the following order:

AB6 > QR1 > AB5 > AB4 > QF8 > AB3 > AB2 > GS4 > QF7 > QR2 > QF9.

The average total risk of cancer by ingestion (1.2 x 10-4) as mentioned in table (6) indicating a possible high risk of developing cancer, and the highest risk of developing cancer by ingestion is (1.8 x 10-4) in the QF1 sample as mentioned in table (6), because the model under study is close to the southern gas isolation station, while its lowest value (5.1 x 10-5) is observed in QF2 as mentioned in table (6). Perhaps the reason is the spread of gypsious soil in the area of current sample. The order of cancer risk by ingestion of the heavy elements under study is as follows: As> Ni > Cr > Cd > Pb pattern .The average total exposure to cancer through dermal exposure (2.6 x 10-4) indicates a high probability of developing cancer, noting that the highest value for the risk of dermal cancer is (1.15 x 10-2) in sample AB6, where the meeting point of Al-Ain Al-Bayda Valley with the main sewage valley for the city of Qayarah, while the lowest value is recorded (3.03 x 10-3) in the QF2 sample, which is characterized by the presence of gypsious soil. The order of cancer risk by dermal exposure to heavy metals is as follows: Cr > Ni > As > Cd. The average ratio of the total risk of cancer by inhalation is (7.85 x 10-3) indicating high potential cancer risk, largest value of inhalation cancer risk (1.15x10-2) is in AB6, where the meeting point of Al-Ain Al-Bayda Valley with the main sewage valley for the city of Qayarah, while lowest (3.03x10-3) is in QF2, which is characterized by the presence of gypsious soil. The order of summation of inhalation cancer risk of studied heavy metals is as follows: Cr>As>Ni>Co>Cd>Pb.

Conclusion

The application of the pollution load index (PLI) show that the current study area is generally below the level of pollution, with the exception of two locations, which are represented by AB6 and QR1 samples. The results of the contamination factor and the enrichment of heavy elements in the study area show the following order: As>Ni>Cd>Cr>Pb> Co. The main source of pollution was the oil and gas processing, so the remnant of industrial zone by-product, and human waste products in the city, and the increase in the mud content within the floodplain sediment of the Tigris River contributed to the adsorption of heavy elements. The natural geomorphology of studied area also contributed through the general direction of the slope of the topography, as well as the direction of the prevailing winds in the study area in the distribution of pollutants from the northwest towards the southwest. The high alkalinity of the soil reduces the dissolution of organic matter and the number of fixed pollutants in soil, and this is the reason for the decrease in the pollution load index, the enrichment and contamination factors. The average total carcinogenic risk by ingestion ($1.2x10^{-4}$) indicates a high environmental carcinogenic risk. The effect of carcinogenic pollutants by ingestion is in the following order: As>Ni>Cr>Cd>Pb, while the average total risk by skin exposure is ($1.2x10^{-3}$), which indicates a high environmental carcinogenic risk, as in the following order: Cr>Ni>As>Cd. The mean of the total carcinogenic risk by inhalation is (7.85×10^{-3}), which indicates a high environmental carcinogenic risk. The carcinogenic effect of the studied pollutants through skin exposure follows the order: Cr>As>Ni>Co>Cd>Pb. The general arrangement of the risk of exposure to heavy metals shows the following order: the carcinogenic risk by: inhalation > the carcinogenic risk by the skin > the carcinogenic risk by ingestion.

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