GEOCHEMISTRY AND ENVIRONMENTAL ASSESSMENT OF HEAVY METALS IN SURFACE SOIL IN AL-HAWIJA, SOUTHWEST KIRKUK

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ABSTRACT

Soil pollution adversely affects the safety and health of the human being. The main objective of the study is to determine the concentrations of heavy metals (As, Cd, Co, Cr, Cu, Fe, Mn, Mo, Ni, Pb and Zn) in surface soil in Al-Hawija, southwestern Kirkuk. Twenty-one samples were collected and analyzed by inductively coupled plasma-mass spectrometry (ICP-MS) to measure the content of heavy metals and assess the soil pollution by using the contamination factor, degree of contamination, geoaccumulation index, pollution load index and ecological risk index (RI). The results indicate that there is high pollution by lead, chromium and copper (78.8, 87.4 and 53.8 mg/kg) respectively, in industrial areas due to anthropogenic sources with the presence of significant ecological risk (Er) of the lead (116) in site S7, due to its high concentrations, while size fraction analysis indicated that all heavy metals are concentrated in the fine parts as a result of adsorption processes by clay minerals.

Keywords: Heavy metals; Pollution; Statistical analysis; Size fraction

INTRODUCTION

Environmental pollution with heavy metals is defined as a background increase in the surface sediments of urban areas caused by anthropogenic activities (Hanfi et al., 2019). Heavy metals are defined as metals with a density greater than 7 g / cm³ (Bjerrum, 1936). Ali and Khan (2018) suggested a more comprehensive definition of the “heavy metals as the element that occurs naturally and has atomic number is greater than 20 and the density is greater than 5g /cm³”. Thousands papers have been published in international journals on various aspects of heavy metals pollution, “heavy metals” has been used in general for elements and metals related to environmental pollution, toxic effects and health risk to organisms and people (Ali and Khan, 2018), because of its ability to accumulate in the human body and causing damage to some of its organs (Lee et al., 2007; Lohani et al., 2008). Soil pollution poses a major threat to

environmental sustainability (Su, 2014), and affects the well-being and economy of society (Jónsson et al., 2016). According to World Health Organization, air, water and soil pollution, chemical materials exposure, climate change, and ultraviolet rays may contribute to more than 100 diseases, as human health is associated with the surrounding environment (WHO, 2016). Soil is one of the most important basic units for all terrestrial ecosystems, as it provides a chemical and biological link in biogeochemical cycles (Pietrzykowski et al., 2014). In addition to the main elements such as C, P, N, Ca, Mg and S, heavy metals also participate in biogeochemical cycles that have toxic effects (Kabata-Pendias and Mukherjee, 2007), and the heavy metals accumulation is affected by environmental variables in the soil, which include source rocks and soil properties (Albanese et al., 2015) mobility and availability depend on the origin of heavy metals, as the metals with lithogenic origin are low in motion due to their dominantly linked with the primary minerals, by contrast, the heavy metals anthropogenic sources that are mostly highly mobile (Kabata-Pendias, 1993). The mobility, activity, and availability of the element also depend on the specifications of that element and the chemical and mineral soil properties such as organic material, clay percent, and pH (Di Giuseppe et al., 2014; Othman et al., 2020). The size fraction affects its distribution in the soil as the clay have high adsorption to these metals due to its possession of large surface area (Sherene, 2010). The Natural sources of heavy metals are geological weathering and erosion of soil, and airborne dust, (Men et al., 2018), under certain geological conditions, releases of heavy metals may occur from volcanic eruptions in the form of gases or lava or from the sea-salt sprays and wind-borne soil particles, fires forests are also natural sources (Masindi and Muedi, 2018) but the anthropogenic sources are mining and disposal of untreated or partially treated liquid pollutants and various industries such as pharmaceutical and excessive use of fertilizers and pesticides containing concentrations of heavy metals (Karbassi and Amirnezhad, 2004; Al-Jaberi et al., 2016). The aims of this research are to study the geochemistry and environmental pollution assessment of heavy metals in surface soil that resulting from anthropogenic activities in Al-Hawija area.

MATERIALS AND METHODS

Study Area

Al-Hawija is located between the longitude (43.755 - 43.79 E) and latitude (35.43 – 35.315 N) away 65 km from Kirkuk to the southwest (Fig. 1), with a population of 118215 people (Ministry of Municipalities and Public Works, 2014). Tectonically, the town falls within the range of low folded zone in the Hemrin-Makhul subzone (Jassim and Goff, 2006). Stratigraphically, covered with quaternary deposits consisting of river deposits forming

floodplains and there is no formation exposed on the surface (Buringh, 1960). The soil of this region in general is silty formed from weathering and sedimentation processes during different stages of river floods (Al-jumaly, 2007).

Fig. 1. Map of the study area and sampling location

Sampling and Chemical Analysis

Twenty-one samples were collected from surface soil (0-20 cm) in Al-Hawija (Table 1) at 10 September 2019. Every 1kg of the sample is collected by Auger and saved in plastic container. In laboratory work the samples were dried using an electric oven on 55°C till completely dry and then grinded and sifted by sieve mesh 200 (75 Micron) then the samples are divided into three groups based on the type of land use in residential, commercial and industrial areas, then 0.5 grams of each sample was sent to ACME laboratories in Canada for the chemical analysis by inductively coupled plasma mass spectrometry (ICP-MS) (Table 2).

Size Fraction

For the purpose of studying the concentration of heavy metals and understanding their behavior in the size fraction of the study area, six soil samples (S1, S5, S9, S11, S15 and S20) were chosen and separated volumetrically into Sand, Silt and Clay using a method of pipet analysis according to (Carver, 1971) and sent to ACME laboratories for the purpose of analyzing the concentrations of heavy metals in them.

Statistical Analysis

Correlation coefficient

The correlation coefficient was calculated to find the correlations between heavy metals, as it is one of the most common statistical processes in the interpretation of geochemical relations between elements and is used to determine the possibility of a similar source of two or more elements (Wang et al., 2012).

Table 1. Longitude and latitude of the samples

Samples	Areas	Longitude	Latitude
S1	Industrial	43°47'4.12"	35°19'18.33"
S2	Industrial	43°47'9.17"	35°19'23.15"
S3	Industrial	43°47'1.13"	35°19'26.64"
S4	Industrial	43°47'8.84"	35°19'27.28"
S5	Industrial	43°46'52.17"	35°19'19.19"
S6	Industrial	43°47'6.00"	35°20'37.00"
S7	Industrial	43°47'4.97"	35°19'24.04"
S8	Commercial	43°47'8.25"	35°20'12.79"
S9	Commercial	43°47'4.75"	35°20'12.07"
S10	Commercial	43°46'18.74"	35°19'37.75"
S11	Commercial	43°46'4.75"	35°19'46.63"
S12	Commercial	43°45'56.91"	35°19'33.44"
S13	Commercial	43°45'42.84"	35°19'3.01"
S14	Residential	43°46'41.91"	35°19'15.05"
S15	Residential	43°46'53.71"	35°20'8.40"
S16	Residential	43°45'27.22"	35°19'15.55"
S17	Residential	43°45'44.46"	35°19'24.46"
S18	Residential	43°46'10.55"	35°19'26.37"
S19	Residential	43°46'2.56"	35°19'10.58"
S20	Residential	43°46'34.29"	35°19'26.84"
S21	Residential	43°46'53.27"	35°19'47.47"

Table 2. Detected limit, accuracy and precision

Metals	Unit	Minimum Detected Limit	STD BVGEO01 Standard	STD BVGEO01 Expected	Soil S1	Repeated Soil S1
As	ppm	0.1	122.5	121	5.8	5.6
Cd	ppm	0.01	6.43	6.5	0.46	0.52
Co	ppm	0.1	25	25	13.3	13.5
Cr	ppm	0.5	167.5	171	77.5	80.5
Cu	ppm	0.01	4380.09	4415	55.62	55.18
Fe	%	0.01	3.63	3.7	2.23	2.23
Mn	ppm	1	719	733	570	589
Mo	ppm	0.01	10.57	10.8	1.15	1.17
Ni	ppm	0.1	154.5	163	94.5	95.7
Pb	ppm	0.01	191.01	187	68.41	67.05
Zn	ppm	0.1	1719.7	1741	184.4	185.6

The higher correlation coefficient value (r) it is possible to rely Accordingly, the strong positive relationship indicates the similarity of the source to those elements, but if the relationship is strong negative, it may indicate different sources, while weak relations, the value of the value (r) from zero indicate the diversity of sources and have no statistical significance (Guo et al., 2019).

Factor analysis

Factor analysis were done using Microsoft Excel (XLSTAT 2019) program as it is one of the most important statistical methods for analyzing multiple variables, as it works to reduce the number of variables while preserving the variations of the original variables and giving joint factors that simplify the relationship between the variables and help explain them.

Indices Assessment

Contamination factor (CF) and degree of contamination (DoC)

The contamination factor is established by Hakanson (1980) and calculated by equation 1, and it is classified into ranges as in Table 3 which can be:

$$CF_i = \frac{C_i}{B_i} \quad (1)$$

Where C_i is the concentration of the element in the soil and B_i is the background of the element in the soil. In this study, the average concentration of elements in the soil was used according to what was previously published (Kabata-Pendias and Mukherjee, 2007). Since the contamination factor only reveals contamination of a single element, the sum of the pollution factors for all the elements examined represents the DoC in the environment (Hakanson, 1980; Inengite et al., 2015), and is divided into four categories as in the Table 3 and calculated by equation 2:

$$DoC = \sum_i^n CF \quad (2)$$

Where CF contamination factor and n number of heavy metals in the study .

Geoaccumulation index (Igeo)

The Geoaccumulation index is proposed by Muller (1969) to assess soil contamination with heavy metals which depends on the concentration of elements in its background of the environment including very low human inputs, and is calculated by multiplying the background value concentration by a factor of 1.5 to get the upper limit than lowest class as in equation 3 (Kowalska et al., 2018; Muller, 1969; Wei and Yang, 2010).

$$I_{geo} = \log_2(C_i/1.5B_i) \quad (3)$$

Where C_i is the concentration of the measured element in the soil and B_i is the background for it in the soil, and the constant 1.5 is added to analyze the natural variation in the environmental units to discover very small human impacts, and it is classified into seven classes as in Table 3.

Table 3. Classification of environmental indicators

Index	Value	Environmental risk grade	Reference
CF	$CF < 1$	Low contamination factor	(Hakanson, 1980)
	$1 \leq CF < 3$	Moderate contamination factor	
	$3 \leq CF < 6$	Considerable contamination factor	
	$CF \geq 6$	Very high contamination factor	
DoC	$Doc < 8$	Low Doc	(Hakanson, 1980)
	$8 \leq Doc < 16$	Moderate Doc	
	$16 \leq Doc < 32$	Considerable Doc	
	$Doc \geq 32$	High Doc	
Igeo	$I_{geo} \leq 0$	Uncontaminated (Class 0)	(Muller, 1969)
	$0 < I_{geo} \leq 1$	Uncontaminated to moderately contaminated (Class 1)	
	$1 < I_{geo} \leq 2$	Moderately contaminated (Class 2)	
	$2 < I_{geo} \leq 3$	Moderately to heavily contaminated (Class 3)	
	$3 < I_{geo} \leq 4$	Heavily contaminated (Class 4)	
	$4 < I_{geo} \leq 5$	Heavily to extremely contaminated (Class 5)	
	$5 < I_{geo}$	Extremely contaminated (Class 6)	
PLI	< 1	Not pollution	(Tomlinson et al., 1980)
	$= 1$	Baseline levels of pollution	
	> 1	Pollution	
Er	$Er < 40$	Low potential ecological risk	(Hakanson, 1980)
	$40 \leq Er < 80$	Moderate potential ecological risk	
	$80 \leq Er < 160$	Considerable potential ecological risk	
	$160 \leq Er < 320$	High potential ecological risk	
	$Er \geq 320$	Very high ecological risk	
RI	$RI < 150$	Low ecological risk	(Hakanson, 1980)
	$150 \leq RI < 300$	Moderate ecological risk	
	$300 \leq RI < 600$	Considerable ecological risk	
	$RI \geq 600$	Very high ecological risk	

Pollution load index (PLI)

Defined as criterion of the total pollution level at the sample site. Developed by Tomlinson et al. (1980). It is possible to estimate heavy metal pollution levels for different sampling sites, and can calculated by equation 4:

$$PLI = (CF_1 \times CF_2 \times \dots \times CF_n)^{1/n} \quad (4)$$

Where n is the number of metals studied, CF is a contamination factor and PLI is classified into three categories (Table 3).

Potential ecological risk index (RI)

It is the an indicator used to determine the potential environmental risks of heavy metals on living organisms in the environment (soil, water and air) (Al-Anbari et al., 2015; Guan et al., 2014; Kowalska et al., 2018 and Tang et al., 2015).

RI is calculated by the sum of the Ecological Risk (Er) of each sample by equation 5 and 6 (Hakanson, 1980).

$$E_r = T_r \times CF \quad (5)$$

$$RI = \sum_i^n E_r^i \quad (6)$$

Where CF represents the contamination factor, Tr represents the coefficient of toxicity of the elements which is As = 10, Cd = 30, Cr = 2, Cu = 5 and Pb = 5 (Hakanson, 1980), n is number of the elements, and was previously classified into the four categories (Table 3)

RESULTS AND DISCUSSION

Geochemical Distribution of Heavy Metals in Surface Soil

Arsenic (As)

It's average in the soil was 6.4 mg/kg (Table 4) which is higher than the background value for it in the earth crust, which is 1.8 mg/kg (Kabata-Pendias and Mukherjee, 2007), the highest concentration was in the industrial areas in the site of S6 represented by Technical Institute workshop which attacked by Military operations (Dvorak et al., 2020), while the sites S2, S3, and S4, may be resulted by industrial waste product from repairing workshops (Thornton, 1996), but in the commercial area was its highest concentration in the site S8 and this is also due to the military operation because it represents the Deanship of the Technical Institute in the northeast of the town (Fig. 2) while the site S14 was related to the heavy traffic because it represents the bus station area in the south the town (Nannoni et al., 2011), and the highest concentration of arsenic in residential areas was at the sites S15 and S21 may be related to the military operations at site S15, while site S21 may be due to the use of pesticides (Thornton, 1996), generally the arsenic in the industrial, commercial and residential areas was relatively high, and this explains the role of military operations.

Cadmium (Cd)

The average concentration of the cadmium in the surface soil of Al-Hawija town (0.31mg/kg) (Table 4) which is higher than its background value for the Earth's crust (0.1 - 0.2mg/kg), As for the average soil concentration (0.5mg/kg) it was relatively normal (Kabata-Pendias and Mukherjee, 2007), the highest concentration was in the industrial area (site S1 and S7) (Fig. 2) due to their proximity to the grain mill and repairing garage as they have chemical's waste product plus heavy traffic (Jaradat and Momani, 1999), and in the site S3 Cd source was due to the military operation there, this is compatible with Islam et al. (2016) as it was stated that the shooting areas increase the percentage of cadmium in the surface soil, in the commercial

areas the highest concentration was in the site S14 (bus station) due to heavy traffic (Yakeem and Onifade, 2012), in residential areas it reached 0.52mg/kg in the site S21 due to the use of fertilizers and pesticides as well as the proximity from an electric generator (small farm) (Adriano, 2001), In general the concentration of cadmium in industrial areas was higher than that of residential and commercial areas, as it reached 0.33> 0.32> 0.26, respectively.

Table 4. Concentrations and of heavy metals in surface soil samples

Sample No	As	Cd	Co	Cr	Cu	Fe	Mn	Mo	Ni	Pb	Zn
	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	%	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg
Industrial Area											
S1	5.8	0.46	13.3	77.5	55.62	2.23	570	1.15	94.5	68.41	184.4
S2	6.7	0.33	18.9	97.2	105.94	3.21	828	1.42	136.2	49.37	186.9
S3	6.7	0.39	16.5	85.1	34.89	2.57	578	0.77	121	53.23	108.6
S4	6.7	0.24	14.5	76.8	23.27	2.29	561	0.62	106.1	8.05	46.5
S5	6.2	0.18	18.1	91.8	38.35	2.78	727	0.7	144.7	14.65	55.3
S6	7.3	0.31	17.5	89.9	27.85	2.62	630	0.8	121.5	9.59	57.8
S7	6.6	0.46	17.9	93.6	90.48	2.59	708	1.55	124.6	347.9	175.4
Average	6.6	0.3	16.7	87.4	53.8	2.6	657.4	1.0	121.2	78.8	116.4
Commercial Area											
S8	7.5	0.28	17.6	89.3	27.24	2.5	609	1.06	119.3	9.82	53.9
S9	6.2	0.26	17.6	90.3	43.89	2.67	699	0.47	136.9	13.37	136.2
S10	6.9	0.27	16.6	79.7	26.15	2.41	651	0.61	122.6	9.33	51.8
S11	6.4	0.32	18.7	93.3	34.16	2.87	669	0.56	134.5	12.11	69.7
S12	6.1	0.27	15.6	71.5	30.89	2.22	713	0.83	103.4	18.46	80.9
S13	6	0.16	17.5	87.2	26.26	2.52	718	0.39	133.1	8.04	47.9
S14	7.3	0.31	17.6	89	32.61	2.47	591	0.85	116.2	27.88	68
Average	6.6	0.3	17.3	85.8	31.6	2.5	664.3	0.7	123.7	14.1	72.6
Residential Area											
S15	6.7	0.32	17.5	93.1	40.55	2.74	663	0.76	125.8	41.23	81.5
S16	6.3	0.24	16.9	80.6	27.92	2.29	598	0.87	113.9	18.65	61.2
S17	6.2	0.36	16	81.1	38.81	2.28	663	0.6	110.2	78	134.4
S18	6.2	0.27	16.1	80.1	28.42	2.4	710	0.53	117.6	17.03	82.2
S19	6.1	0.29	16.2	89.7	32.54	2.6	702	0.47	119.4	28.04	77.56
S20	5.7	0.27	17.2	88.8	33.09	2.57	631	0.45	125.8	68.75	101.2
S21	6.7	0.52	17.6	87	31.26	2.5	614	0.68	114.4	24.38	82.2
Average	6.3	0.3	16.8	85.8	33.2	2.5	654.4	0.6	118.2	39.4	88.6
Max	7.5	0.52	18.9	97.2	105.94	3.21	828	1.55	144.7	347.9	186.9
Min	5.7	0.16	13.3	71.5	23.27	2.22	561	0.39	94.5	8.04	46.5
Average	6.4	0.31	16.9	86.3	39.5	2.54	658.7	0.77	121.0	44.1	92.5
(Kabata-Pendias and Mukherjee, 2007)	1.8	0.5	4.5 – 14	54	20	3.5	10 - 9000	1.8	22	25	64

Fig .2. Spatial distribution of As, Cd, Co, Cr, Cu, Fe, Mn and Mo in the top soil of the study area

Cobalt (Co)

Its average concentration was 16.9 mg/kg (Table 4), which is higher than the background of the soil (4.5 to 14 mg/kg) (Kabata-Pendias and Mukherjee, 2007), it was relatively similar in the most of sites of industrial area, it was higher in the site S2 and S7 (18.9, 18.1 mg/kg)

respectively, due to car's emissions and industrial liquid waste product (oils and chemical detergents) (Al-Khashman, 2007). For the commercial areas its concentration reached was 18.7mg/kg in the site S11 (Fig. 2) which represent vegetables and fruits store, phosphatic fertilizers are a source of cobalt that may be carried with these crops (Zadnipyany et al., 2017). In residential areas (S21 and S15 sites) its concentration was 17.6 mg/kg and 17.5 respectively, due to sewage sludge and the construction debris (Leyssens et al., 2017), in the commercial areas that's located in the east and north of the town was higher than it is in residential and industrial areas.

Chromium (Cr)

The average concentration of the Cr in the surface soil (86.3 mg/kg) (Table 4) was higher than the background value in the soil and reached 54 mg/kg (Kabata-Pendias and Mukherjee, 2007), the highest concentration of the element in the industrial areas of the site S2 was due to the liquid waste product containing dyes, because the chromium is used in the production of steel, electroplating and some specialized chemical materials (Ertani et al., 2017), sites S7 and S5, which may also due to chemical waste product and dyes, while residential areas have higher concentration in the site S11 and S9 as a result of military operations against terrorism (Mishra and Bharagava, 2016; Idzelis et al., 2006), which lead to an increase in mineral waste in the surface soil, in residential areas the chromium component was concentrated in the north of Al-Hawija in site S15 (Fig. 2), which also returns to the Technical Institute near the student's housing, (attacked by military operations), in general the average concentration of chromium in the industrial areas (87.4 mg/kg), which is higher than that in the commercial and residential areas (85.7 mg/kg).

Copper (Cu)

The average of copper concentration was 39.53 mg/kg (Table 4) which is higher than the background value of 20 mg/kg (Kabata-Pendias and Mukherjee, 2007), as the highest concentration was in the southeast of the town (Fig. 2) specifically at S2 and S7 sites and this may be related to the liquid and solid industrial waste there (Rajaganapathy et al., 2011), and it's also appeared in high concentration in the S1 site and this may be due to its proximity to the high way (Kabadayi and Cesur, 2010). For the residential areas, its highest concentration was in the S15 site, which is near the student housing of the Technical Institute, or may be due to the military operations in the area. In the commercial areas reached its highest concentration in the S9 site (near the building of the Deanship of the Technical Institute, Al-Hawija), due to military operation occurred there (Dvorak et al., 2020; Vasarevičius and Greičiūte, 2004), and

in general the industrial areas show higher concentrations than the residential and commercial areas, its sequence was $53 > 33 > 31$, respectively.

Iron (Fe)

Its average concentration in surface soil reached 2.54% (Table 4) and these concentrations are less than the background value of the elemental concentration in the soil, which is 3.5% (Kabata-Pendias and Mukherjee, 2007), its concentration in industrial areas in the site S2 is 3.2 % (Fig. 2), this is probably due to the presence of waste product of cars repairing garage, in addition to the results of the frictions of the brakes (Thorpe and Harrison, 2008), for the rest of the industrial and commercial sites of residential areas all of them were less than 2.87% and this percentage is relatively low because iron is a widespread element in the soil as it is the third most common metal in the Earth's crust (Wedepohl, 1995), in general the variation in rates was relatively slight as the element showed a concentration in soil sites of industrial areas were higher than the commercial and residential areas, which was $2.61 > 2.52 > 2.48$, respectively.

Manganese (Mn)

Its average soil surface concentration was 658mg/kg (Table 4) which is within soil background value of 10 - 9000 mg/kg (Kabata-Pendias and Mukherjee, 2007). There is no contamination of manganese in the surface soil in Al-Hawija town.

Molybdenum (Mo)

The average of molybdenum concentration was 0.76 mg/kg (Table 4) which is less than background in the soil (1.8mg/kg) (Kabata-Pendias and Mukherjee, 2007), it was the highest concentrations in the industrial areas in the site of S7 and S2 as compared to other sites (Fig. 2) and this may be due to liquid waste originating from car's repair and the use of chemical detergents (Liang et al., 2017; Xu et al., 2013). For the commercial and residential areas, Mo concentration was relatively normal to its concentration in the background, in general the rate in the industrial areas was higher than that the commercial and residential areas, its sequence was $1 > 0.68 > 0.62$, respectively.

Nickel (Ni)

Its average concentration in soil reached 121 mg/kg (Table 4), which is higher than the background value of the element (20mg/kg) (Kabata-Pendias and Mukherjee, 2007), Ni is highly affected by paedogenic (Sun et al., 2018) it was observed in the town but more in the residential areas (located in the center, north and the southeast area of the town), its highest concentration in the industrial site S2 and S5 (136.2, 144.7 mg/kg) respectively (Fig.3), due to its waste product, Terry and Banuelos (2000) mentioned that nickel is used in steel industry, nickel-cadmium batteries and in electroplating. In commercial and residential areas its highest

concentration was in the sites S 20, 15, 13, 11 and 9 respectively this may be due to domestic waste and car's emissions (Rathor et al., 2014), generally the concentration of nickel in the soil of commercial areas was higher than in industrial and residential areas, which was $123.7 > 121.2 > 118.1$ respectively (Source rocks may be rich in nickel)

Lead (Pb)

The average of the lead concentration was 44.11 mg/kg (Table 4) which is higher than globally published (Kabata-Pendias and Mukherjee, 2007) which is 25 mg/kg and it was in high concentration in the southeastern part of the town (Fig. 3) in particular site S7, due to its proximity to the repair and garage dyeing car that have high emission of exhausts, liquid waste of oils and fuels (Awadh and Al-Hamdani, 2019; Liang et al., 2017). S1 site is the second area of the higher concentration due to its proximity to the grain mill that's work by fuel contain lead (García-Lestón et al., 2012) or may be due to the military operations occurred there (Vasarevičius and Greičiūtė, 2004), and in the site S2 the concentration of the lead was reached 49.36 mg/kg and the reason due to its proximity to the car washing garage, for the site S3 which has a concentration of 53.23 mg/kg. This is due to its proximity to Al-Hawija electric substation and Al-Taleea fuel station (de Miguel et al., 1997), the fuel contains lead increase its emission, in residential areas it's higher concentration in the site S17 due to its proximity to an electric generator, for the commercial areas the higher concentration at the site S14, which represents bus station (high traffic emissions), generally the industrial areas show higher concentrations than in commercial and residential areas, its sequence was $78.75 > 39.44 > 14.14$, respectively.

Zinc (Zn)

The average concentration of zinc in Al-Hawija surface soil is 92.55 mg/kg (Table 4), which is higher than its average in the soil (64mg/kg) (Kabata-Pendias and Mukherjee, 2007), the highest concentration in the industrial areas are in sites S2, S1 and S7 (Fig. 3), This is may be due to the friction of the tires and multiple use of brake as zinc is used in their manufacture (Taghavi et al., 2019), In addition to that zinc can be produced from car's oil, cooling fluids and road erosion (Saeedi et al., 2009), The commercial area was the highest concentration (136.2 mg/kg) in the site S9 that's may be due to military operations (attacked by heavy weapons) (Islam et al., 2016), and in residential areas the highest concentration was 134.4 mg/kg in the site S17 due to its proximity to un electric generator and the presence of domestic waste product (Al-Jumaily and Rasheed, 2018), in general the rate of its concentration in industrial areas was higher than that in residential and commercial areas $116.4 > 88.6 > 72.6$, respectively.

Fig. 3. Spatial distribution of Ni, Pb and Zn in the top soil of the study area

Size Distribution Effect

The size of soil particles has an important and effective role in determining the content and movement of heavy metals in the soil (Rinklebe et al., 2016; Shaheen and Rinklebe, 2014), as these elements are concentrated in the clay part more than in the silty and sandy part (Bhattacharyya and Gupta, 2008), this is due to the fact that iron oxides, manganese, clay minerals and organic matter are concentrated in the fine parts that adsorption, absorption, sedimentation, and ion exchange of heavy metals (Awadh et al., 2015; Liu et al., 2018), Gong et al. (2014) stated that there is an inverse proportion between heavy metal concentration and the size of the soil grains, the soil grain was of silt loam category and all the studied heavy metals were focused on very fine granular, as their concentration increased in clay more than silt and sand, the concentrations of copper, zinc and lead in the clay fraction were increased due to its adsorption on clay minerals, and those metals were adsorbed on Bentonite and Montmorillonite minerals (Table 5) (Jin et al., 2014; Akpomie and Dawodu, 2016; El Adraa et al., 2017), while nickel rose in Clay as a result of replacing iron and magnesium in the crystal structure of kaolinite and montmorillonite minerals (Addy et al., 2012; Mohammed and Al-Mashaikie, 2018), and the cobalt is adsorbed on the surfaces of smectite and clay minerals (Shawabkeh et al., 2007), also cadmium may be was adsorbed by kaolinite (Awadh and Yousif, 2015), arsenic and cobalt may be concentrated in the clay part due to the high adsorption of clay minerals in general (Argyaki et al., 2017; Xu et al., 2019).

Table 5. Results of the analysis of the heavy metals in size distribution for the soil

Size	Metals	Mo	Cu	Pb	Zn	Ni	Co	Mn	Fe	As	Cd	Cr
	Units	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	%	mg/kg	mg/kg	mg/kg
Sand 8.9%	Max	1.76	99.9	47.79	166.8	120.7	16.3	726	2.94	5.9	0.38	92.1
	Mine	0.26	19.69	6.03	35.8	95.2	12.1	582	2.18	4	0.16	74.3
	Average	0.62	39.08	21.91	81.1	111.2	14.4	621	2.44	4.9	0.27	79.4
Silt 79.5%	Max	1.13	83.92	56.53	154.5	124.5	16.3	717	2.91	6.2	0.32	84.8
	Mine	0.35	22.2	6.88	38.9	113.9	14.6	552	2.28	5	0.14	79
	Average	0.57	39.95	23.23	87.7	118.8	15.4	614	2.49	5.4	0.25	81.4
Clay 11.5%	Max	1.65	156.	114.5	271.8	216.1	31	1153	4.08	10.6	0.4	133.6
	Mine	0.61	50.57	19	90.9	170.6	23.7	790	3.53	8.3	0.28	122.8
	Average	1.04	77.53	54.95	155.6	187.2	26.8	962	3.82	9.4	0.36	127.4

Statistical Analysis

Correlation coefficient

The results of the correlation coefficient showed that the metals were divided into two groups (Table 6) where molybdenum was correlated with copper, lead, zinc and cadmium with positive relationships, and this may be due to the geochemical affiliation of molybdenum with copper in the copper minerals carrying it (Jeldres et al., 2017) and with the zinc and cadmium due to the similarity of their industrial sources (Liang et al., 2017; Wang et al., 2007). As for the correlation of lead with zinc, it may be due to the similarity of their anthropogenic of fuel combustion and tire friction (Lee et al., 2005; Al-Hamdani et al., 2016).

Table 6. Correlation coefficient of heavy metals in the top soil

	Mo	Cu	Pb	Zn	Ni	Co	Mn	Fe	As	Cd	Cr
Mo	1										
Cu	.775**	1									
Pb	.612**	.641**	1								
Zn	.595**	.837**	.600**	1							
Ni	-.131	.230	-.017	-.079	1						
Co	.099	.274	.080	-.087	.833**	1					
Mn	.129	.542*	.138	.282	.592**	.490*	1				
Fe	.199	.542*	.039	.217	.812**	.775**	.604**	1			
As	.327	-.037	-.063	-.287	.037	.336	-.245	.163	1		
Cd	.485*	.407	.510*	.589**	-.389	-.123	-.247	-.039	.126	1	
Cr	.211	.462*	.236	.176	.776**	.825**	.405	.875**	.260	.066	1

** Correlation is significant at the 0.01 level

* Correlation is significant at the 0.05 level

Nickel is positively correlated with cobalt, manganese, iron and chromium, nickel correlation with cobalt may be due to the entry of the two elements in the steel industry and some household appliances (Ertani et al., 2017), or it may be attributed to the adsorption of these elements on clay minerals as well as the presence of iron oxides in its crystal structure (Gitari, 2014).

Factor analysis

Four factors were chosen, which explain 74.04% of the total variance of the variables (Table 7)

Table 7. Loading factors

	F1	F2	F3	F4		F1	F2	F3	F4
Mo	-0.166	0.781	-0.164	-0.293	SO ₃	-0.604	0.204	0.351	0.073
Cu	0.157	0.941	0.111	-0.120	Cl	-0.363	-0.363	0.111	-0.374
Pb	-0.113	0.747	-0.121	-0.068	K ₂ O	0.671	-0.175	-0.559	0.321
Zn	-0.138	0.882	0.129	0.229	CaO	-0.747	0.120	-0.081	0.220
Ni	0.891	0.086	0.198	-0.224	TiO ₂	0.856	-0.064	0.040	0.085
Co	0.820	0.211	-0.200	-0.219	V ₂ O ₅	0.449	-0.041	0.467	0.417
Mn	0.572	0.393	0.517	-0.078	Cr ₂ O ₃	0.310	-0.070	0.837	0.029
Fe	0.830	0.395	-0.034	-0.166	MnO	0.622	0.179	0.665	0.012
As	0.099	-0.075	-0.638	-0.528	Fe ₂ O ₃	0.884	0.250	0.062	-0.144
Cd	-0.249	0.551	-0.567	0.351	LOI	-0.312	0.133	-0.171	-0.612
Cr	0.755	0.431	-0.202	-0.148	PH	0.283	-0.238	-0.348	-0.059
Na ₂ O	-0.450	0.143	0.782	-0.038	O.M	0.250	0.558	-0.359	0.198
MgO	0.799	-0.498	-0.164	-0.022	Eigenvalue	9.428	4.821	4.221	2.264
Al ₂ O ₃	0.852	-0.297	-0.264	0.032	Variability %	33.670	17.217	15.076	8.085
SiO ₂	0.840	-0.187	0.250	0.274	Cumulative%	33.670	50.887	65.963	74.048
P ₂ O ₅	0.045	0.178	-0.405	0.746					

Factor 1

There was a positive loading of the elements of nickel, cobalt, manganese, iron, and chromium, (Fig. 4) due to the similarity of their sources which may be mostly natural, iron and manganese have associated geochemically in clay minerals, or may be attributed to military sources which show high loading in the first factor of the sites (S5 and S15) which attacked by military operations (Table 8) noted that the anthropogenic metals such as lead, zinc and cadmium appeared with negative loads.

Fig. 4. Loading factor 1

Table 8. Factor scores

Samples	F1	F2	F3	F4	Samples	F1	F2	F3	F4
S1	-6.602	2.365	1.392	2.487	S12	-2.230	-1.211	1.512	0.031
S2	3.392	5.628	1.551	-1.553	S13	1.927	-1.693	4.286	-0.439
S3	-0.457	-0.186	-1.314	0.138	S14	-0.835	-0.332	-2.778	0.080
S4	-4.452	-2.747	-0.173	-2.407	S15	4.582	-0.728	-1.453	1.120
S5	5.165	-1.279	3.519	-0.231	S16	-3.984	-0.714	0.685	-0.461
S6	0.588	-1.151	-2.351	-2.046	S17	-2.177	0.571	0.981	2.693
S7	-0.613	6.201	-1.186	-1.609	S18	-0.953	-0.891	1.467	1.737
S8	-0.810	-0.463	-1.730	-1.993	S19	-0.468	-0.116	0.849	0.138
S9	2.182	0.116	2.021	-0.419	S20	0.028	0.354	-0.521	0.630
S10	-0.283	-2.699	-0.429	-1.635	S21	-0.150	-0.208	-3.832	1.608
S11	6.149	-0.818	-2.495	2.130					

Factor 2

The second factor shows positive loads of the elements of molybdenum, copper, lead, zinc, cadmium, and chromium in Table 7) which may indicate the anthropogenic sources such as industrial waste, emissions of vehicles exhaust and oils waste, as these activities are the main sources of heavy metals polluting the environment also that there are no strong positive loads of oxides that represent the main natural components of the soil (Fig. 5) (Table 8), high positive loading of sites S1, S2 and S7 (Fig. 6) represents industrial areas near the grain mill, car wash and repairing garage , respectively, in the study area.

Factor 3

The third factor gives positive loads for manganese, chromium and vanadium oxide as in Table 7) and Fig. 7. This may be due to the use of chromium in industrial activities such as dyes and steel. For manganese, it may be due to the different natural sources of the soil, as manganese is one of the main components of it, there is a high load of the sites S13 and S5 because, the S13 represents a football stadium and its soil was brought from other sites, as for S5 represents the industrial area in the study area.

Fig. 5. Loading factor 2

Fig. 6. Biplot F1 and F2

Fig. 7. Loading factor 3

Factor 4

The fourth factor, positive loading of cadmium and phosphorus oxide is determined (Fig. 8) and it may be due to the anthropogenic source, such as agricultural pesticides and liquid wastes, as there was a high load in the sites (S11 and S21) (Table 8) which represents fruits and vegetables store and small farm, S1 which represents the industrial area, and S17 represents a residential area near the electricity generator in the study area.

Fig. 8. Loading factor 4

Indices Assessment

Contamination factor (CF) and degree of Contamination (DoC)

Through the results of the contamination factor (CF) for the heavy metals studied in the surface soil of Al-Hawija Town, there was a high pollution element with copper in the two sites (S7, S2) and may be due to industrial waste product in this area (Devi and Yadav, 2018) (Table 9). For the lead it was highly polluted at the sites of S1, S2, S3, S7, S17 and S20 this may be due to emissions from heavy traffic (Szwalec et al., 2020), zinc has been recorded as mild pollution at sites S1, S2, S7, S9 and S17 due to industrial and sewage waste product (Liu et al., 2020), for the nickel all sites indicated high pollution and it's reason may be due to the release of large amount of it as a result of human activities, such as car's emissions and domestic waste (Terry and Banuelos, 2000). Cobalt show mild contamination in all locations except (S1, S4, S12) and this may be due to liquid waste product, used in fertilizers phosphate, car's emissions and exhaust vehicles (Leyssens et al., 2017; Suh et al., 2016). Arsenic has recorded moderate pollution in all locations as a result of high traffic density (Sosa-Rodríguez et al., 2020). As for the chromium all sites represent low pollution category, which may be related to industrial uses (Ihedioha et al., 2017). For the elements of molybdenum, iron, and cadmium all sites show no pollution category except in the cadmium at site S21 was from the category of low pollution. By calculating the DoC, the sites (S2 and S7) were within the category of High contamination, this may be due to industrial activities contaminated with heavy metals because sites of S2 and S7 represent industrial areas.

Geoaccumulation index (Igeo)

There is medium to high pollution with the nickel element in the industrial area, This was attributed to industrial waste product and heavy traffic, for the copper it has the geoaccumulation index for the sites was between class 0 to class 1 (uncontaminated to moderately contaminated) except for the sites S2 and S7 it was class 2 (moderately contaminated) and this is due to industrial waste product in the industrial district, and the lead was in most of the sites within the class 0 and class1 category except for the sites S1, S2 and S3 within the class 2 category, the site S7 within the class 4 category (heavily contaminated) due to the emissions of the gasoline burning as well as industrial waste from solid oils and waste, while the zinc was between class 0 and class 1, and the nickel in all models of class 2 except for sites S2, S5, S9, S11 and S13 were in the class 3 category this may be due to industrial and domestic wastes as well as car's emissions. For the cobalt, arsenic, and chromium, all sites were in class 1 category, and for the molybdenum, manganese, iron and cadmium there were in the class 0 category (Table 10) and (Fig. 9).

Table 9. (CF) and (DoC) values in the top soil of the study area

Sample No	Mo	Cu	Pb	Zn	Ni	Co	Mn	Fe	As	Cd	Cr	DoC
S1	0.64	2.78	4.56	2.93	4.30	1.66	0.80	0.64	2.32	0.92	1.44	23.0
S2	0.79	5.30	3.29	2.97	6.19	2.36	1.16	0.92	2.68	0.66	1.80	28.1
S3	0.43	1.74	3.55	1.72	5.50	2.06	0.81	0.73	2.68	0.78	1.58	21.6
S4	0.34	1.16	0.54	0.74	4.82	1.81	0.78	0.65	2.68	0.48	1.42	15.4
S5	0.39	1.92	0.98	0.88	6.58	2.26	1.02	0.79	2.48	0.36	1.70	19.4
S6	0.44	1.39	0.64	0.92	5.52	2.19	0.88	0.75	2.92	0.62	1.66	17.9
S7	0.86	4.52	23.20	2.78	5.66	2.24	0.99	0.74	2.64	0.92	1.73	46.3
S8	0.59	1.36	0.65	0.86	5.42	2.20	0.85	0.71	3.00	0.56	1.65	17.9
S9	0.26	2.19	0.89	2.16	6.22	2.20	0.98	0.76	2.48	0.52	1.67	20.3
S10	0.34	1.31	0.62	0.82	5.57	2.08	0.91	0.69	2.76	0.54	1.48	17.1
S11	0.31	1.71	0.81	1.11	6.11	2.34	0.93	0.82	2.56	0.64	1.73	19.1
S12	0.46	1.54	1.23	1.28	4.70	1.95	0.99	0.63	2.44	0.54	1.32	17.1
S13	0.22	1.31	0.54	0.76	6.05	2.19	1.00	0.72	2.40	0.32	1.61	17.1
S14	0.47	1.63	1.86	1.08	5.28	2.20	0.83	0.71	2.92	0.62	1.65	19.2
S15	0.42	2.03	2.75	1.29	5.72	2.19	0.93	0.78	2.68	0.64	1.72	21.2
S16	0.48	1.40	1.24	0.97	5.18	2.11	0.84	0.65	2.52	0.48	1.49	17.4
S17	0.33	1.94	5.20	2.13	5.01	2.00	0.93	0.65	2.48	0.72	1.50	22.9
S18	0.29	1.42	1.14	1.30	5.35	2.01	0.99	0.69	2.48	0.54	1.48	17.7
S19	0.26	1.63	1.87	1.23	5.43	2.03	0.98	0.74	2.44	0.58	1.66	18.8
S20	0.25	1.65	4.58	1.61	5.72	2.15	0.88	0.73	2.28	0.54	1.64	22.0
S21	0.38	1.56	1.63	1.30	5.20	2.20	0.86	0.71	2.68	1.04	1.61	19.2
Average	0.43	1.98	2.94	1.47	5.50	2.12	0.92	0.73	2.60	0.62	1.60	20.9

Table 10. Igeo value in the top soil of the study area

Sample No	Mo	Cu	Pb	Zn	Ni	Co	Mn	Fe	As	Cd	Cr
S1	-1.23	0.89	1.60	0.96	1.52	0.15	-0.91	-1.24	0.63	-0.71	-0.06
S2	-0.93	1.82	1.13	0.98	2.05	0.66	-0.38	-0.71	0.84	-1.18	0.26
S3	-1.81	0.22	1.24	0.20	1.87	0.46	-0.89	-1.03	0.84	-0.94	0.07
S4	-2.12	-0.37	-1.48	-1.02	1.68	0.27	-0.94	-1.20	0.84	-1.64	-0.08
S5	-1.95	0.35	-0.62	-0.77	2.13	0.59	-0.56	-0.92	0.73	-2.06	0.18
S6	-1.75	-0.11	-1.23	-0.71	1.88	0.54	-0.77	-1.00	0.96	-1.27	0.15
S7	-0.80	1.59	3.95	0.89	1.92	0.58	-0.60	-1.02	0.82	-0.71	0.21
S8	-1.35	-0.14	-1.20	-0.81	1.85	0.55	-0.82	-1.07	1.00	-1.42	0.14
S9	-2.52	0.55	-0.75	0.53	2.05	0.55	-0.62	-0.98	0.73	-1.53	0.16
S10	-2.15	-0.20	-1.27	-0.87	1.89	0.47	-0.72	-1.12	0.88	-1.47	-0.02
S11	-2.27	0.19	-0.89	-0.44	2.03	0.64	-0.68	-0.87	0.77	-1.23	0.20
S12	-1.70	0.04	-0.29	-0.22	1.65	0.38	-0.59	-1.24	0.70	-1.47	-0.18
S13	-2.79	-0.19	-1.48	-0.98	2.01	0.54	-0.58	-1.06	0.68	-2.23	0.11
S14	-1.67	0.12	0.31	-0.47	1.82	0.55	-0.86	-1.09	0.96	-1.27	0.14
S15	-1.83	0.43	0.87	-0.21	1.93	0.54	-0.70	-0.94	0.84	-1.23	0.20
S16	-1.63	-0.10	-0.27	-0.63	1.79	0.49	-0.84	-1.20	0.75	-1.64	-0.01
S17	-2.17	0.37	1.79	0.51	1.74	0.42	-0.70	-1.20	0.73	-1.06	0.00
S18	-2.35	-0.08	-0.40	-0.20	1.83	0.42	-0.60	-1.13	0.73	-1.47	-0.02
S19	-2.52	0.12	0.32	-0.29	1.86	0.43	-0.61	-1.01	0.70	-1.37	0.15
S20	-2.58	0.14	1.61	0.10	1.93	0.52	-0.77	-1.03	0.60	-1.47	0.13
S21	-1.99	0.06	0.12	-0.20	1.79	0.55	-0.81	-1.07	0.84	-0.53	0.10
Average	-1.91	0.27	0.15	-0.17	1.87	0.49	-0.71	-1.05	0.79	-1.33	0.09

Fig. 9. Geoaccumulation index in surface soil of Al-Hawija area

Pollution load index (PLI)

The average pollution load index in the surface soil of Al-Hawija town is 1.4 (Table 11) which indicates that all sites were higher than 1 (polluted according to the load index classification), as it was the highest pollution in the site S7 was 2.3 this may be due to the high pollution of the lead in the southeast of the town which represented the industrial area (Fig. 10).

Table 11. Pollution load index (PLI) value

Sample No	PLI	Sample No	PLI
S1	1.7	S12	1.2
S2	2.0	S13	1.0
S3	1.5	S14	1.4
S4	1.0	S15	1.5
S5	1.3	S16	1.2
S6	1.2	S17	1.5
S7	2.3	S18	1.2
S8	1.2	S19	1.3
S9	1.3	S20	1.4
S10	1.1	S21	1.4
S11	1.3	Average	1.4

Fig. 10. Spatial distribution of risk index (RI) and pollution load index (PLI) in the top soil of Al-Hawija area

Potential ecological risk index (RI)

The ecological risk index for the studied heavy metals was calculated and Er value of the elements (Cr Cu, Pb, As, Cd) was less than 40 except for the lead element in the site S7 where Er value was 116 which represent considerable potential ecological risk, and the environmental risk quotient index was calculated for the following elements (Cr Cu, Pb, As, Cd,) (Table 12) and (Fig. 10) and it was found that all sites were less than 150 (under the Low category Ecological Risk) except for the site S7 was in the category of moderate ecological risk ,This may be due to the high ecological risk index with lead, copper and arsenic in that site.

Table 12. The (Er) and (RI) value for some heavy metals in the soil of the study area

Sample	Cu	Pb	As	Cd	Cr	RI	Sample	Cu	Pb	As	Cd	Cr	RI
S1	13.9	22.8	23.2	27.6	2.9	90.4	S12	7.7	6.2	24.4	16.2	2.6	57.1
S2	26.5	16.5	26.8	19.8	3.6	93.1	S13	6.6	2.7	24.0	9.6	3.2	46.1
S3	8.7	17.7	26.8	23.4	3.2	79.8	S14	8.2	9.3	29.2	18.6	3.3	68.5
S4	5.8	2.7	26.8	14.4	2.8	52.5	S15	10.1	13.7	26.8	19.2	3.4	73.3
S5	9.6	4.9	24.8	10.8	3.4	53.5	S16	7.0	6.2	25.2	14.4	3.0	55.8
S6	7.0	3.2	29.2	18.6	3.3	61.3	S17	9.7	26.0	24.8	21.6	3.0	85.1
S7	22.6	116	26.4	27.6	3.5	196.1	S18	7.1	5.7	24.8	16.2	3.0	56.7
S8	6.8	3.3	30.0	16.8	3.3	60.2	S19	8.1	9.3	24.4	17.4	3.3	62.6
S9	11.0	4.5	24.8	15.6	3.3	59.2	S20	8.3	22.9	22.8	16.2	3.3	73.5
S10	6.5	3.1	27.6	16.2	3.0	56.4	S21	7.8	8.1	26.8	31.2	3.2	77.2
S11	8.5	4.0	25.6	19.2	3.5	60.8	Average	9.9	14.7	26.0	18.6	3.2	72.3

CONCLUSIONS

- 1- The results of heavy metal concentrations in the surface soil show a significant increase in lead, chromium, copper and zinc concentrations in industrial areas due to anthropogenic sources
- 2- Through the spatial distribution maps of heavy metals, it was found that copper, lead, chromium, molybdenum, zinc, cadmium and iron had increased in industrial areas more than commercial and residential areas as a result of industrial waste product and heavy traffic, while for the nickel, cobalt, manganese and arsenic they increased in commercial areas as a result of anthropogenic waste and agricultural activities and military operations.
- 3- An analysis of the size fraction of the soil showed that all studied heavy metals increased in the fine parts (clay) as a result of the presence of iron and manganese oxides and clay minerals adsorption and absorption.
- 4- The correlation coefficient showed that there is a positive correlation between the molybdenum, copper, lead, zinc and cadmium which indicated their participation in anthropogenic sources.

- 5- The factor analysis of the heavy metals in the soil showed that 17.21% of the total variation of the elements was the result of anthropogenic activities in the region and that the greatest was in the industrial areas in the town.
- 6- Indices assessment showed high pollution of the lead element in the site S7 (CF= 23.20) and (Igeo= 3.95) as a result of industrial waste product, also a high ecological risk in the same site.

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