AL-Heety et al. Iraqi Journal of Science, 2021, Vol. 62, No. 4, pp: 1077-1087
DOI: 10.24996/ijs.2021.62.4.4

ISSN: 0067-2904

Heavy Metal Pollution and Ecological Risk Assessment in Soils Adjacent to Electrical Generators in Ramadi City, Iraq

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Received: 21/5/2020 Accepted: 5/8/2020

ABSTRACT

This study aims to evaluate the concentration of the heavy metals (Co, Cd, Cr, Cu, Ni, Pb, and Zn) and their ecological risk in soils adjacent to the power generators of Ramadi city, Iraq. The soil samples were collected from a depth of 20cm. The obtained results showed that the mean concentrations of heavy metals (HMs) are ranked as in the following order: Cr (360.90mg/kg) > Ni (283.65mg/kg) > Zn (190.96mg/kg) > Pb (130.75 mg/kg) > Cu (36.54 mg/kg) > Co (16.62 mg/kg) > Cd (2.55 mg/kg). The mean values of HMs concentration exceed the international guidelines. The result of correlation matrix analysis at $P \leq 0.05$ showed significant correlations between the concentrations of HMs. These correlations are interpreted in the context of a common source of pollution and/or common origin. Results of the potential ecological risk factor assessment of metal i (E^{i}_{r}) in soil adjacent to the power generators of Ramadi city showed that the E^{i}_{r} values take the following descending order: Ni (354.56, very severe) > Cd (255.31, severe) , Co (207.77, severe) > Zn (88.69, heavy) > Cu (25.73, light) > Cr (17.43, light) > Pb (12.0, light). The potential ecological risk index (RI) values are classified as severe ecological risk for all studied heavy metals. This study provides the environmental protection managers and decision-makers with important information about the risk of using electrical generators in residential neighborhoods.

KEYWORDS: Heavy metal; Soil; ecological risk; Iraq

التلوث بالعناصر الثقيلة وتقييم المخاطر الايكولوجية في الترب المجاورة للمولدات الكهربائية في مدينة الرمادي، العراق

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الخلاصة:

يمثل التلوث بالعناصر الثقيلة مشكلة عالمية خطيرة. أعتبرت الانبعثات من محطات توليد الطاقة الكهربائية واحد من المصادر الرئيسة لتحرير العناصر الثقيلة. تهدف هذه الدراسة الى تقييم تراكيز العناصر الثقيلة (الكادميوم، الكوبالت، الكروم، النحاس، النيكل، الرصاص والخارصين) و تخمين مخاطرها الايكولوجية في التربة المجاورة للمولدات الكهربائية في مدينة الرمادي، العراق. جمعت في هذه الدراسة احدى وخمسون عينة من التربة من عمق 20 سم وتم تحضيرها للتحليل باستخدام مطياف الامتصاص الذري. أظهرت النتائج

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المكتسبة أن متوسط تراكيز العناصر الثقيلة تأخذ الترتيب الآتي: الكروم (360.90 ملغ/كغم) > النيكل (283.65 ملغ/كغم) > الخارصين(190.96ملغ/كغم) > الرصاص (130.75 ملغم/كغم) > النحاس (36.54 ملغم/كغم) > الكوبالت (16.62 ملغم/كغم) > الكادميوم (2.55 ملغم/كغم) . تجاوزت القيم المتوسطة لتراكيز العناصر الثقيلة المعايير الدولية. أظهرت نتائج تحليل مصفوفة الارتباط علاقات ارتباط مهمة بين العناصر الثقيلة عند مستوى الأهمية أقل أو يساوي 0.05 . فسرت علاقات الارتباط الموجبة المهمة المرتفعة والمتوسطة في سياق المصدر المشترك للتلوث و/أو الأصل المشترك. أظهرت نتائج تخمين المخاطر الايكولوجية المحتملة للعناصر الثقيلة في الترب المجاورة للمولدات الكهربائية في مدينة الرمادي الترتيب التنازلي الآتي: النيكل (354.56, قاسية جدا)> الكادميوم(255.31, قاسية) والكوبالت (207.77, قاسية)> الزنك (88.73 ,خطيرة) > النحاس (25.73, خفيفة) > والكروم (17.43, خفيفة) > والرصاص (12.01, خفيفة). اعتمادا على قيم معامل المخاطر، تصنف المخاطر الايكولوجية كمخاطر قاسية لجميع العناصر الثقيلة في منطقة الدراسة. تزود هذه الدراسة مدراء حماية البيئة وصناع القرار بمعلومات مهمة حول مخاطر استخدام المولدات الكهربائية في الأحياء السكنية والحاجة الى التقليل من استخدامها من خلال تحسين شبكة الطاقة الوطنية.

INTRODUCTION

One of the serious global environmental problems is the heavy metal pollution of air, water, and soil. The seriousness of the heavy metal pollution is due to toxicity, bioaccumulation, abundance, and persistence of these metals [1]. Heavy metals are widespread in the environment and whilst some of the metals are of geogenic origin (rock weathering and volcanic eruptions), the majority are released from anthropogenic activities. These include industrial, agricultural, and domestic activities. The accelerating urbanization and industrialization over recent years have increased both ecological and human health interests for environmental pollution by heavy metals [2]. In recent years, soil pollution with heavy metals has received great attention as a global environmental issue. The sources of releases of heavy metals that are introduced to the soil, especially urban soils, are the industrial activities, coal and fuel burning, vehicle emissions, mining operations, fertilizers and pesticide usage, municipal solid waste disposal, and other wastes [3]. Coal and fuel combustion releases fly ash, particulate matter, and potentially dangerous heavy metals, which have harmful effects on humans and wildlife [4]. Currently, the predominant emitters of mercury, acid gases, and many toxic metals in the United States are power plants [5]. Data from the United States Environmental Protection Agency (USEPA) show that 62% of As, 28% of Ni, 50% of Hg, 22% of Cr, 13% of NO_x, and 60% of SO_2, that are toxic air pollutants, come from power plants [6]. Many researchers investigated emissions of heavy metals from thermal power plants and diesel engine generators and assessed their risks to human health and environment, along with their ecological risks on soil and water [5, 7-11]. The heavy metals are transported from the soil, accumulated in the plant tissues, and then consumed by humans. The heavy metals accumulate in fatty tissues and affect the activities of nerves, endocrine and immune systems, normal cellular metabolism, etc. [12]. There is an increasing use of diesel engine generators to generate and supply electrical power for the citizens, due to the governmental inability in Iraq. Since 2003, the government has been unable to meet the citizen's needs for electrical power from the large power plants. This inability prompted private investment in the use of diesel engine generators to supply citizens with the electrical power. The motivation to carry out the current study is that most of these generators are located within residential neighborhoods, causing human health and environmental risks. The current study is the first attempt in Iraq to investigate the heavy metals emitted from diesel electrical generators and their effects on the surrounding soils. The effects of lead pollution on soil and plants around four power generators in Baghdad were investigated [13]. The aims of our study are , firstly, the evaluation of concentrations of heavy metals in neighboring soils of power generators in Ramadi City, the capital of Al-Anbar Governorate, Iraq, and, secondly, the assessment of ecological risks of heavy metals in neighboring soils of power generators. The obtained results provide decision-makers and environmental managers with important information to deal seriously with the risks of using power generators in the residential neighborhoods on the human environment and health. The also emphasize the need to find environmentally friendly alternatives.

MATERIALS AND METHODS

Study Area

Ramadi is a city in Iraq, about 110 km west of Baghdad. It is located at 33° 25′ 11″ N, 43° 18′ 45″ E (Figure-1). It is the capital of Al-Anbar Governorate. Ramadi is stretched

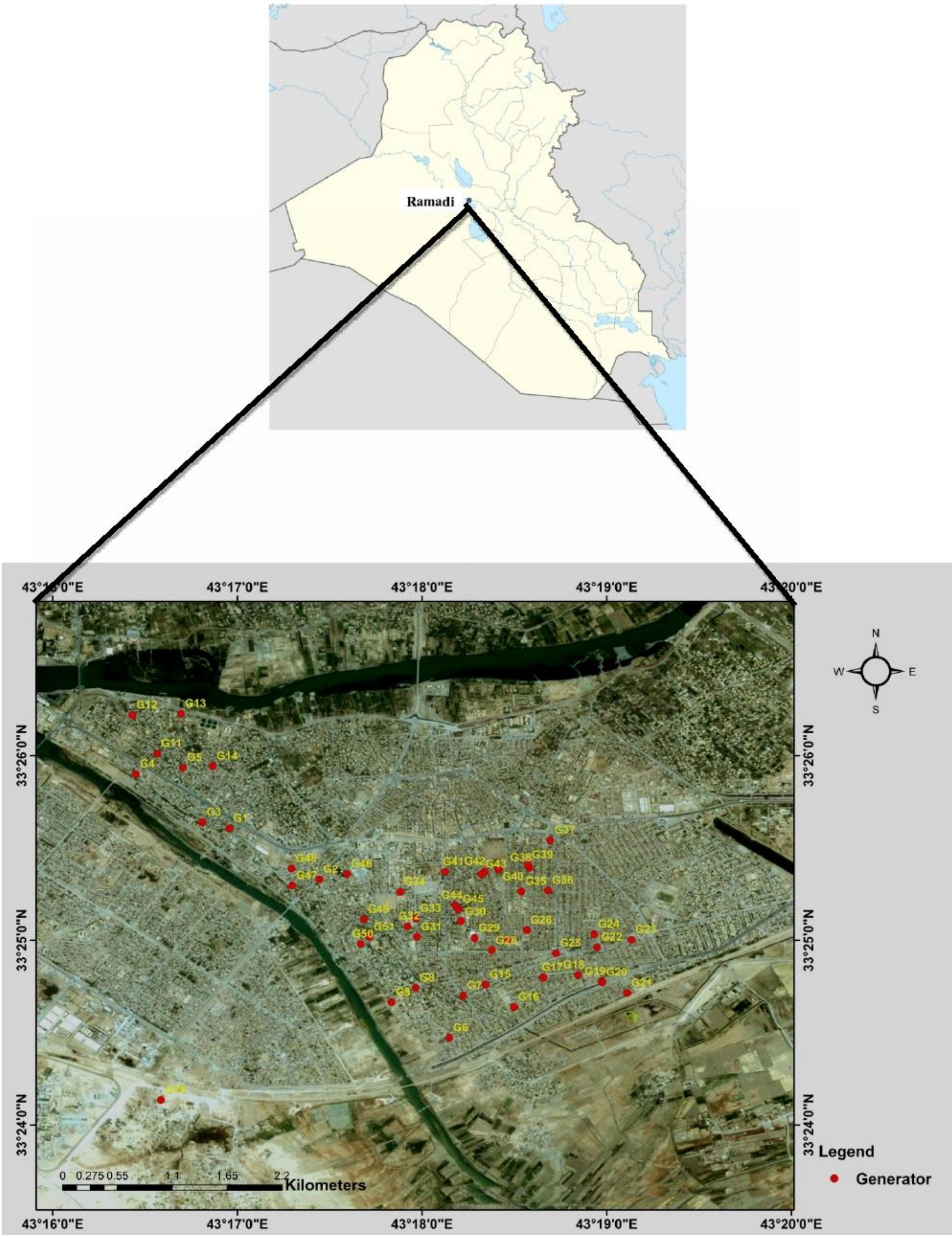

Figure 1- Location map of the study area and the power generators

over an area of about 180 km^2. The data of Anbar Governorate Statistics Directorate demonstrated that the population of Ramadi City in 2018 is 458280 capita. Ramadi is surrounded by the Euphrates to the north, the suburbs to the east, the Baghdad/Al-Qaim railway line to the south, and the Warar Canal to the west. More suburbs exist to the west and northwest of the canal and north of the Euphrates. Ramadi City has a hot desert climate where the typical annual temperature being 22.4 °C. Most rain falls occur in the winter, with an annual of precipitation rate of about 115 mm. Fifty - one generators operate daily at an average of 12 hours. The total production capacity of these generators is 21.486 MV.

Samples Collection and Analysis

Soil samples were collected from the adjacency of the locations of the generators at a depth of 0-20 cm, using shovel devices. Every soil sample consisted of 4 subsamples. The sampling site locations were recorded by the use of Garmin 72 GPS, USA. In every sampling site, an aggregated sample was made through the mixing of the four subsamples. Plastic bags were used to keep the soil samples. These samples were then dried in the oven in the laboratory at 105˚C for 24 h, and after that, they were sieved using a 106 μm stainless steel sieve. The sieving process was carried out to remove large debris, gravel-sized materials, plant roots, and other waste materials. The samples were then homogenized with porcelain pestle and mortar. They were kept in polyethylene containers, being ready for digestion and analysis. Closed vessel microwave-assisted acid digestion technique under high temperature and pressure has become routine [14], which avoids the external contamination and requires shorter time and smaller quantities of acids, thus improving detection limits and overall accuracy of the analytical method [15]. 0.5g of soil sample was placed into the reference vessel. A volume of 25 ml of mixture ($HCl:H_2SO_4: HNO_3$, 3:2:2) was then added to the reaction vessel which was inserted into the microwave unit. The digested solution was cooled and filtered. The filtered sample was then made up to 50ml with distilled water and kept in special containers. AAS (Atomic Absorption Spectrometry) instrument (Phoenix - 986, USA) was utilized to detect and measure heavy metal content in the soil samples.

Potential Ecological Risk Assessment

Hakanson [16] proposed the potential ecological risk factor (E^i_r) to assess the ecological risk posed by heavy metals in sediments and soils. The E^i_r is calculated using the following equations:

$$C_f^{\ i} = \frac{C_s^{\ i}}{C_r^{\ i}} \tag{1}$$

$$E_r^{\ i} = T_f^{\ i} x \ \frac{C_s^{\ i}}{C_r^{\ i}} \tag{2}$$

$$E_r^{\ i} = T_f^{\ i} x \ C_f^{\ i} \tag{3}$$

where $E_r^{\ i}$ is the potential ecological risk factor of metal *i* and $T_f^{\ i}$ is the toxic response factor of metal *i*. The T_f values of heavy metals are 30, 5, 2, 5,1, 5, 5, and 1 for Cd, Co, Cr, Cu, Mn, Ni, Pb, and Zn, respectively. $C_s^{\ i}$ is the metal *i* concentration in a sediment or soil sample and $C_r^{\ i}$ is the reference value of metal *i*. The potential ecological risk index (RI) is the sum of the risk factor values of all heavy metals at the sampling sites:

$$RI = \sum_i^n E_r^{\ i} \tag{4}$$

$E_r^{\ i}$ is categorized into five classes: light ($E^i_r< 40$), moderate ($40 \leq E^i_r < 80$), heavy ($80 \leq E^i_r < 160$), severe ($160 \leq E^i_r < 320$), and very severe ($E^i_r \geq 320$). RI is classified into four grades: light ($R_i < 150$), moderate ($150 \leq R_i < 300$), heavy ($300 \leq R_i < 600$), and severe ($R_i \geq 600$).

Data Processing

Descriptive statistics, including mean, minimum, maximum, standard deviation, standard error, and covariance, as well as the correlation matrix analysis, were carried out using Statistica 13 software. Calculations of E_r^i and RI were conducted using Microsoft Excel. Geospatial distribution maps of E_r^i, and RI were drawn using Surfer 11 software.

RESULTS AND DISSCUSION

Concentrations of Heavy Metals

The descriptive statistics of the analyzed HMs, as well as those for the international guidelines, are given in Table-1. All mean values of HM concentrations exceeded the guidelines. The values of concentrations of heavy metals take a descending order, as follows: Cr > Ni > Zn > Pb > Cu > Co > Cd. The coefficient of variance (CV) values of Cu (65.97%), Pb (64.99%), Zn (63.70%), and Cd (30.34%) are higher than those of Ni, Cr, and Co. This result suggests that Cu, Pb, Zn, and Cd had greater variations among the soil samples and, hence, may be influenced by external factors, such as anthropogenic activities [17]. When comparing the mean concentrations of HMs in the soil of the study area with those reported for urban soils in a number of Iraqi cities, we find them to be either higher or lower, Table-2.

Table 1-Results of descriptive statistics analysis of HMs in soils adjacent to electrical generators in Ramadi City, along with values of the international guidelines

HMs	**Mean mg.kg^{1}**	**Minimum**	**Maximum**	**Std.Dev.**	**Coef.Var.**	**Brazilian SQG [18]**	**USEPA SQG [19]**	**CCME SQG [14]**
Cd	2.55*	1.46	3.92	0.77	30.43	0.3	0.6	0.6
Co	16.62*	12.25	21.09	2.32	13.96	0.4	-	-
Cr	360.90*	124.60	584.82	84.75	23.48	41.1	25	37.4
Cu	36.54*	9.79	86.67	24.11	65.97	7.1	16	35.7
Fe	1592.33*	921.10	2818.06	398.74	25.04	1500	30	30
Ni	283.65*	159.87	397.37	66.73	23.52	4.0	16	-
Pb	130.75*	15.63	295.12	84.98	64.99	54.4	40	35
Zn	190.96*	17.98	443.73	121.65	63.70	10.4	110	123

***Higher than guidelines**

Table 2- Mean heavy metal concentrations (mg/kg) in soil samples for the study area with comparisons with other studies in Iraqi cities

City	Cd	Co	Cr	Cu	Ni	Pb	Zn	Reference
Ramadi	2.55±	16.62±	360.90*	36.54±	283.65*	130.75*	190.96±	present study
Al-Nasiriya		27.50	116.3	27.30	147.10	16.84	57.30	[20]
Baghdad	18.64	-	3.65	15.64	30.71	1.99	23.71	[21]
Basrah	2.8	-	60.9	-	36.90	-	-	[22]
Duhok	3.42	40.54			78.73	88.28	308.86	[23]
Erbil	0.35		66.3	53.1	67.6	25.63	98.41	[24]
Fallujah	0.64	3.43	11.59	2.01	8.96	3.82	5.50	[25]
Hawega		36.29	310.5	35.7	152.3	-	51.33	[26]
Kirkuk	10	-	61.30	6.70	38.20	10	-	[27]
Wasit	2.2	13.4	226	54.7	188.9	32.2	117.6	[28]
Tikrit		20.33	108.66	23.66	113.66	37.16	57	[29]

***Higher; ± Higher or Lower**

Cd concentration in the study area ranges from 1.46 to 3.92 mg/kg, with a mean value of 2.55 mg/kg. The mean value of Cd concentration exceeded the guidelines. Weathering of Cd-rich rocks increases soil Cd content [30]. High concentrations of Cd were recorded in soils around power plants that use fossil fuel of various types as energy sources [5, 11]. The source of Cd in diesel fuel is likely from fuel and engine wear [31]. The magnitude of Cd emissions from diesel fuel depend on its Cd content, thus being either detectable or undetectable [32]. The Cd sources in soil of the study area might be anthropogenic (fuel combustion emissions) or geogenic.

Co concentration in the soils adjacent to the power generators in Ramadi city ranges from 12.25 to 21.09 mg/kg, with a mean value of 16.62 mg/kg. The mean value of Co concentration exceeded the guidelines. The diesel fuel content of Co is either free of Co or with very low content, depending on its type [31, 32, 33], thus the Co emission from diesel fuel is very low. Anthropogenic sources of cobalt in soils include industrial processes, and leather and tannery factories [34]. Due to the lack of leather and tannery factories, low emission of Co from diesel fuel, and the urbanized nature of the study area, the Co in the soil samples is considered of geogenic source.

Cr content in soil samples adjacent to the power generators in Ramadi city ranges from 124.60 to 584.82 mg/kg, with a mean value of 360.90 mg/kg. The mean value of Cr content exceeds the guidelines. Diesel exhaust emissions elevate Cr content in the soil. Diesel fuel contains different concentrations of Cr, depending on the type of fuel. In experimental studies, several authors inverstigsted the Cr emissions from diesel fuel using different fuel types [31, 32, 33]. The Cr content in the soil adjacent to the electricity generators might originate from weathering products of the ultramafic igneous rocks in Turkey and Syria that were brought by the Euphrates River, in addition to its emissions from diesel generators.

Cu concentration in the soil adjacent to the power generators in Ramadi city ranges from 9.79 to 86.67 mg/kg, with a mean value of 36.54 mg/kg. The mean value of Cu concentration exceeded the guidelines. Significant Cu emissions as oil residue (waste) from fuel oil were reported by Reddy *et al*. [33]. Cu accumulates in the top horizon of the soil profile, which reflects its bioaccumulation and the recent anthropogenic sources of the metal [35]. The increase of Cu content in the soil samples of the study area is possibly due to its emissions from diesel fuel used to generate the electricity by generators.

Ni content in soil samples adjacent to the power generators in Ramadi city ranges from 159.87 to 397.37 mg/kg, with a mean value of 283.65 mg/kg. The mean value of Ni concentration exceeded the guidelines. Oil- and coal-fired power plants as well as trash-incinerators also release Ni into the environment [35]. In previous experiments, many authors reported Ni emissions from diesel fuel [31, 32, 33]. Significant Ni emissions as oil residue (waste) from fuel oil were reported, and the enrichment factors were higher than those of the other heavy metals [33]. The high concentration of Ni in soil of the study area can be explained in terms of its close proximity to the source ultramafic rocks, in addition to the Ni emissions as oil residues and bottom ash from the diesel engine generators.

Pb content in soil samples adjacent to the power generators in Ramadi city ranges from 15.3 to 295.12 mg/kg, with a mean value of 130.75 mg/kg. Pb enters the environment when it is released from mining fields of lead and other metals, factories producing or using leadand its alloys, lead compounds from coal combustion, and vehicle exhaustion [36]. In earlier investigations, high Pb emissions as oil residue of fuel oil used in the power plants were reported [33]. The high concentrations of Pb in the soils adjacent to the power generators in the study area are mainly caused by diesel generators emissions.

Zn concentration in the soil adjacent to the power generators in Ramadi city ranges from 17.98 to 443.73 mg/kg, with a mean value of 190.96 mg/kg. The anthropogenic sources of Zn include traffic emissions, mechanical friction of vehicles, mining, steel processing from oil pools , coal and waste combustion, and fuel emitted from generators [4, 37]. Reddy *et al*. [33] found that Zn shows higher enrichment factors for oil residue in fuel oil-based power plants . The lubricant oil combustion is a source of Zn emission [38]. The high content of Zn in soils adjacent to the power generators in Ramadi City can be attributed to the engine diesel oil and lubricant oil combustion by generators.

Correlation Matrix Analysis

Correlation matrix analysis is an effective tool to show the relations between multiple variables and to understand the influencing factors as well as the chemical parameter sources [39]. The correlation relations between heavy metals provide important information about sources and pathways of heavy metals [40]. In general, a correlation coefficient > 0.70 is interpreted as a strong correlation, while the value between 0.50 and 0.70 reflects moderate correlation, and the value less than 0.50 is interpreted as low correlation [41]. The results of correlation matrix analysis at a significant level ($p \leq 0.05$) are listed in Table-3. The strong and moderate correlations are interpreted in terms of the common origin or source, while the low correlation refelects the different origin or source. The results showed a positive strong correlation of Cu and Pb with the other metals (except for Cr), with the highest correlation coefficient being between Cu and Pb, implying that these latter two metals originated from the same source. The deposition of these metals in the soil is associated with the emissions of fuel engines [42].

Table 3-Correlation matrix analysis for HMs in soils adjacent to the electrical generators in Ramadi City

Metal	Cd	Co	Cr	Cu	Ni	Pb	Zn
Cd	1						
Co	**0.34***	1					
Cr	0.11	0.15	1				
Cu	**0.66***	**0.45***	0.01	1			
Ni	0.11	**0.34***	0.25	**0.37***	1		
Pb	**0.54***	**0.42***	-0.20	**0.68***	**0.46***	1	
Zn	**0.47***	0.13	-0.12	**0.53***	-0.08	**0.34***	1

[*]Marked correlations are significant at $p < 0.05$.

Spatial Distribution of Heavy Metals in Soli

Spatial distribution maps of heavy metals were conducted by using surfer 13 software and the interpolation method used was IDW (Inverse Distance Weighting), ass demonstrated in Figure-2. The spatial distribution maps showed three high anomalies (hot spots) of Cd, two of Co, one of Cr, four of Cu, three of Ni, two of Pb, and five of Zn. These hot spots describe the high concentration of heavy metals in the soil sampling sites as compared to their surroundings. These high anomalies are

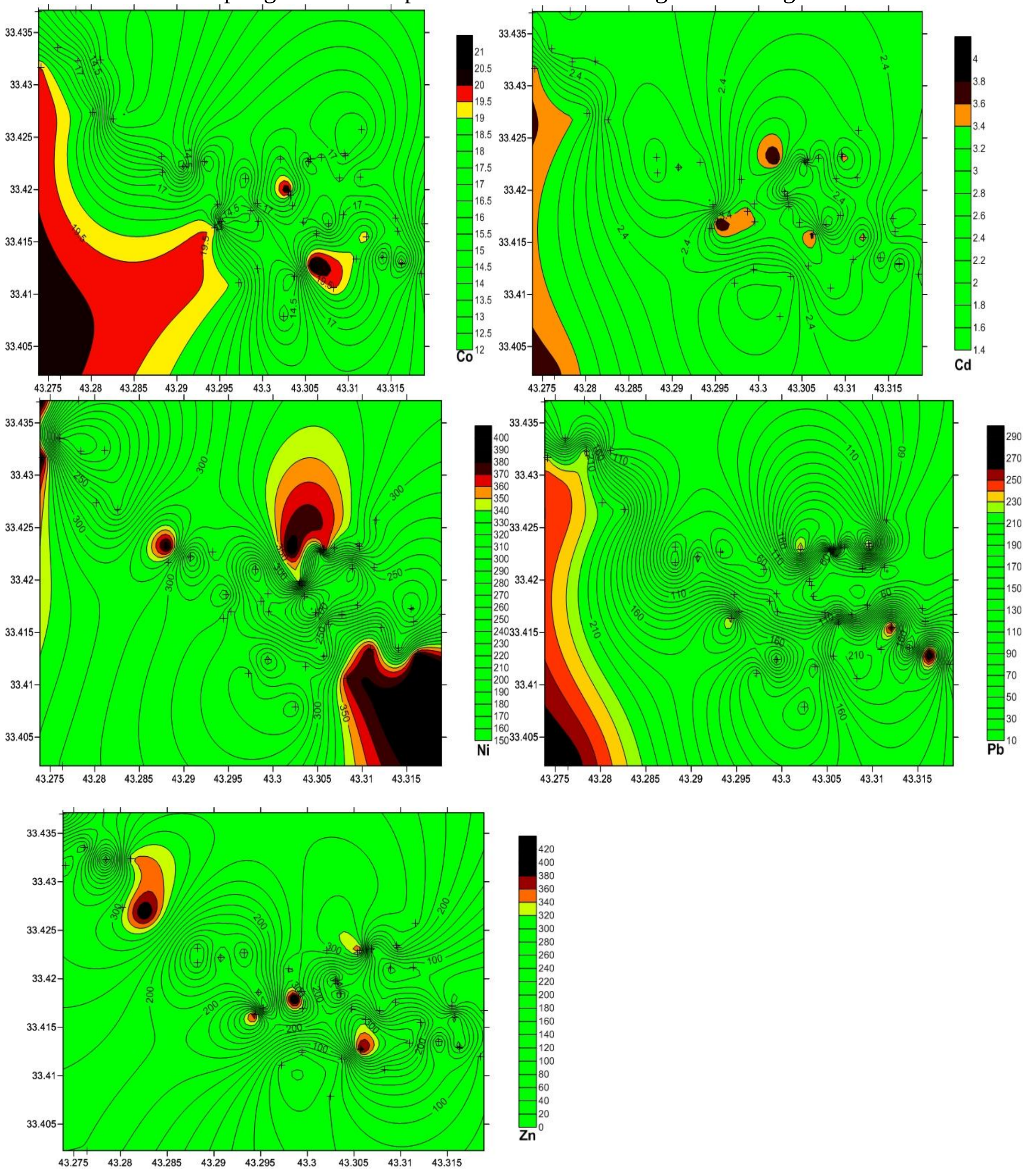

Figure 2-Spatial distribution of HMs in soils adjacent to electrical generators in Ramadi City.

explained in terms of the widespread distribution of the generators and/or the proximity of a number of them to the streets of Ramadi City. This, in turn, indicates the impact of traffic emissions, in addition to diesel generators emissions, in the elevation of the studied HMs concentrations.

Ecological Risk Assessment

The descriptive statistics results of E_r^i and RI of HMs in urban soils of Ramadi City are listed in Table

-4. The descending mean values of E_r^i are ranked as follows: Ni > Cd > Co > Zn > Cu > Cr > Pb. The mean values of E_r^i for Ni, Cd, Co, and Zn indicate very severe, severe, severe, and heavy potential ecological risks, respectively. The mean values of E_r^i for Cu, Cr, and Pb are classified as light potential ecological risk.

Al-Heety and Saod [43] calculated E_r^i of different HMs in the urban soils for several Iraqi cities. They found that the mean value of E_r^i for Cd in soils of Baghdad, Duhok, Basrah, Erbil, and Fallujah cities are classified as severe, severe, heavy, heavy, and light potential ecological risks, respectively. The mean value of E_r^i for Ni and Zn in the soil samples of the current study is more than that reported earlier [43]. The light potential ecological risk for Cu, Cr, and Pb in the soils of the study area is consistent with that inferred previously [43]. The high values of E_r^i for Ni, Co, and Zn depend on their concentrations, while the E_r^i for Cd depends on its toxic response factor and concentration.

The RI value ranges from 697.28 to 1347.33, with a mean value of 961.54. According to the categories of RI [16], the RI values are classified as severe ecological risk. The contributions of the single ecological risk E_r^i in RI take the following descending order: Ni > Cd > Co > Zn > Cu > Cr > Pb. There is a relation between the IR value and the type, concentration, and toxicity of the HM, while the lower RI reflects a lower content of the HM and slight toxicity [44]. The obtained RI value for the urban soils in Ramadi City was higher than that reported previously [43] for soils in Baghdad. The high RI value in the urban soils of Ramadi City can be attributed to the anthropogenic activities, such as emissions from the power generators, traffic emissions, atmospheric deposition, and other human activities. The spatial distribution of RI in the urban soil of the study area is shown in Figure-3. There are two hot spots that reflect more severe risks than the surroundings. These hot spots are surrounding and including a larger number of electrical generators, and in turn, are more exposed to emissions of HMs from the burning of fossil fuels used in power generation.

Table 4-Results of descriptive statistical analysis of potential ecological risk index (Eri) and risk index (RI) values of HMs in soils adjacent to electrical generators in Ramadi City.

Metal	Mean	Minimum	Maximum	Std.Dev.	Coef.Var.
Cd	255.31	146.70	392.23	77.69	30.43
Co	207.77	153.20	263.65	29.01	13.96
Cr	17.43	6.01	28.25	4.09	23.48
Cu	25.73	6.89	61.04	16.97	65.97
Ni	354.56	199.84	496.72	83.41	23.52
Pb	12.01	1.43	27.12	7.81	64.99
Zn	88.69	8.64	213.33	56.90	64.15
RI	961.54	697.28	1347.33	183.92	19.10

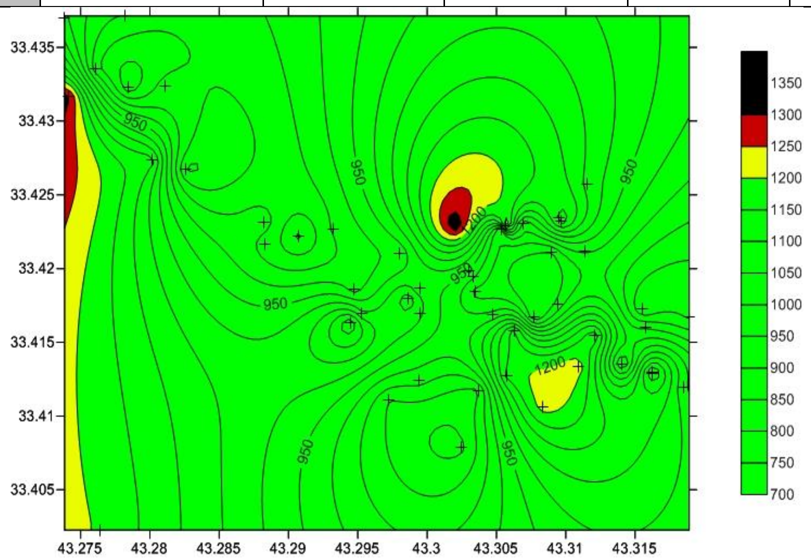

Figure 3-Spatial distribution of ecological risk index (RI) of HMs in soils adjacent to the electrical generators in Ramadi City

CONCLUSIONS and RECOMMENDATIONS

The studied soil is polluted by Cd, Co, Cr, Cu, Ni, Pb, and Zn, which are released by the burned diesel and traffic emissions. The HMs in the soils adjacent to the electrical generators in Ramadi city showed different grades of potential ecological risk (E_r^i), ranging from very severe to light, along with severe ecological risk index (RI). We recommend the decision makers to focus on rehabilitation and development of the national electricity network to reduce the dependence on electrical generators for supplying households with electrical power, which, in turn, reduces HM release into the environment.

ACKNOWLDGEMENTS

The authors express their gratitude to Mr. Ahmed Al-Rawi, Lecturer in Department of Chemistry, College of Science / University of Anbar for his generous help in samples preparation and analysis.

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