APPLICATION OF SOME SINGLE AND INTEGRATED INDEX EQUATION TO ASSESS HEAVY METAL IN DIFFERENT SOILS IN ERBIL GOVERNORATE

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ABSTRACT

The aim of this study was to application of some single and integrated index equation to assess heavy metal in different soil within Erbil governorate. The 15 different locations (Bahare new, Newroz, New Hawler, Hesarok, Azadi1, Zen city, Atconz city, Pank village, Binaslawa, Darato, Qushtapa, Shaways, Kasnazan, Bahirka, Pirzin) were specifically selected to identify the effects of traffic activities on soil properties. Different heavy metal distribution patterns (As, Cd, Cu, Cr and Zn) were determined from distance 5, 25, 50m roadside. Soil pollution was assessed using many indices including: contamination factor (CF), degree of contamination (Cdeg), Ecological Risk Factor and Potential Ecological Risk Index. The results showed that concentrations of As, Cd, Cr, Cu, and Zn in street dust ranged from (4.60, 1.80, 217.83, 62.14 and 215.18) mg.kg⁻¹ which recorded in Qushtapa, Kasnazan, Atconze city, Hasarok5 and Zen city respectively. The contamination factor and degree of contamination of the trace elements As, Cd, Cr, Cu ,and Zn of soil samples was indicating considerable contamination factor for Oushtapa moderate contamination factor for Kasnazan, while Atconze city, Hasarok5, Zen city showed very high contamination factor, while degree of contamination considerable low degree of contamination. According to the ecological risk factor and RI results Owshtapa was indicate as low potential ecological risk, Kasnazan had moderate potential ecological risk while Hasarok5 and Zen city considerable high potential ecological risk, except Atconze considerable very high ecological risk, on the other hand for RI index shown considerable very high ecological risk recorded in Hasarok 5 soil samples.

Keywords: contamination factor (CF), degree of contamination (Cdeg), ecological risk factor and potential ecological risk index.

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تطبيق بعض معادلات الأدلة الفردية والمتكاملة لتقييم معادن تقيلة في الترب مختلفة لمحافظة أربيل شاكار جمال عويز دلها عثمان عبدالة عثمان الماكار عبدالة عثمان الماكار جمال عويز الماكار عبدالة عثمان الماكار عبدالة عثمان الماكار عبدالة عثمان الماكار عبدالله الماكار عبدالله عثمان الماكار عبدالله الماكار الما

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المستخلص:

الكلمات المفتاحية: تقييم المعادن الثقيلة، عامل تلوث المعادلة الفردية والمتكاملة (CF)، درجة التلوث (Cdeg)، عامل الخطر البيئي ومؤشر المخاطر البيئية المحتملة المحتملة

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INTRODUCTION

Soil is the basis of all agroecosystems; it is an important part of the Earth. Most of soils were endangered with various types of erosion and pollution. Heavy metals and hazardous elements play a significant role among the pollutants. The pollution of soil with metals due to the aerial transportation is a worldwide issue. Metals were released during various processes, such as combustion or component wearing. Lead, copper, zinc and cadmium have been considered as major inorganic pollutants. Concerning the railroad transport, the pollution depends on an engine type. Diesel locomotives use fuel combustion, similarly to the road vehicles, they also release polycyclic aromatic hydrocarbons in contrary, electric locomotives are considered environmentally friendly, however, the railroad presence of the itself could significantly increase metal concentrations in nearby soils, in addition, particle abrasion from wheels, tracks and pantographs can get metals into aerosols and pollute the wider railway, surroundings cleaning bays and railway sidings are also heavily polluted areas; concentrations of Pb, Cu, Zn, Fe, Cr and Hg in soils could be several times higher than at relatively clean control areas outside studied sites (8). Heavy metals emission sources in the environment are both; natural ,such as soil ,rock erosion and dust or anthropogenic, such industrial activities, mining, organization, transportation and pesticides (6). Rapid economic development has led to rapid expansion of the highway transportation industry which has resulted in increases in the emissions of such contaminants as heavy metals, roadside soils tend to accumulate pollutants directly emitted from vehicle exhaust, and soils can easily come into contact with pedestrians and inhabitants near the roads, either via inhalation of suspended particles or by direct contact exposure to inhalable emissions from roadways has been implicated as a threat to human health and is associated with an increased risk of respiratory illness (22). Emitted dusts are naturally eliminated as deposits to earth surface through dry or wet deposition in rainfall (2). Exposure to heavy metals is normally chronic because of food chain transfer, Acute (immediate)

poisoning through ingestion of or dermal contact with heavy metals is rare, but it is possible, chronic problems associated with long-term heavy metal exposures are mental lapse caused by Pb exposure; Cd effects on the kidney, liver, gastrointestinal tract; and As poisoning of the skin, kidneys, and central nervous system. The contamination by heavy metal of soil increases risks and hazards to human and the ecosystem through food or direct contact, as soil plant human or soil plant animal human interaction is inevitable leading to phytotoxicity and decrease in agricultural yield causing food insecurity (3). Numerous studies link the presence of heavy metals in soil to industrialization. A part from industries, roadways and automobiles are emerging as major contributors of heavy metal contamination in soil. It is now well established that a variety of motor vehicles introduce a number of toxic metals into the environment, most of which are released adjacent to roadways. Their concentration in the soil is a major concern because of their toxicity and threat to human life and the environment. Combustion of fuel, engine oil, wear and tear of brakes, tires, leakage of oils, are some of the contributing factors for the contamination of soil (19). This study is aimed to investigating the possible problems of pollution with heavy metals deposited from the different location of road side of Erbil city. The analysis will be done using different contamination index methods of contamination factor (CF), Ecological risk factor, degree of contamination (Cdeg) and potential ecological risk factor.

MATERIALS AND METHODS Study area

Erbil governorate situated 414 meters above the sea level, on longitude 43° 15' E and latitude 35° 11' N to 37° 24 N' (21). Erbil's soil are calcareous, originating from limestone and dolomite in different formations. The topsoil is calcareous with a 1-2% organic matter and exists in areas with hot-dry summers and cold rainy winters (4). The Erbil climate is somehow similar to the Irano-Turanian type of the semi-arid zones, characterized by cold winters, mild-growing periods in spring and hot summers (8). The local public transportation for Erbil city is

provided by buses and taxis. Sample collect from fifty sites (S1-S15) along the roadside were selected (Table 1). Soil samples were taken 5, 25, 50 m from the road edge, GPS was used to record the coordinates of the sample locations. At each sampling location five surface soils (0-5 cm, approximately 1,000 g each) at all 15 location were take respectively, and mixed. The soil samples were stored in polyethylene bags transportation and storage then air-dried at room temperature (25 C°), crushed and sieved through 2-mm stainless sieve to remove debris (17). As shown in Table 1 (S1, S2, S3, S4, S5, S6, S7 and S8) were located inside Erbil (Bahare new, Newroz, New Hawler, Hesarok, Azadi1, Zen city, Atconz city, Pank village and (S9, S10, S11, S12, S13, S14 and S15) Binaslawa, Darato, Qushtapa, Shaways, Kasnazan, Bahirka, Pirzin) located outside Erbil city.

Table 1. Sampling locations

G! 4	C!	Coordinatio	n Location		
Site	Site name	Coordination Location			
No.		North	East		
S1	Bahari	36° 18'	44° 03'		
S2	Newroz	36° 17'	43° 97'		
S3	New	36° 22'	44° ′∩6′		
S4	Hesarok	36°17′	44°707°		
S5	Āzadi 1	36°16'	44° 01'		
S6	Zen City	36° 25'	44° 06'		
S7	Atconz	360 241	44° 61'		
S8	Pank	36° 26'	430-001		
S9	Binaslaw	36° 16'	<u>4</u> 4°~11¹		
S1	Darato	36°12'	44°7157		
S1	Oushtap	35° 99 1	44°773′		
S1	Shaways	36° 251	44°708°		
S1	Kasnaza	36° 021	<u> 1</u> 2° 174°		
\$1	Bahirka	36° 31'	44° 03'		
\$1	Pirzin	₹ 6°′261	<i>44</i> °^06′		

Sample preparation and analysis

All samples were air dried and passed through a 2-mm polyethylene sieve to remove rocks, leaves, and other debris, then ground with an agate mortar and sieved through a 0.15-mm polyethylene sieve. All handling procedures were carried out without contacting any metals to avoid potential cross-contamination of the samples. Approximately 1.0 g of each soil sample was digested primarily in a mixture solution of HNO₃ -HCl (1:3), then added HClO₄ for further digestion. The total concentrations of Pb, Cu, Ni, and Zn in the digested samples were determined by using flame atomic absorption spectrophoto-metry, and Cd was determined through using graphite furnace atomic absorption spectrometry. materials Standard reference GSS-6 (geochemical standard soil) was used for quality assurance and quality control. The recovery rate of the metals ranged from 90% to 110%.

Determination of heavy metal concentration in the soils

The soil samples were analysed for five metals including: arsenic (As), cadmium (Cd), cobalt (Co), chromium (Cr), copper (Cu) and zinc (Zn) and digested in aqua regia using 3:1 nitric to hydrochloric acids as given in (1). Metals in the final solutions were determined using ICP-Mass Spectroscopy (ICP-MS).

Soil pollution index

Pollution index is a powerful tool for ecological geochemistry assessment, the pollution indices which used for determining or assessing pollution or contamination heavy metals in soils and sediments were classified to two types of single index and integrated index in an algorithm point of view. The pollution indices for assessing heavy metal contamination are classified into three types: (i) Contamination indices, (ii) background enrichment indices, and (iii) Ecological risk indices (14).

Table 2. Pre-industrial reference level (pg/g) and toxic- response factor (5)

Elements	Hg	Cd	As	Cu	Pb	Cr	Zn
Pre-industrial reference level	0.25	1.0	15	50	70	90	175
Toxic- response factor	40	30	10	5	5	2	1

Single indices

Single indices are indicators used to calculate or assess only one contamination metal, which include contamination factor, ecological risk factor, enrichment factor, and index of geo-accumulation (14), thus only four methods illustrated as follows:

Contamination factor

A contamination factor (C_f^l) used to describe the contamination of a given toxic substance in a lake or a sub-basin is

$$C_f^t = \frac{\overline{C}_{0-1}^t}{C_-^t}$$

Where $C_{\text{o-1}}$ is the mean content of the substance i in at least 5 sample sites, and is the pre-industrial reference level for the substance. The following terminologies are

used to describe the contamination factor: $C_f^i < :$ low contamination factor, $1 \le C_f^i < 3:$ moderate contamination factors, $3 \le C_f^i < 6:$ considerable contamination factors and $C_f^i \ge 6:$ very high contamination factor. Here, contamination factor (C_f^i) was expanded to be defined as

$$C_f^i = C_i / C_{ri}$$

Where C_i is the metal content (i) instead of mean content from at least 5 sample sites; C_{ri} is the reference value of (baseline level), or national criteria of metal (i). When the sediment quality guideline was selected for the C_{ri} , the concentration factor (CF) is equal to the sediment quality guidelines such as effect range low (ERL) per effect range median (ERM), and threshold effect level (TEL) per probable effect level (PEL).

Ecological risk factor

An ecological risk factor (Er') quantitatively express the potential ecological risk of a given contaminant, which is suggested by Hakanson (5) is:

$$Er^{i}=Tr^{i}\cdot C^{i}_{f_{i}}$$

Where Tr is the toxic-response factor for a given substance, and C_f^i is the contamination factor. The Tr values of heavy metals concluded by (5). The following terminologies used to describe the risk factor: Er < 40; low potential ecological risk, $40 \le Er < 80$; moderate potential ecological risk, $80 \le Er < 160$; considerable potential ecological risk, $160 \le Er < 320$; high potential ecological risk and $Er \ge 320$; very high ecological risk. It was use to assessing the quality of sediments and soils in environment by heavy metals.

Integrated indices

Integrated indices are indicators used to calculate more than one metal contamination, which based on the single indices. Each kind of integrated index might been composed by the above single indices separately. According to algorithm, eight integrated methods illustrate as following.

Sum of pollution index

A sum of pollution index (PI_{sum}) might be defined as

$$PI_{sum} = \sum_{i=1}^{m} p_i$$

Where P_i is the single pollution index of heavy metal i, and m is the counted heavy metal species. The sum of pollution index was widely used in soil and sediment quality assessment by heavy metals such as the degree of contamination and the potential ecological risk index. (14).

Degree of contamination (C_d)

The degree of contamination $(C_{\rm d})$ was originally defined as the sum of all contamination factors

$$C_d = \sum_{i=1}^m C_f^i$$

Where C_f^i is the single index of contamination factor, and m is the counted heavy metal species. For the description of contamination degree, the following terminologies have used $C_d < m$; low degree of contamination, $m \le C_d < 2m$; moderate degree of contamination, $2m \le C_d < 4m$; considerable degree of contamination and $C_d > 4m$; very high degree of contamination (14).

Potential ecological risk index (RI)

The potential ecological risk index (RI) was in the same manner as degree of contamination defined as the sum of the risk factors

$$RI = \sum_{i=1}^{m} Er^{i}$$

Where Er is the single index of ecological risk factor, and m is the counted heavy metal species. The following terminology or ranges were used for the potential ecological risk index: *RI*<150; low ecological 150≤*RI*<300; moderate ecological risk, 300≤RI<600; considerable ecological risk and RI>600; very high ecological risk when the toxic-response factors were used for the eight elements (5).

Statistical analysis

Experimental designed in completely randomized design (CRD) data was statistically analyzed using SPSS version 24. All data expressed as mean value. The difference among the means of compost types

compared by applying Duncan multiple comparison tests at level of significant 5% (20).

RESULTS AND DISCUSSION

Soil metal contents

Non-essential trace metals detection in soil is great important for soil properties, not only because these elements necessary for protect the soil and water resource from pollution, but also their impact on human health. Results in Table 3 shown that heavy metal concentration in soil were changed significantly at (p<0.05) influenced by roadside pollution. The highest values were (4.60, 1.80, 217.83, 62.14 and 215.18) mg.kg⁻¹, for (As, Cd, Cr, Cu and Zn) were recorded in $(S_{11}, S_{13}, S_7, S_4 \text{ and } S_6)$ respectively. This result indicate that roadways and automobiles were emerge as major contributors of heavy metal contamination in soil, it was established that a variety of motor vehicles introduce a number of toxic metals into the environment, most of which are released adiacent to roadways. concentration in the soil is a major concern because of their toxicity and threat to human life and the environment, combustion of fuel, engine oil, wear and tear of brakes, tires, leakage of oils etc. are some of the contributing factors for the pollution of soil, recorded result were similar to (13) which, noticed that heavy metals might been transferred to human bodies by way of ingestion, inhalation and dermal contact, or through the food chain. Khudhur (9) reported that out of the forty heavy metals in the earth, As, Cd, Cr, Cu, Pb, Hg and Ni were the most common heavy metals that are considered pollutant, in particular the metals arsenic, antimony, lead, mercury, copper, chromium and chromium VI, as the soluble compound of chromium, can have adverse harmful effects on human health and the environment.

Table 3. The concentration of some trace metals in different site in Erbil city

Sites	Heavy metals mg.kg ⁻¹						
	As	Cd	Cr	Cu	Zn		
1	4.51	1.34	80.44	48.65	202.50		
2	3.30	1.19	111.04	27.28	191.03		
3	2.83	1.17	109.37	17.10	208.41		
4	4.30	1.43	107.44	62.14	177.04		
5	2.81	0.85	136.93	20.71	197.35		
6	2.53	0.49	99.71	29.54	215.18		
7	4.50	0.22	217.83	32.45	130.56		
8	3.28	1.08	122.90	16.91	188.24		
9	1.79	1.33	116.64	28.83	152.11		
10	3.06	1.14	128.07	41.48	141.07		
11	4.60	1.25	136.61	30.82	144.77		
12	2.82	1.14	132.50	43.57	165.96		
13	1.66	1.80	131.20	19.81	114.88		
14	1.92	1.18	184.12	22.01	179.38		
15	3.18	1.42	128.89	18.21	148.09		
LSD	1.49	0.68	62.69	20.24	89.77		
(0.01)							

Results in Table 4 indicate that different distance from roadside was significantly at heavy $(p \le 0.05)$ affected on metal concentration of soil. The highest values were (3.99, 1.51, 153.31, 40.71 and 194.11) were recorded in distance (2). Investigated result indicate that distance near road-side soil shows a high concentration of heavy metal that can be attributed to motor vehicles, vehicular discharge of numerous gases and trace metal contaminants due to incomplete combustion of petroleum fuel, adversely affects the microbial population and their activities in the soil. Mineral filler materials in road surfaces contain different heavy metal species, which can be transported into the road-side soils by atmospheric precipitation or road runoff, the bio-availability and environmental mobility of the metals are dependent upon the form in which the metal was associated with the soil, those metals could been directly harm public health by entering the body via soil, dust and through the food chain. The result were similar to those recorded by Sripathy (19) which, road-side heavy reported that concentration was influenced by multiple factors, including traffic properties, highway characteristics, road-side terrain, road-side distance, rainfall and wind direction, etc., normally the heavy metal content in roadside soils have a belt-shaped distribution in terms of distance to the road edge, increasing/decreasing with exponentially distance from the road.

Table 4. The concentration of some trace metals in different distance from roadside

Distance m	Heavy metals mg.kg ⁻¹					
	As	Cd	Cr	Cu	Zn	
1	2.61	1.04	143.27	27.70	162.51	
2	3.99	1.51	153.31	40.71	194.11	
3	2.82	0.85	92.16	23.49	154.70	
LSD (0.01)	0.67	0.31	28.03	9.05	40.14	

Results soil pollution index

Contamination factor and degree of contamination

Results in Table 5 indicates that there were roadside pollution significantly at (p≤0.05) affected on contamination factor and degree of contamination. The highest contamination factor and degree of contamination values were (0.307, 1.803, 1.243, 2.42 and 1.191), while for degree of contamination was (5.165) for (As, Cd, Cr, Hg, Ni, Pb) were recorded in $(S_{11}, S_{13}, S_7, S_4 \text{ and } S_3)$ and degree of contamination was recorded (S_4) . respectively. According to contamination factor and degree of contamination index. indicate considerable contamination factor for (Qushtapa) and moderate contamination factor (Kasnazan), while (Atconze Hasarok5, Zen city) showed very high contamination factor, with considerable low degree of contamination in (Hasarok 5). This result can be attributed to the influences of crowded traffic, because traffic was regarded as a source of heavy metal content in soil, wear and corrosion of vehicle parts (brakes, tyres, radiators, body and engine parts) is one of the potential sources of many heavy metals. This result and interpretation were similar to the result reported by Seda et al., (16) that indicated CF of the trace elements (Al, As, Co, Cr, Mn, Ni, Ti and V) of soil samples in the studied areas based on the local soil background was showed low to moderate contamination.Mlitan, (12) showed CF values between 0.5 and 1.5 indicate that the metal was entirely from crust materials or natural processes; whereas CF values greater than 1.5 suggest that the sources were more likely to be anthropogenic. The Cf revealed that soils show highest contamination factors for Pb and Cu ranging from considerable contamination to very high contamination, while Zn, Mn and Cd had minimal to moderate contamination, on the other hand, demonstrated Ni might been

moderate to considerable contamination. Likuku et al., (11) noted that overall windward at the SelebiPhikwe copper and nickel mine in eastern Botswana, based on the CF values indicate that soils have been considerably contaminated with Cu and Ni, moderately contaminated with Fe, Mn, Pb and Zn, while, showed signs of low contamination with Co. In case degree of contamination, the windward soils fall under considerable contamination. Compared to the average soil backgrounds, the sites (2, 3, 4, 5 and 7) have a moderate degree of contamination (8 < C_{deg} < 16), while the sites 6 and 8 have a considerable degree of contamination (16< C_{deg}<32). Based on both local and average soil backgrounds, Sardasht and garden soil (control) have a moderate degree of contamination, while the Erbil Steel Company has a very high degree contamination (C_{deg}) ≥32) same results concluded by Seda et al., (16).

Table 5. Contamination Factor and Degree of Contamination

Sites		Cdeg				
	As	Cd	Cr	Cu	Zn	
1	0.301	1.343	0.894	0.973	1.157	4.668
2	0.22	1.187	1.234	0.546	1.092	4.277
3	0.189	1.167	1.215	0.342	1.191	4.103
4	0.287	1.43	1.194	1.243	1.012	5.165
5	0.187	0.85	1.521	0.414	1.128	4.101
6	0.168	0.493	1.108	0.591	1.23	3.59
7	0.3	0.223	2.42	0.649	0.746	4.339
8	0.219	1.077	1.366	0.338	1.076	4.075
9	0.119	1.332	1.296	0.577	0.869	4.193
10	0.204	1.14	1.423	0.83	0.806	4.402
11	0.307	1.25	1.518	0.616	0.827	4.518
12	0.188	1.143	1.472	0.871	0.948	4.623
13	0.11	1.803	1.458	0.396	0.656	4.424
14	0.128	1.18	2.046	0.44	1.025	4.819
15	0.212	1.423	1.432	0.364	0.846	4.278

Ecological risk factor and potential ecological risk index

Results in Table 6 indicate that road side pollution significantly at (p \leq 0.05) affected the ecological risk factor and RI. The highest ecological risk factor and RI values were (3.07, 54.10, 435.67, 310.68 and 215.18) and for RI was (748.38) for (As, Cd, Cr, Cu and Zn) were recorded in (S₁₁, S₁₃, S₇, S₄ and S₆) respectively, with potential ecological risk respectively recorded in (S₄). According to ecological risk factor and potential ecological risk index, was indicate low potential ecological risk in (Qushtapa) moderate potential ecological risk in (Kasnazan) while (Hasarok 5, Zen city) considerable high

potential ecological risk, on the other hand, (Atconze) considerable very high ecological risk, while potential ecological risk index considerable very high ecological risk recorded in (Hasarok 5). This result indicates metals in soil have been shown to be associated with ambient particles released by roadside dust, their discharge of heavy metal into the environment especially in soil varies across time, location, the intensity of human activities and traffic volume, mobility and bioavailability of the metals and can cause the production and release of inflammatory mediators by the respiratory tract epithelium, studied results and interpreting partially agreed with those reported by Jiang et al., (7). Results concluded that, the potential ecological risk arrayed in the order of ER (Cd) > ER (Pb) > ER(Cu) > ER(Cr) > ER(Zn), Cd was the key influence factor to cause the potential ecological risk, and its mean value of ER was up to 72.92, all of the sampling points have strong potential ecological risk of Cd, whereas other heavy metals only showed slight potential ecological risk to the environment. Li et al., (10) indicated that the potential ecological risk of sediments in Lower River, estuary and Jinzhou bay was at very high level, and Cd contributed more than 95% of RI in the sediment samples. The estuary was the most polluted area, and their RI value was as high as 34.6 times of that in line value for very high ecological risk level.

Table 6. Ecological Risk Factor and Potential Ecological Risk Index

Sites	Ecological Risk Factor					
	As	Cd	Cr	Cu	Zn	RI
1	3.01	40.30	160.87	243.27	202.50	649.95
2	2.20	35.60	222.07	136.42	191.03	587.32
3	1.89	35.00	218.73	85.50	208.41	549.53
4	2.87	42.90	214.89	310.68	177.04	748.38
5	1.87	25.50	273.86	103.53	197.35	602.11
6	1.68	14.80	199.42	147.70	215.18	578.79
7	3.00	6.70	435.67	162.27	130.56	738.20
8	2.19	32.30	245.79	84.57	188.24	553.09
9	1.19	39.96	233.29	144.13	152.11	570.68
10	2.04	34.20	256.13	207.40	141.07	640.84
11	3.07	37.50	273.21	154.08	144.77	612.64
12	1.88	34.30	264.99	217.87	165.96	685.00
13	1.10	54.10	262.40	99.03	114.88	531.52
14	1.28	35.40	368.24	110.05	179.38	694.35
15	2.12	42.70	257.79	91.07	148.09	541.77

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