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Using Pollution Indices to Assess Heavy Metals Contaminated Soil in some Libyan Regions

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ABSTRACT

Soil pollution by heavy metals is an important challenge facing many countries around the world, including Libya. This investigation was carried out across a heavy metals pollution in Libyan soil using pollution Indices such as Geo-accumulation index (i-GEO), contamination factor (CF), pollution load index (PLI), Contamination degree (CD), Modified contamination degree (mCD), Metal pollution index (MPI), overall metal contamination index (MCI). These pollution indices shed light on the quality of soil in Libya, and indicate that some of the heavy metals were unpolluted to severely extremely polluted with regard to i-GEO especially for Ni Cu & Pb, and the contamination factor were low to very high contamination status. the Most of the polluted soils fell within the industrial region. In particular, some of the sites in the industrial region showed high i-GEO. CF showed significant to very high contaminated for Ni, Cr, Zn, Cu and Pb for most of the sampling from the industrial area and also because they are closer to a major road intersection with a large traffic volume such as Benghazi, Al-marij Tripoli, Misurata & Khomes. The high CF index of heavy metals in soil made significant contribution recorded based on pollution load index (PLI). A very high pollution recorded in soils of Al-marij, Benghazi, Sirt, Zwara & Khomes with PLI ≥ 3. Also, very high contamination degree (CD > 24) was found in soils of Al-Marj, Benghazi, Misurata, Ejmail, Sirt, Zwara, Albayda & Khomes. Furthermore, the study confirmed that Al-Marj & Benghazi had the highest levels of overall metal contamination index (MCI). The results demonstrated that the values of MPI < 1 for all soils studied inducted that the overall of ecosystem is still non-polluted dilution and dispersion of heavy metals content due to large of the study area. However, the soil surrounding the biggest cities is heavily influenced by human activities, which causes massive accumulation of heavy metals in the soil in most regions. So, Monitoring and environmental audit should start into action to boost the environmental quality of Libyan soils

الملخص العربي

يعد تلوث التربة بالمعادن الثقيلة تحديا هاما يواجه العديد من البلدان في جميع أنحاء العالم ، بما في ذلك ليبيا. تم إجراء هذا البحث عبر تلوث المعادن الثقيلة في التربة الليبية باستخدام مؤشرات التلوث مثل مؤشر التراكم الجغرافي (i-GEO) ، عامل التلوث (CF) ، مؤشر حمل التلوث (PLI) ، درجة التلوث (CD) ، درجة التلوث المعدلة (mCD) ، مؤشر تلوث المعادن (MPI) ، مؤشر تلوث المعدن الكلى (MCI). تسلط مؤشرات التلوث هذه الضوء على جودة التربة في ليبيا ، وتشير إلى أن بعض المعادن الثقيلة كانت غير ملوثة لتلوث شديد للغاية فيما يتعلق بـ i-GEO خاصة بالنسبة إلى Ni Cu & Pb ، وكان عامل التلوث منخفضًا إلى مرتفع للغاية. الحالة. تقع معظم التربة الملوثة داخل المنطقة الصناعية. على وجه الخصوص ، أظهرت بعض المواقع في المنطقة الصناعية ارتفاع i-GEO. أظهر التليف الكبريت نسبة كبيرة إلى عالية الملوثة في النيكل والكروم والزنك والنحاس والحصى في معظم العينات من المنطقة الصناعية وأيضًا لأنها أقرب إلى تقاطع طريق رئيسى مع حجم مرور كبير مثل بنغازي والمريج طرابلس مصراته والخمس. قدم مؤشر CF العالي للمعادن الثقيلة في التربة مساهمة كبيرة مسجلة على أساس مؤشر حمل التلوث (PLI). تم العثور على تلوث عالٍ جدًا في تربة المريج وبنغازي وسرت وزوارة والخمس مع PLI ≥ 3. كما تم العثور على درجة تلوث عالية جدًا (CD> 24) في تربة المرج وبنغازي ومصراته وإلجميل ، سرت ، زوارة ، البياضة والخمس. علاوة على ذلك تؤكد الدراسة كذلك أن المرج وبنغازي لديهما أعلى مستويات مؤشر تلوث المعادن (MCI). أوضحت النتائج أن قيم MPI <1 بالنسبة لجميع أنواع التربة التى تمت دراستها حثت على أن إجمالي النظام البيئى لا يزال مخففًا وتشتت غير محتوي لمحتوى المعادن الثقيلة نظرًا لوجود مساحة كبيرة من مساحة الدراسة. ومع ذلك فإن التربة المحيطة بالمدن الكبرى تتأثر بشدة بالأنشطة البشرية ، مما يسبب تراكمًا هائلاً للمعادن الثقيلة في التربة في معظم المناطق. لذلك يجب أن تبدأ المراقبة والمراجعة البيئية في العمل لتعزيز الجودة البيئية للتربة الليبية.

INTRODUCTION

Soil is a vital source for humans because its chemical and physical conditions affect agricultural production. It is commonly accepted that soil contamination with heavy metals is potentially damaging ecosystems (Liu *et al*., 2013). Typically, the accumulation of heavy metals in soil is related to the direct and indirect anthropogenic activities (Mazurek *et al*., 2017; Aishah *et al*., 2018). High levels of heavy metals in soils do not necessarily reflect that influence, but instead may be of a diagenetic origin or grain size effects. Since metals from both natural and anthropogenic sources accumulate in soils. A crucial step for pollution assessment of soil is to establish the expected natural background concentration levels, from which various approaches can be used to quantify inputs (Ololade, 2014). A study of the distribution, enrichment and accumulation of heavy metals in soils is particularly important, especially in developing countries like Libya. However, the environmental problem of soil pollution by heavy metals has received increasing attention in the last few decades in both developing and developed countries throughout the world (Sodango, *et al* 2018). Increased inputs of heavy metals in the terrestrial environment due to rapid industrialization coupled with inadequate environmental management in the developing country. Soil plays an important role in global metal cycling. Due to continuous human activities, these soils are highly contaminated (Luo *et al*. 2012). The rapid population growth, agricultural and industrial activities has brought the risk of increasing the soil pollution (Sun, 2017). Soils are usually regarded as the ultimate sink for heavy metals discharged into the environment. Thus, soil pollution may cause human health risk through its effects on the hygiene quality of food and drinking water. Also soil pollution affect air quality through enrichment of heavy metals content in air borne particles originating from soil. The study of heavy metal pollution is of increasing interest because of the awareness that heavy metals present in soil may have negative consequences on the human health and whole environment. In order to determine the degree of contamination of soil levels with heavy metals, their concentration is compared with the content of the local geochemical background, and by calculation of the geo-accumulation index (i GEO), pollution index (PI), pollution load index (PLI), metal pollution index (MPI), condemnation degree (CD), elemental contamination index (ECI), overall metal contamination index (MCI) (Weissmannová and Pavlovský, 2017). A number of previous studies have reported for the assessment of heavy metal contamination in soils on many developing countries using different pollution indices, but those studies are very limited especially in Libya, However, those studies were found that the evaluation of the heavy metal level in the environment is useful and powerful for environmental protection. Heavy metal assessment in Libyan soils has become urgently needed due to an increasingly serious threat to both humans and environments from different anthropogenic metal contribution in Libyan cities. Rising heavy metal concentration in soil is a serious and current concern for regulatory bodies for environmental risk assessment. Therefore, the use of pollution indices methods for monitoring heavy metals has a great importance among the environmental studies. The anthropogenic metal contribution in soil can be estimated from the enrichment relative to un polluted reference materials or widely accepted background (pre-industrial) levels, such as the average values for continental shale or crustal abundances (Devanesan *et al*., 2017). Several authors have widely assessed heavy metals pollution in soils. But information on pollution load of heavy metals, contamination degree and overall metal contamination in Libyan soils is rare in literature. Therefore, this study is aimed to investigate the pollution states of heavy metals in Libyan soil using several pollution indices such as geoaccumulation index (i-GEO), contamination factor (CF), pollution load index (PLI)contamination degree (CD), Metal pollution Index (MPI).

MATERIALS AND METHODS

Libya is located in Northern Africa and lies between latitudes 33 & 200 °N and longitudes 200 & 25 °E. Libya covers an area of approximately 1,775,500 km2. 19 cities were selected to evaluate some heavy metals contaminations soils (GPS coordination shown in Table 1) namely; cadmium (Cd), lead (Pb), chrome (Cr), nickel (Ni), zinc (Zn), & copper (Cu). These sites were selected to cover different regions in Libya.

One kg of soil was collected from each zone, using soil auger at depth 0-30 cm. The samples were brought to laboratory where they were air dried. Soil samples were then passed through 2 mm sieve in order to collect the fraction of coarse particles. Five grams of each of samples were digested using aqua-regia, and then analyzed for various heavy metals, i.e., Cd, Pb, Cr, Ni, Zn & Cu. Average values of three replicates were taken for each determination.

Aiming to understand the pattern of metal contamination, several useful pollution indices were used to calculate heavy metals concentration in soil such as; Geoaccumulation Index (i-GEO), Contamination factor (*Cf*), Load Pollution Index (LPI), Contamination degree (CD). Metal pollution index (MPI), Metal contamination Index (MCI); i.e.,

Table 1. The GPS coordination of Sampling Sites

Site	Location
Al-Marj	*"59.26'28°32N 20°49'56.15" E*
Benghzi	*"17.97'06°32N 20°06'52.13" E*
Misurata	*"45.34'20°32N 15°06'20.85" E*
Abougrain	*"56.61'26°31N 15°15'13.80" E*
Zliten	*"29.54'27°32N 14°34'35.31" E*
Tripoli	*"53.59'50°32N 13°14'12.80" E*
Sabrata	*"08.52'48°32N 12°23'27.87" E*
Ejmail	*"15.36'31°32N 11°54'47.68" E*
Houn	*"30.03'07°29N 15°56'47.39" E*
Brack	*"02.90'33°27N 14°16'12.06" E*
Sebha	*"21.82'02°27N 14°25'29.08" E*
Murzuq	*"29.69'55°25N 13°55'17.06" E*
Ubari	*"24.53'35°26N 12°47'28.27" E*
Ghat	*"57.55'46°25N 10°33'45.54" E*
Sirt	*"28.88'10°31N 16°36'24.72" E*
Zwara	*"42.15'55°32N 12°05'11.20" E*
Albayda	*"44.24'45°32N 21°45'30.84" E*
Khomes	*"01.91'39°32N 14°15'49.62" E*
Kufrah	*"53.43'11°24N 23°17'09.20" E*

- Geo-accumulation index (i GEO)

A common approach to estimate the enrichment of metal concentrations above background or baseline concentrations is to calculate the geo accumulation index **(i GEO).** This method assesses the metal pollution in terms of seven (<0 to >5) enrichment classes ranging from background concentration to a very heavily polluted., as follows:

$$\textbf{i-}\text{EGO} = \mathbf{\log_2 (Cn/1.5\ Bn)}$$

where:

Cn is the concentration of the heavy metals in the samples (mg kg^{-1}).

Bn is the background concentration of the heavy metals (mg kg^{-1}).

Background values are the natural contents of substance in the soil completely dependent on the compositional and mineralogical characteristic of the parent/source geological material (Abbaslou *et al*., 2014).

- Contamination factor (CF)

, contamination factor **(CF)** was used to quantify the enrichment of heavy metals in contaminated soils with respect to soil background; a contamination factor (Cf) of each metal was attributed to each metal using equation of (Thambavani and Mageswari, 2013).

$$\mathbf{CF} = \text{Cn}/\ \mathbf{Bn}$$

Where:

Cn is the measured concentration of each heavy metal (mg kg^{-1})
Bn is background value for each metal (mg kg^{-1}).

The background is refers to the concentration of metal indicates the concentration of metal (of interest) in the soils when there was no anthropogenic input.

- Pollution load index (PLI):
Pollution load index (PLI) was used to indicate the degree of integrated heavy metal pollution in affected soils (Liu *et al*., 2013), this parameter is expressed as:

$$\mathbf{PLI} = (\mathbf{CF_1} \times \mathbf{CF_2} \times \mathbf{CF_3} \ldots\ldots\ldots \times \mathbf{CF}_n)^{1/n}$$

- Contamination Degree (CD)
The CD is aimed at providing a measure of the degree of overall contamination in a particular sampling site (Thambavani and Mageswari, 2013). This index is calculated as:

$$\mathbf{CD} = \sum_{i=1}^{n} \mathbf{CF}$$

- Modified Contamination Degree (mCD)
Modified and generalised forms of the equation for the calculation of the overall degree of contamination are presented by equation given by (Thambavani and Mageswari, 2013). The modified formula is generalized by defining the degree of contamination (*mCD*).

$$\boldsymbol{mCD} = \frac{\sum_{i=1}^{n} \mathbf{CF}}{n}$$

- Metal pollution index (MPI)
The MPI has been calculated to enable presentation of all results from the metal concentrations (Cd, Pb, Cr, Ni, Zn and Cu) as one value if possible, this implies that the six metal concentrations must be normalised to make it possible to sum up and average the different metal concentrations into one value (Thambavani and Mageswari, 2013). MPI has been calculated as:

$$\text{MPI} = \mathbf{log}\, \frac{\sum_{i=1}^{n} [\mathbf{X}]}{refi}$$

- Elemental contamination index (ECI) and overall metal contamination index (MCI)
Elemental contamination index (ECI) and overall Metal Contamination Index (MCI) are expression of single metal contamination within a sample or combined metal contamination for a sample (Cx) relative to the background values of the respective metal (B) (Thambavani and Mageswari, 2013) , and are expressed as:

$$\text{ECI} = \frac{(C_X - B)}{B}$$
$$\text{MCI} = \sum \frac{(C_X - B)}{B}$$

RESULTS AND DISCUSSION

The assessment of heavy metal contamination can be conducted using various methods such as total heavy metal concentration. Table (2) lists the concentrations and the background values of heavy metals in soils of the study regions. The concentration level of heavy metals in the Libyan soils is variable owing to the heterogeneity of soil types and parent material. Also, the variation in concentrations of heavy metals reflects the influence of different factors such as traffic density, microclimatic condition and nature of anthropogenic inputs.
According to Table (2), the concentrations of Cd were higher than background value Almarj, Tripoli, Sirt, Zwara, Albayda & khomes. Cd showed highest concentrations in Almarj, which Cd was about 5.557-fold higher than background. the importance sources of Cd are fossil fuel combustion iron and steel production, cement production, phosphate fertilizer. Cadmium compared to other heavy metals, relatively soluble and are therefore generally more mobile and toxic (Salah *et al*., 2013, Mayouf *et al*., 2014). Also, our results indicated that the concentrations of Pb in Benghzi, Tripoli, Sabrata, Ejmail, Sirt, Zwara, Albayda & Khomes were higher than background value. Pb exhibited highest concentrations in Sirte, which Pb was about 6.97-fold higher than background. Pb in contaminated sites can originate from a wide variety of anthropogenic activities in the form of disposal of high metal wastes, leaded gasoline and lead-based paints, land application of fertilizer, sewage sludge, pesticides, petrochemicals, and atmospheric deposition. However, it worthy of note that the concentrations of Cr in Almarj, Benghzi, Misurata, Zliten, Tripoli, Sabrata, Ejmail, Houn, Brack, & Albayda were higher than background value, the highest concentration of

Cr was found in soil from Benghzi (111.540 mg.kg^{-1}), about 25.292 fold higher than background. The high level of soil metals in the same regions may be a result of precipitation of industry such as iron industry steel factory dusts in Miusurata.

Also, it is important of note that the concentrations of Ni were higher than background value in all soils under study. The highest Ni concentration was in soil from Almarj (135.460 mg.kg^{-1}) about 30.786- fold higher than background (Table 2). Nickle recorded high concentrations when compared with other studied metals, this is may be attributed to the increase of industrial activities in these regions, such as cement industry which undergo process and production require energy from burning fossil fuel and vehicle emission (Barbieri, 2016). Moreover, Zn concentrations were higher than background value in all soils under study excepted soils from Misurata, Sebha & Murzuq. The highest concentration was in Benghazi (90.130 mg.kg^{-1}), about 6.997-fold higher than background. In addition,

the result showed that concentrations of Cu were higher than background value in Almarj, Benghzi, Misurata, Abougrain, Zliten, Tripoli, Sabrata, Ejmail & Houn The highest concentration was in Almarj (80.531 mg.kg^{-1}), about 21.417- fold higher than background.

Our results indicated that Cd, Pb, Cr, Ni, Zn, Cu were highly distributed on Almarj, Sirt, Benghzi. These cities were located near the industrial area and near major road that loads a heavy traffic. The problem of industrial pollution lay with the large number of small industries (food, dairy, garment, metallic paints detergent, and soap. According to Weissmannová and Pavlovský (2017), the amounts of heavy metals in soils are different and worldwide average concentrations vary. As a consequence of rapidly growing amounts of heavy metals in soils, the contaminated soils become unavailable for plant growing crop cultivation, and the quality of soils change in terms of biodiversity, water cycles. Thus, pollution of soil can change the whole ecosystems. However, with the rapid industrialization and economic development, heavy metals are continuing to be introduced to soils via several pathways, such as atmospheric deposition, fertilization, runoff, and point sources (Zhang *et al*., 2019).

Quantification of Heavy Metal Pollution in the Soil

Pollution indices are a powerful tool for environmental assessment. In the present study, we are assessing the soil contamination based on the i.GEO, CF), CD, mCd, PLI, MPI & MCI to assess environmental risk of the activities leading to pollution

i. Geo-accumulation index (i-GEO)

To quantify the degree of elemental accumulation in soil, geochemical index (i GEO) was calculated. Geoaccumulation index (i-GEO) is typically used to assess the degree of anthropogenic accumulated pollutant loads (Bhutiani *et al*., 2017) The calculation of environmental geochemical baselines is necessary to assess the current state of the environment and to provide guidelines and quality standards in environmental legislation and policy-making, especially in the evaluation of contaminated soils and in environmental risk assessment (Jia *et al*., 2018). The results of recent study showed that the i-GEO grades for the studied heavy metals varies from metal to metal and site to site (Fig.1 & 3). The background concentrations of heavy metals are dependent on the soil characteristics with regard to texture and structure. This could also explanation for the variation in the i-GEO among the studied region.

Table 2. Heavy metals concentrations mg Kg^{-1} in the studied soils

Site	Cd	Pb	Cr	Ni	Zn	Cu
Almarj	5.113	4.809	44.343	135.460	82.190	80.531
Benghzi	0.503	22.932	111.540	45.630	90.130	52.416
Misurata	0.655	0.725	71.357	31.167	3.065	13.057
Abougrain	0.281	3.697	0.995	22.815	74.880	14.391
Zliten	0.222	0.211	34.098	29.519	31.298	4.212
Tripoli	1.287	36.270	14.040	6.435	35.100	8.190
Sabrata	0.152	17.550	11.694	15.210	88.920	14.040

Ejmail	0.257	32.760	9.364	22.230	88.810	18.720
Houn	0.222	1.720	6.318	15.912	44.577	20.241
Brack	0.847	7.097	6.329	11.980	14.940	3.529
Sebha	0.007	0.120	0.023	26.987	0.171	0.036
Murzuq	0.060	0.710	0.210	19.531	2.040	0.100
Ubari	0.070	6.150	0.193	22.852	40.000	2.250
Ghat	0.613	0.777	0.189	12.801	31.199	2.098
Sirt	3.523	53.675	3.527	36.845	23.552	25.027
Zwara	4.281	51.700	4.171	38.978	29.099	27.837
Albayda	3.192	45.330	4.824	20.303	13.114	25.909
Khomes	3.216	43.687	4.281	31.569	13.649	24.094
Kufrah	0.711	0.849	0.232	11.462	29.451	3.155
Ghat	0.613	0.777	0.189	12.801	31.199	2.098
background	**0.920**	**7.700**	**4.410**	**4.420**	**12.880**	**3.760**

According to the i-GEO values, Cd i-GEO states remain unpolluted in Benghazi, Misurata Abougrain, Zliten, Tripoli, Sabrata, Ejmail, Houn, Brack, sebha, Murzuq, Ubari Kufrah and Ghat, suggesting that the soil in these cities are in background value with respect to this metal. While, attain in other cities which indicates that soil of these cities were slightly polluted by Cd such as soil of Al-Marj, Sirt, Zwara, Albayda and Khomes with i-GEO values 0.420-1.10. The anthropogenic activities has led to higher contents of Cd in the soil of the studied area. Cadmium in soils is derived from deferent sources such as sewage sludge and phosphate fertiliser application, fossil fuel combustion, metallurgical works, wastes from cement industr. Cadmium is a highly toxic metal that can cause harmful reactions even in low concentration (Khan *et al*., 2017)

Lead is the environmentally most toxic, it is significantly accumulated in the soils, as indicated by their respective average. According to our results, i-GEO values (2.076-2.788) inducted moderately severely polluted in soils of Tipoli, Ejmaill , Zwara, Albayda & Khomes. While the i-GEO states in Benghazi, Sabrata was moderately polluted (i-GEO 1.175-1.561). An increased amount of lead in these cities comes from human activities such as lead in gasoline, coal burning, paints. Lead is non-biodegradable toxic metal in the environment and now, it has become a global health issue (Mishra *et al*., 2019). Pb is a widespread heavy present in soils, it is mostly present in top layer of soil due to the deposition from air containing smoke from vehicles. In contrast, the unpolluted i-GEO statues was found for soils of Al-Marj, Misurata, Abougrain, Zliten, Houn, Brack, Sirt, Sebha, Murzuq, Ubari, Kufrah, & Ghat suggesting that the Pb concentration in soil of these cities under stile under the background value of Pb. the concentrations of heavy metals can be affected by soil properties, such as SOC and pH. These studied regions with low i-GEO are low OM and CEC suggesting a low absorbing capacity of surface soil to Pb.

From Fig.1 & 3, it was also observed that Cr i-GEO values were belonged to the category of unpolluted in soils of Abougrain, Houn, Sirt,, Zwara, Albayda, Khomes, Brack Sebha, Murzuq, Ubari, Kufrah & Ghat , which mean that the Cr concentration in soil of these cities are in Cr background. It is worth noting that values of i-GEO in other examined soils have indicated different levels of Cr contamination. Where the i-GEO value (4.076) in soil of Benghazi classified as severely extremely polluted. The highest concentration of Cr could have resulted from the disposal and application of untreated waste. While, i-GEO (2.745, 2.366) for soil of Al-Marj and Zliten was moderately severely polluted. Furthermore, Cr i-GEO (3.431) in Misurata was classified as severely polluted. i-GEO 1.086 in soils of Tripoli was moderately polluted, and slightly polluted for soil of Sabrata and Ejmail (i-GEO 0.822 and 0.561 respectively). Chromium has attained wide attention because of its toxicity to environmental ecosystems.

According the Fig.1 & 3, the soil of Tripoli was considered as non-polluted suggesting that the Ni concentration stile under the background value of Ni. However, our results showed that values of i-GEO in other examined soils have indicated different levels of Ni contamination. The Ni i-GEO valuse (0.790-0.949) in Brack, Kufrah and Ghat were classified as slightly polluted. While i-GEO (1.198-1.785) classified as moderately polluted in

Abougrain, Sabrata, Ejmail, Houn, Albayda, Murzuq & Ubari. Whereas, i-GEO (1.198-1.785) for soils of Misurata, Sirt, Zwara,Khoumes and Sebha were moderately severely polluted. The highest value of Ni i-GEO value 2.745 was for soil from Al-Marj which considered as severely extremely polluted. The major sources of nickel contamination in the soil are metal plating industries, combustion of fossil fuels, and and electroplating. For Zn i-GEO status (Tables 3 & 4), the soils of Misurata, Albayda, Khomes, Brack, Sebha & Murzuq were considered as non-polluted. While i-GEO (0.286-0.862) was slightly polluted for soils of Zliten, Tripoli, Sirt, Zwara, Kufrah & Ghat. The i-GEO values of Abougrain, Houn and Ubari were (1.050-1.955) classified as moderately polluted. The results indicated that the i-GEO statuses of Al-Marj, Benghazi, Sabrata & Ejmail soil were moderately severely polluted with values ranged between 2.089 and 2.222. there has been significant concern regarding soil contamination by Zn due to expanding industrialization and urbanization. The excessive input of heavy metals into soils may lead to changes in soil physicochemical and biology properties which may create other environmental problems (Islam *et al*., 2017; Aishah *et al*., 2018).

Fig.1 & 3 showed Cu i-GEO status. The soils of Zliten, Brack, Sebha, Murzuq, Kufrah & Ghat considered as non-polluted. Slightly polluted i-GEO status was recorder in Misurata & Tripoli with i-GEO 1.211 and 0.538 respectively. The i-GEO values of Abougrain, Sabrata, Ejmail & Houn were (1.316-1.844) classified as moderately polluted. While, moderately severely polluted i-GEO status was in Sirt, Zwara, Albayda & Khomes with values ranged between 2.095 and 2.303. For soils of Al-Marj and Benghazi i-GEO status was belonged to the category of severely polluted with i-GEO values 3.836 and 3.216 respectively.

The comparison of data obtained in the present study showed that there are variances in anthropogenic sources of elements in tested soils, it could be concluded that the Cd of these cites soils has a geological source but human activity leads to rise the Cu concentration. Additionally, the extent of heavy metals influenced by climate conditions; e.g., temperature and precipitation. However, to avoid possible risks for the soil environment, close monitoring of Cd, Pb, Cr, Ni Zn and Cu is needed.

ii. Contamination factor (CF)

To assess the intensity of elemental contamination in soils, the contamination factor was calculated. CF is a powerful tool for processing, analyzing, and conveying raw environmental information to decision makers, managers, technicians, and the public. Therefore, CF index is able to consider, concentration of metal, its bioavailability and also its toxicity (Roudposhti *et al*., 2016). As showed by Tables 3 & 4, the contamination factor index results indicate that the soils were considerable contamination with respect to Cd (3.22) in Al-Marj. Moderate contamination in Sirt, Zwara, Albayda and Khomes with CF between 2.01 and 2.69. Cadmium is present as an impurity in several products, including phosphate fertilizers, detergents and refined petroleum products. Also, the fertilizers, pesticides, sewage sludge, the disposal of industrial wastes or the deposition of atmospheric contaminants increases the total concentration of Cd in soils. Cd enrichment in soil occurs from both natural and anthropogenic sources, and is considered to be of great environmental concern, according to results (Fig.2 & 3), Cd showed low contamination (CF < 1) for soils of Benghazi, Misurata, Abougrain, Zliten, Tripoli, Sabrata, Ejmail, Houn, Brack, Sebha, Murzuq, Ubari, Kufrah & Ghat.

Increasing the concentration of Pb is a major problem in developing countries. Lead showed very high contamination index (6.32-10.36) in Tripoli, Sirt, Zwara, Albayda & Khomes. The Cf values of Pb classified as considerable contamination in Benghazi with 4.43. While it was moderate contamination in soils of Brack (1.37) and Ubari (1.19). Pb is one of the less mobile heavy metals so its compounds tend to accumulate in soils. The sources of lead contamination are paints, lead waste, cell batteries and local industries. In contrast, the contamination factor of pb indicated low contamination (CF < 1) for soils of Ejmail, Misurata, Abougrain, Zliten, Houn, Sebha, Murzuq, Kufrah & Ghat. However, at the present time there are concerns regarding the possible human and ecotoxicological risks of soils polluted with Pb.

Recently, concern about Cr as an environmental pollutant has been escalating due to its build up to toxic levels in the environment as a result of various industrial and agricultural activities. Our results (Fig.2 & 3) revealed that CF value for Cr are > 6 in Al-Marj, Benghazi, Misurata and Zliten which indicates very high Cr contamination states due to use Cr in some industries such as tanning of animal hides, inhibition of water corrosion, pigments, ceramic glazes, refractory bricks.

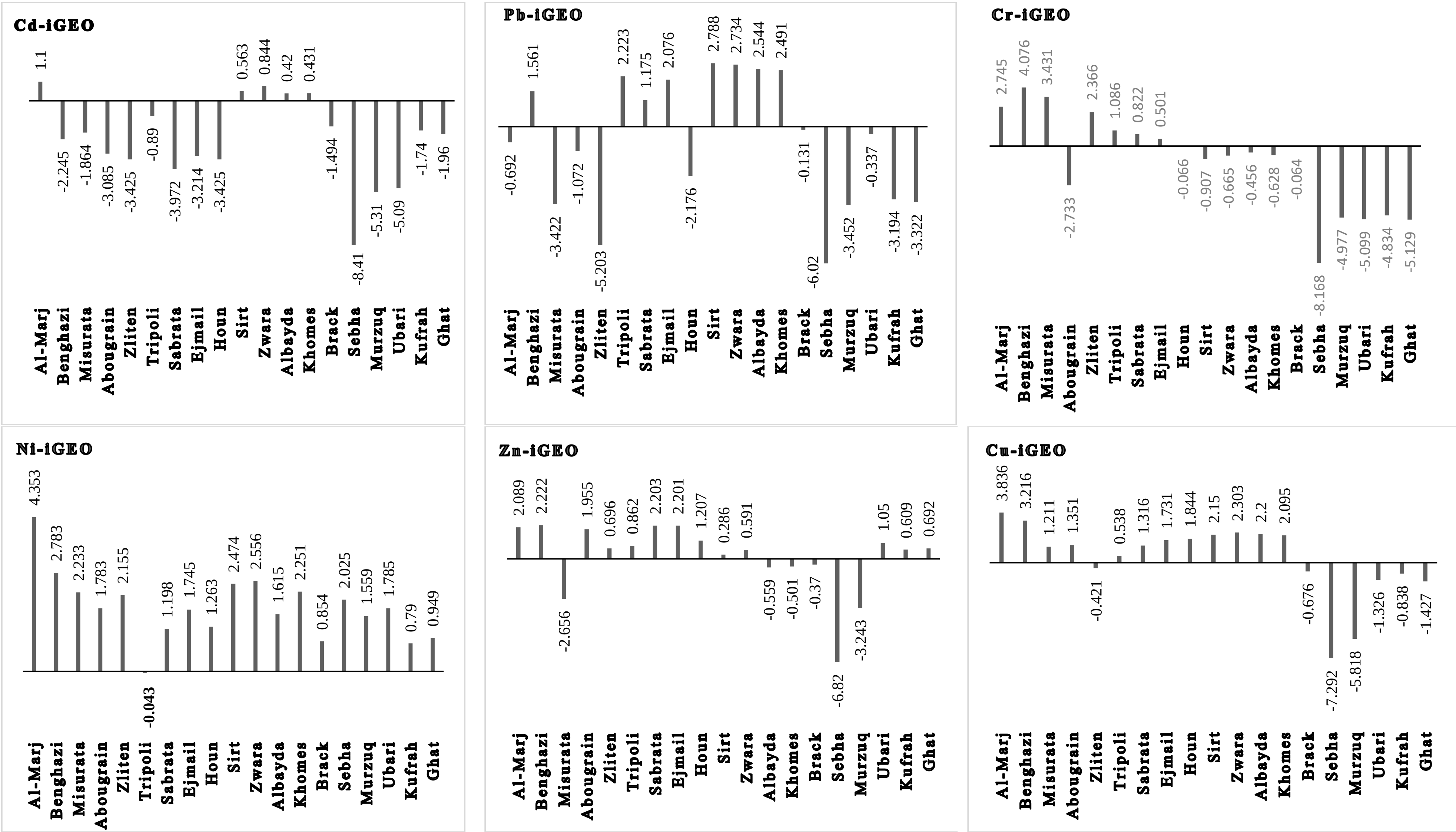

Figure (1) : i-GEO values calculated for heavy metals studied in soils

Table 3: the categories of Pollution Indices used

Index	≤ 0	0- 1	1 - 2	2- 3	3-4	4-5	> 5	Reference
Geo-accumulation index(i-GEO)	unpolluted	slightly polluted	moderately polluted	moderately severely polluted	severely polluted	severely extremely polluted	extremely polluted	Abbaslou *et al.*, 2014

Index	<1	1-3	3-6	>6	Reference
contamination factor (Cf)	Low Contamination	Moderate Contamination	Considerable Contamination	Very high Contamination	Thambavani and Mageswari, 2013)

Index	<1	1 - 2	2 -3	≥ 3	Reference
PLI	no pollution	moderate pollution	high pollution	very high pollution	Liu *et al.*, 2013

Index	<6	6-12	12-24	>24	Reference
Contamination degree (Cd)	Low contamination	Moderate contamination	Considerable contamination	Very high contamination	Thambavani and Mageswari, 2013

Index	<1.5	1.5-2	2-4	4-8	8-16	16-32	>32	Reference
Modified contamination degree(mCd)	Very Low degree	Low degree	Moderate degree	High degree	Very high degree	Extremely degree	Ultra-degree	Thambavani and Mageswari, 2013

Index	<1	>1	Reference
Metal Pollution IndexmpI	non-polluted ecosystem	polluted ecosystem	Thambavani and Mageswari, 2013

Index	<5	5–10	10–25	25–50	50–100	>100	Reference
MCi	very low contamination	low contamination	medium contamination	high contamination;	very high contamination	extremely high contamination	Thambavani and Mageswari, 2013

Also, the CF showing considerable contamination with value 3.18 in Tripoli which indicating the presence of serious Cr pollution. The CF values of soils from Sabrata, Ejmail, Houn, Albayda & Brack were (1.09-2.65) classified as moderately contamination. However, the source of Cr appears to be anthropogenic from the existing tannery industries, where they are using chromium and its compounds Cr is widely used in industry as plating. On other hand, the CF value was <1 for soils of Abougrain, Sirt, Zwara, Khomes, sebha, Murzuq, Ubari, Kufrah & Ghat which indicates low Cr contamination states. Due to the wide anthropogenic use of Cr, the consequent environmental contamination increased and has become an metal concentration in soil is serious and current concern for governmental and regulatory bodies for environmental risk assessment

For Ni, contamination factor indicates very high contamination of Ni with CF >6 for soil of Al-Marj, Benghazi, Misurata, Zliten, Sirt, Zwara, Khomes & sebha. The very high level of Ni contamination is due to the anthropogenic activities such as cement manufacturing, paint making, refining and petroleum industries, smelting industry, combustion of coal, diesel oil and fuel oil, the incineration of waste and sludge as well as application of some fertilizers. On the other hand, the CF values were (3.44 -5.17) showing considerable contamination in soils of Abougrain, Sabrata, Ejmail, Houn, Albayda & Ubari. While, CF (1.46 -2.90) for soil of Tripoli, Brack, Kufrah & Ghat indicated moderate contamination. The major concern for the impact Ni in soils arises apparently from the role of soil as an ultimate sink for heavy metals and the consequence transfer through the food-chain to crops, fruits and vegetables grown in contaminated soils and their possible consumption by animals or humans.

For Zn CF status, the soils of Al-Marj, Benghazi, Sabrata & Ejmail, were considered as very high contamination with **(**CF > 6). Zn concentrations are rising unnaturally, due to anthropogenic additions such as industrial activities, for example coal and waste combustion and steel processing. On other hand, the CF showed considerable contamination in soils of Abougrain, Houn & Ubari with CF values 5.82,03.46 and 3.11 respectively. The CF values (1.02-4.42) classified as moderately contamination for soils from Zliten, Tripoli, Sirt,Zwara, Albayda, Khomes, Brack,Kufrah & Ghat. The main sources of Zn pollution are industries and the use of liquid manure, composted materials and agrochemicals such as fertilizers and pesticides in agriculture. on other hand, Zn- CF states remain low contamination (<1) in soils of Misurata, Sebha & Murzuq. However, in the soil, zinc is bound to the soil complex (clay, organic material, etc.) depending on different physicochemical soil factors such as pH and organic matter content and other factors like cation exchange capacity, redox potential, mineral composition, and moisture content.

Copper is the third most used metal in the world, and the results of current showed the CF indicated very high contamination conditions in soils of Al-Marj, Benghazi, Zliten, Sirt, Zwara, Albayda & Khomes. The Cu content of these soils has been built up to high concentration from industrial soures and agriculture activities especially in permanent crops such as olive groves and vineyards. In addition, the CF values (3.47-5.38) classified as considerable contamination in soils of Miusrata, Abougrain, sabrata,Ejmal & Houn. Also, CF values were within moderately contamination in Zliten (1.12) and Tripoli (2.18). While, Cd showed low contamination (CF < 1) for soil of Brack, Sebha, Murzk, Ubari , Kufrah & Ghat. Copper is restricted mainly in the top layer of soil because of its ability to tightly bind with carbonates, clay minerals, hydrous oxides of Al, Fe and Mn and organic matter. Heavy metals in soils have been considered as powerful tracers for monitoring impact of anthropogenic activity such as industrial emission (cement plant, fossil fuel and coal combustion chemical plants) and vehicular emission.

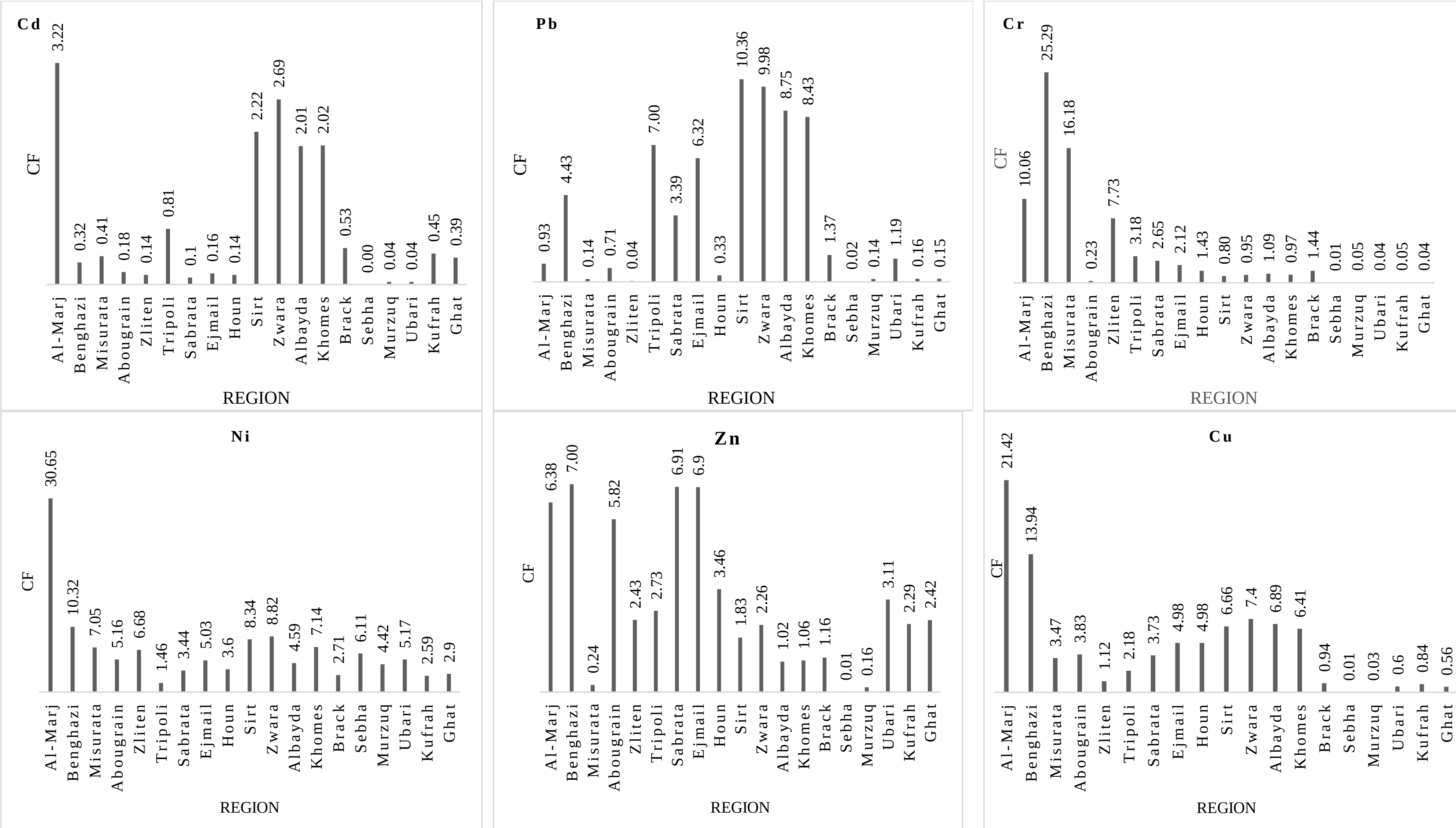

Figure (2)：CF values calculated for heavy metals studied in soils

iii. Pollution load index PLI.

Pollution Load index of soil is useful to assess the pollution level in soil. The PLI index was used to measure the degree of overall contamination in sample stations. In order to give proper assessment of the degree of contamination, attempts were made to calculate the PLI value for each city (Tables 3 & 4). According to the results, very high pollution recorded in soils of Al-marij, Benghazi, Sirt, Zwara & Khomes. Soils from Tripoli, Sabrata, Ejmal & Albayda were found to be high polluted. The possible explanation is that the toxic-response factor of Cd, Pb, Cr Ni, Zn and Cu. Therefore, we predict that, at least in the near future, adverse biological effects caused by heavy metals. Also, the PLI values of soils from Miusrata, Abougrain, Huon & Brack were (1.212 -1.334) indicating moderate pollution. While, the lowest PLI value (<1) was recorded for soils of Zliten, Sebha, Murzuq, Ubari, Kufrah & Ghat indicated no pollution environments. Lower values of PLI imply no appreciable input from anthropogenic sources. There is, in general, a decrease in PLI values of study area indicating dilution and dispersion of heavy metals content with increasing distance from source areas. Thus from the overall result, we can state that pollution load index still in control level, just on certain location that located near industrial areas and major road that produce high level of heavy metal. the rise in the emission of heavy metals in urban regions (e.g. Tripoli and Benghazi) is due to increasing population and urban growth. From the environmental point of view, heavy metals are largely immobile in the soil system, so they tend to accumulate in soils for a long time. The most reported heavy metals with potential hazards in soils are Cadmium, Chromium, Lead, zinc and copper. greater focus must give to the amount of emissions of Pb, Cd, and Cr due to their high toxicity, prevalence, and persistence in the environment. To that end, close monitoring of the application of agrochemicals and application of sustainable agriculture practices can help to mitigate the prevalent pollution of soils.

iv. Contamination degree (CD):

The contamination degree CD is aimed at providing a measure of the degree of contamination in sampling sites. the CD values are presented in Tables 3 & 4. Very high contamination degree (CD > 24) was found in soils of Al-Marj, Benghazi, Misurata, Ejmail, Sirt, Zwara, Albayda & Khomes due to the rapid industrialization and economic development in these cities, Meanwhile, considerable contamination degree was recorder for soils of Abougrain, Zliten, Tripoli, Sabrata & Houn, which means the increasing anthropogenic influences on the environment have caused negative changes in natural ecosystems. Moderate contamination degree was found in soils of Brack, Sebha, Ubari & Ghat with values (6.161- 10.150). low contamination degree (CD < 6) was recorder in Murzuq.

v. Modified contamination degree (mCD)

Tables 3 & 4 summarizes the modified contamination degree of soil samples collected. A close look at results shows that the modified contamination degree was very high degree for soil of Al-marj and Benghazi, while mCD values (3.369-5.350) present a high degree of contamination for soils from Misurata, Sabrata, Ejmal, Sirt, Zwara, Albayda & Khomes. The soil samples of Abougrain, Zliten, Tripoli & Houn registered moderate degree of contamination, with mCD values between 2.392 to 3.024, these results demonstrated that the distribution of metals concentration in the studied cities have come about as a result of anthropogenic influences. However, low contamination degree found in soil of Ubari with mCD value equal 1.692, and very low contamination degree with mCD < 1.50 for soils of Brack, Sebha, Murzuq & Ghat. Modified contamination degree is presented the overall degree of contamination.

Table 4 the Values of Pollution indices PLI, CD, mCD, MCI & MPI

REGION	PLI	CD	mCD	MCI	MPI
Al-Marj	7.361	72.647	12.108	66.647	0.708
Benghazi	5.942	61.300	10.217	55.300	0.658
Misurata	1.334	27.495	4.582	21.495	-0.133
Abougrain	1.223	15.921	2.653	9.921	-0.289
Zliten	0.963	18.142	3.024	12.142	-1.013
Tripoli	2.360	17.355	2.893	11.355	0.341
Sabrata	2.089	20.216	3.369	14.216	0.275
Ejmail	2.739	25.515	4.252	19.515	0.411
Houn	1.289	14.350	2.392	8.350	-0.188
Sirt	3.597	30.199	5.033	24.199	0.515
Zwara	4.051	32.101	5.350	26.101	0.553
Albayda	2.983	24.355	4.059	18.355	0.446
Khomes	3.118	26.037	4.340	20.037	0.463
Brack	1.212	8.147	1.358	2.147	-0.310
Sebha	0.025	6.161	1.027	0.161	0.972
Murzuq	0.124	4.826	0.804	-1.174	0.727
Ubari	0.523	10.150	1.692	4.150	0.220
Sirt	3.597	30.199	5.033	24.199	0.515
Kufrah	0.511	6.383	1.064	0.383	0.235
Ghat	0.455	6.456	1.076	0.456	0.304

vi. Overall metal contamination index (MCI)

The results in Tables (3 & 4) showed that there are differences between the values of MCI calculated for the studied soils. The results inducted that the soils of Al-Marj and Benghazi were very high contamination with MCI values 66.647 and 55.300 respectively. The high overall metal contamination was recorder in Zwara soil. While the medium overall metal was found for soils of Misurata, Zliten, Tripoli, Sabrata, Ejmail, Sirt, Albayda & Khomes with values between 11.355 and 24.199. The high level of overall soil metal contamination may be a result of precipitation of agriculture activities, highway and industry factory dusts over the year. Low overall metal contamination was recorder in Aboguran (9.921) and Houn (8.350). The very low overall metal contamination was recorder in soils Brack, Sebha, Murzuq, Ubari, Kufrah & Ghat with values ranged between -1.174 and 2.147

vii.Metal pollution index (MPI)

The **metal pollution index** has been used to enable presentation of all results from the metal concentrations studied as one value, this implies that the six metal concentrations were normalised to sum up and average the different metal concentrations into one value. The results demonstrated that the values of MPI were < 1 for all soils studied inducted that the overall of ecosystem is non-polluted. Our results (Tables 3 & 4) showed that the tested metals do not pose any ecosystem risk to the environment. The low values of MPI indicating dilution and dispersion of heavy metals content due to large of the study area. Also, dilution and dispersion of heavy metals with increasing distance from source areas. However, it must be stressed that the heavy metals pollution in these cities should be under routine check to avoid being polluted in the near future. The contaminated soil destabilizes the functioning of whole ecosystems and it has toxic effects on the food webs and the structure of biotic communities. Furthermore, the recent development of economy has resulted in an increase types and content of heavy metals in soils, and in particular, contamination of agricultural soils has increased due to the extensive use of chemical fertilizers, pesticides, , irrigation waste water and sewage sludge, solid waste, agrochemicals and atmospheric deposition. Further, Industrial expansion has increased the amount of heavy metals released into soils (Artiola *et al*., 2019).

CONCLUSION:

The main conclusion that can be drawn from this study is that variety risk level of heavy metal in the Libyan soils. Urban soil is more affected due to the high anthropogenic influence in the form of industrial, commercial, and domestic activities. The study further stated that some studied cities were more seriously polluted than others (e.g. Tripoli, Bengazi Almarj). Soils from Al-Marj, Benghazi, Misurata, Ejmail, Sirt & Zwara had very high contamination degree (CD > 24) owing to its geochemical characteristics and anthropogenic activities. The study confirmed that Al-Marj and Benghazi had the highest levels of overall metal contamination index (MCI). The results demonstrated that the values of MPI were < 1 for all soils studied inducted that the overall of ecosystem is still non-polluted. Heavy metal pollution effects not only crop production and health, but also the quality of the atmosphere, water bodies, climate and ecosystems. However, Continuous monitoring of the environment for heavy metal contamination is still needed

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