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Levels and Distribution of Trace Metals in Surface Soils of Al-Diwaniya, Iraq

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In this work, monitoring of monthly variation (from May 2016 to October 2016) in the concentration of the metals (Co, Zn, Cd, Pb, Ni and Fe) from Al-Diwaniya city of Iraq. Investigation about the pollution with these metals was achieved from five selected sites locate in study area by flame atomic absorption spectroscopy. The results showed a wide variation in the levels of heavy metals from site to site and from month to month. A total of 180 surface soil samples were analyzed to detecting the pollution with selected samples. The results showed that the highest concentration with Ni was 6.290 mg kg^{-1} while the lowest concentration detected with Ni was 0.080 mg kg^{-1}. The results of pollution index (enrichment factor, contamination factor, pollution load index and geo-accumulation) of heavy metals (Co, Zn, Cd, Pb, Ni) had the following order: Zn > Cd > Ni > Pb > Co.

Keywords: Heavy metals, Surface soil pollution, Al-Diwaniyah.

INTRODUCTION

Heavy metals pollution of soils is a wide area from the researchers as an environmental problem affecting agricultural production, threatening human health and food quality [1]. The heavy metals are interfering with agro-ecosystem by both natural and anthropogenic activities. Naturally soil inherits heavy metals from its geological parent materials [2], while anthropogenic sources vary with usage of organic manures, industrial wastes, fertilizers, irrigation, municipal wastes, and wet and/or dry deposits [3]. Heavy metals are one of the most persistent of pollutants in ecosystem, because of their resistance for decomposition in natural conditions. Toxicity appears after increasing the levels of indispensability. Heavy metals act as toxic materials when they are not metabolize by the human body and then accumulate in the tissues of the human body [4].

Generally in unpolluted environment, most of the heavy metals are in low levels. Main source of pollution with heavy metals is by anthropogenic origin such as mining, disposal of partially treated and/or untreated effluents include toxic metals as well metal form chelates with organic compounds from several industrial factories and unsystematic use of fertilizers contain heavy metals [5,6]. More than 50 elements of heavy metals are classified as heavy metals, only 17 elements are considered toxic [7]. Several techniques are used for determination of heavy metals in environmental studies, such as inductive coupled plasma coupled with mass spectrometry (ICP-MS) [8-13], inductively coupled plasma optical emission spectrometry (ICP-OES) [14-18], flame and graphite furnace atomic absorption spectrometry [19], electro thermal vaporization inductively coupled plasma mass spectrometry (ETV-ICP-MS) [20], neutron activation analysis [21] , flow injection solid phase extraction inductively coupled plasma mass spectrometry [22], *etc*. Several manners were used for remediation of heavy metals in contaminated soil, such as soil washing, immobilization and phytoremediation [23]. The cost of these methods and environmental safety roles are very effective for application in real polluted soils, those reasons made of these methods are limited in use [24].

The Al-Diwaniyah city having an area of 8153 km^2 located on Euphrates river between latitudes 31.17-32.24 ºN and longitudes 44.24-45.49 ºE. The objectives of this work is determination the heavy metals and elucidate the distribution of it using an index of enrichment factor (EF), contamination factor

(CF), pollution load index (PLI) and geo-accumulation (I_{geo}) in surface soils samples from Al-Diwaniya city of Iraq.

EXPERIMENTAL

The city of Al-Diwaniyah located on Euphrates river has a climate semi-arid to arid. The study area was chosen in the lands located within Qadisiyah Province at the latitude 31.17 and 32.24º north, longitude 44.24º and 45.49º east (Table-1). Five agricultural soil sites: Al-Shafeiyah (S_0 as control), Al-Saniyah (S_1), Al-Hamza (S_2), Al-Daghara (S_3) and Affak (S_4) were selected. Soil samples were taken from surface depths (0-30 cm) according to specific locations and collected in nylon bags size of 2-3 kg. The coordinates of each site were taken by a GPS device for the purpose of mapping representing the study area (Fig. 1).

TABLE-1
COORDINATES OF STUDIED SOILS LOCATIONS

No.	Sampling station	N. coordinates	E. coordinates
1	S_0 – Al-Shafeiyah (cont.)	31.945075°	44.844762°
2	S_1 – Al-Saniyah	32.054986°	44.776454°
3	S_2 – Al-Hamza	31.730018°	44.970796°
4	S_3 – Al-Dagharah	32.143069°	44.930613°
5	S_4 – Affak	32.069775°	45.231438°

Soil samples: The concentrations of total heavy metals (Co, Zn, Pb, Cd, Ni and Fe) were extracted from soil by using a digestion method of Jones *et al*. [25]. Then the concentrations of total heavy metals were measured by using atomic absorption spectrophotometer (AAS).

Pollution indices: To interpret and assess the contamination status for heavy metals in soil samples, four soil pollution indices were used *viz*., enrichment factor (EF), contamination factor (CF), pollution load index (PLI) and geoaccumulation index (I_{geo})].

Enrichment factor (EF): Enrichment factor of an element in the samples is based on the standardization of measured element against a reference element [26]. In this study, enrichment factor was used to assess the level of contamination and the possible anthropogenic impact in soils.

To identify anomalous metal concentration, geochemical normalization of heavy metals data to a conservative element, such as Al, Fe and Si were employed. Several authors have successfully used iron to normalize heavy metals contaminants [27,28]. In this study, iron was also used as a conservative tracer to differentiate natural from anthropogenic components. The metal enrichment factor (EF) is defined [29,30] as follows:

$$EF = \frac{(C_m/C_{Fe})\ \text{Sample}}{(C_m/C_{Fe})\ \text{Background}} \quad (1)$$

where EF is the enrichment factor, (M/Fe) sample is the ratio of metal and Fe concentration of sample and (M/Fe) background is the ratio of metals and Fe background reference concentration, not as an pollutant. The background concentrations of metals were taken from soils from an undisturbed area.

Enrichment factor categories [31] for eqn. 1 are outlined as follows: (a) EF < 2 minimal enrichment; EF = 2-5 moderate enrichment; EF = 5-20 significant enrichment; EF = 20-40 very high enrichment; and EF > 40 extremely high enrichment.

Contamination factor (CF): The level of contamination of soil by metal is expressed in terms of a contamination factor (CF) is calculated as:

$$CF = \frac{C_m\ \text{Sample}}{C_m\ \text{Background}} \quad (2)$$

where, C_m sample is the concentration of a given metal in soil sample. C_m background is concentration of an element in the background soil sample [32]. Similarly, contamination factor categories [32] for eqn 2 are outlined as follows: (a) CF < 1 refers to low contamination; 1 ≤ CF < 3 means moderate contamination; 3 ≤ CF ≤ 6 indicates considerable contamination and CF > 6 indicates very high contamination.

Pollution load index (PLI): Each site was evaluated for the extent of metal pollution by employing the method [33] based on pollution load index (PLI) as follows:

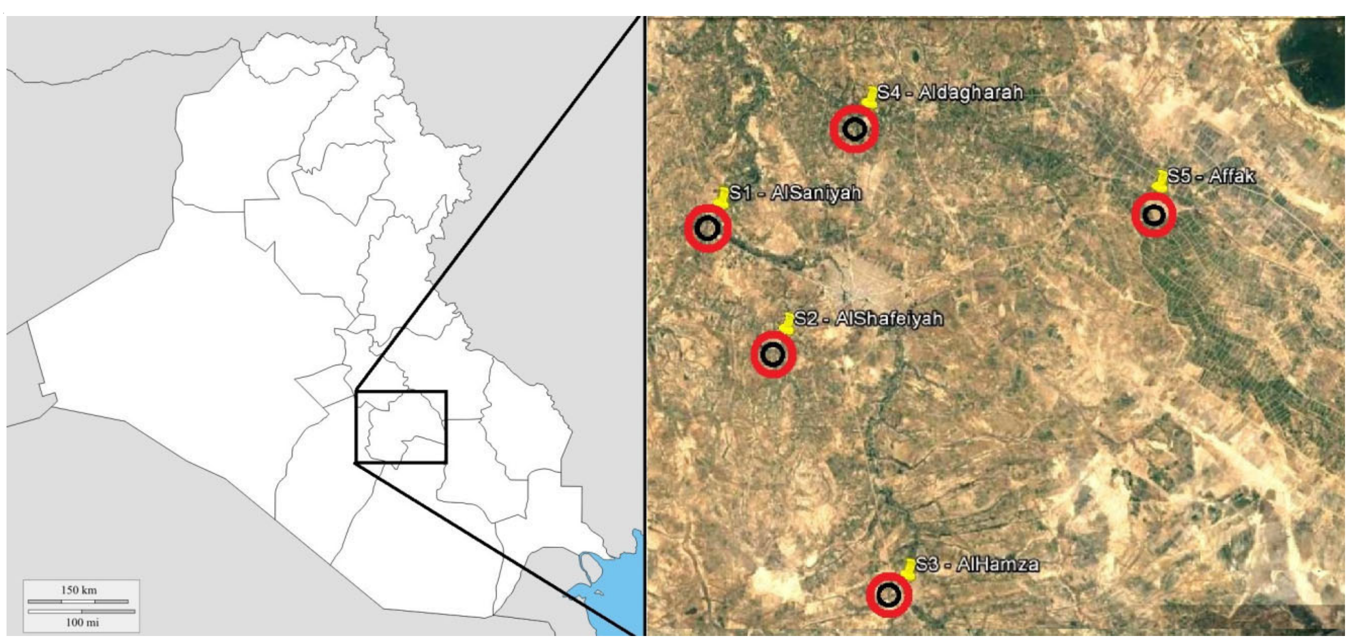

Fig. 1. Map showing the positions of soil samples

$$PLI = (CF_1 \times CF_2 \times CF_3 \times .... \times CF_n)^{1/n} \quad (3)$$

where n is the number of metals studied (five in present study) and CF is the contamination factor calculated as described in eqn. 2. The PLI provides simple but comparative means for assessing a site quality, where a value of PLI < 1 denote perfection; PLI = 1 present that only baseline levels of pollutants are present and PLI >1 would indicate deterioration of site quality [33].

This type of measure has however been defined by some authors in several ways, for example, Hakanson [34] reported the numerical sum of eight specific contamination factors [34], whereas, Abrahim [35] assessed the site quality as arithmetic mean of the analyzed pollutants. In this study, the authors found it appropriate to express PLI as the geometric mean of the studied pollutants, since this method tends to reduce the outliers, which might bias the reported results.

Geoaccumulation index (I_{geo}): The geoaccumulation index is generally used to determine the anthropogenic contamination in sediments as introduced by Muller [36,37] and corroborated by various researchers [38-40]. This index allows us to evaluate the contamination levels by comparing present concentrations with background levels (Table-2).

TABLE-2
I_{geo} CLASSES WITH RESPECT TO SOIL QUALITY

I_{geo} value	I_{geo} class	Designation of soil quality
$5 \geq I_{geo}$	6	Very strongly polluted
$4 \leq I_{geo} < 5$	5	Strongly to very strongly polluted
$3 \leq I_{geo} < 4$	4	Strongly polluted
$2 \leq I_{geo} < 3$	3	Moderately to strongly polluted
$1 \leq I_{geo} < 2$	2	Moderately polluted
$0 \leq I_{geo} < 1$	1	UNP to moderately polluted
$I_{geo} \leq 0$	0	Unpolluted (UNP)

Geoaccumulation index (I_{geo}) introduced by Muller [36] was also used to assess metal pollution in soils. It is express as:

$$I_{geo} = \log_2 \frac{C_m \text{ Sample}}{1.5\, C_m \text{ Background}} \quad (4)$$

The factor 1.5 is introduced in this equation to minimize the effect of possible variations in the background values, C_m Background, which may be attributed to lithogenic variations in soils. The seven proposed descriptive classes for I_{geo} values are given in Table-2.

RESULTS AND DISCUSSION

Basically, soil heavy metals content depends on different resources such as anthropogenic, geochemical, and pedogenic processes. However, they accumulate in high quantities within the soil body and non-biodegradable [41]. The total concentration of heavy metals is very different in contaminated soils by the source of contamination [42]. The results of Co, Zn, Pb, Cd, Ni and Fe in the studied area are listed in Table-3.

Cobalt: Total concentration of cobalt in soils sites ranged from 0.090-0.240 mg kg^{-1} at S_3 site. The results in Table-3 showed the highest value of cobalt was 0.240 mg kg^{-1} in June month of year 2016 at S_3 site.

Zinc: Total concentration of zince in soils sites ranged from 0.090-5.400 mg kg^{-1}. The results in Table-3 showed the highest value of zince is 5.400 mg kg^{-1} in September month at S_2 site.

Cadmium: The concentration of cadmium in soils sites ranged from 0.016-1.440 mg kg^{-1} and the highest value of cadmium was recorded in June month at S_4 site (Table-3).

Lead: Total lead concentration in soils site ranged from 0.200-3.750 mg kg^{-1}. The results in Table-3 showed the highest value of lead as 3.750 mg kg^{-1} appeared in May month at S_4 site.

Nickel: The nickel concentration in soils site ranged from 0.080-6.290 mg kg^{-1}. Table-3 showed that the highest value 6.290 mg kg^{-1}, appeared in June month at S_4 site.

Iron: The iron concentration in soils site ranged from 0.008-7.460 mg kg^{-1}. Table-3 showed that the highest value 6.290 mg kg^{-1}, appeared in August month at S_2 site.

TABLE-3
TOTAL METAL CONCENTRATIONS IN SOIL SAMPLES (mg kg^{-1})

Site No.	May-16	Jun-16	Jul-16	Aug-16	Sep-16	Oct-16	Min.	Max.	May-16	Jun-16	Jul-16	Aug-16	Sep-16	Oct-16	Min.	Max.
	Cobalt (mg kg^{-1})								Zinc (mg kg^{-1})							
S_1	0.120	0.230	0.170	0.130	0.180	0.110	0.110	0.230	1.600	0.090	0.750	0.100	1.700	0.700	0.090	1.600
S_2	0.140	0.190	0.170	0.180	0.120	0.110	0.110	0.190	0.100	0.340	0.420	0.100	5.400	0.100	0.100	5.400
S_3	0.110	0.240	0.090	0.150	0.130	0.120	0.090	0.240	1.000	0.160	1.000	0.100	0.690	1.000	0.100	1.000
S_4	0.110	0.120	0.146	0.160	0.130	0.150	0.110	0.160	2.000	0.120	0.250	0.100	2.700	0.100	0.100	2.700
S_0	0.150	0.130	0.140	0.160	0.170	0.120	0.120	0.170	0.800	0.120	0.500	0.100	5.200	0.100	0.100	5.200
	Cadmium (mg kg^{-1})								Lead (mg kg^{-1})							
S_1	0.550	1.350	0.220	0.060	0.100	1.000	0.060	1.350	1.500	2.340	1.280	0.400	0.280	0.200	0.200	2.340
S_2	0.100	1.400	0.220	0.250	0.040	0.800	0.040	1.400	1.900	1.980	0.700	0.400	0.350	0.400	0.350	1.980
S_3	0.260	1.340	0.034	0.250	0.016	0.900	0.016	1.340	3.250	2.440	2.280	0.500	0.210	0.900	0.210	3.250
S_4	0.290	1.440	0.022	0.130	0.100	1.000	0.022	1.440	3.750	3.400	2.600	0.400	0.350	0.700	0.350	3.750
S_0	0.065	1.300	0.220	0.180	0.100	0.400	0.065	1.300	2.000	2.800	1.280	0.300	0.350	0.800	0.300	2.800
	Nickel (mg kg^{-1})								Iron (mg kg^{-1})							
S_1	1.110	6.290	0.240	0.360	0.100	0.300	0.100	6.290	0.310	0.014	0.200	6.600	1.500	0.250	0.014	6.600
S_3	0.100	2.900	0.120	0.160	0.700	0.150	0.100	2.900	0.200	0.008	0.200	7.460	2.300	0.100	0.008	7.460
S_4	1.560	3.400	0.080	0.400	0.190	0.430	0.080	3.400	0.310	0.009	0.200	5.000	0.530	0.150	0.009	5.000
S_5	1.300	3.600	0.200	0.160	0.220	0.320	0.160	3.600	0.220	0.200	0.200	5.460	0.050	0.300	0.050	5.460
S_0	0.920	2.800	0.200	0.460	0.100	0.430	0.100	2.800	0.130	0.013	0.187	6.300	0.050	0.150	0.013	6.300

Contamination factor (CF): Table-4 showed the values of cobalt of the studied soils. These values ranged from 0.059 to 1.846, with the lowest value at S_1 site and the highest value at S_3 site and those values were at the first and second levels close or equal to 1, which can be classified within the low and moderately contaminated with cobalt. The results also showed that the values of CF of zinc ranged between 0.125-10,000, with the lowest value at S_2 site and the highest value at S_3 soil, CF for the study soil falls within the first and fourth levels so that the level of contamination of zinc in all soils is between low and high contamination. While the values of cadmium ranged between 0.031-8.462 with the lowest value at S_3 site and the highest value at S1 site. The results showed that the CF values fall within the first and fourth levels so that the level of contamination of cadmium was between the low and the high contamination with cadmium.Table-4 showed that the values of CF of lead ranged between 0.250-2.031, with the lowest value at S_1 site and the highest value ate S_4 stie and the values were within the first and second levels. Thus, the level of contamination was between the low and the moderately contaminated with lead. While the results showed that the values of nickel ranged between 0.109-7.000, with the lowest value and the highest values were at S_2 site, which classified in the first and fourth levels of CF, thus the level of contamination with nickel was between low and high contamination.

Enrichment factor (EF): Table-4 showed the values of EF of cobalt which ranged from 0.015-2.200, the lowest and highest values were at S_2 sitel and at the first level EF < 2 all study soils and then increased to the second level (EF = 2-5), thus enrichment factor of those soils at low level with the contamination by cobalt average. Also, the results showed EF values of zinc which ranged from 0.011 to 10,000, with the lowest value at S_1 site and the highest value at S_3 site. According to the results, EF values of zinc were mostly at the first level EF < 2 and then increased to the third level (EF = 5- 20) at S_3 site, thus the level of pollution with zinc ranged from low, medium, to high contaminated with zinc for study soils. Table-4 showed the values of EF factor of cadmium for the study area soil. The values ranged between 0.009-3.548. The lowest value was shown in the soil at S_2 site region and the highest value at S_3 site. As the results showed that these values were within the first level EF < 2 means low contaminated and then increased to the second level EF = 5-20 that moderately contaminated with cadmium. The results showed that the values of EF of lead in the studied soils ranged between 0.022-2.375. The lowest value was shown in the soil of S_0 site and the highest value in soil present at S_2 site. The results showed that the EF values of lead in these soils were low and at the first level EF < 2. Thus, the level of contamination with lead was found at low level. While the results showed the values of EF of nickel ranged between 0.033-2.543 and that the lowest value appeared in at S_3 site and the highest value in soil at S_4 site, which showed that the EF values of nickel were within the first and second levels, so the level of contamination of these soils was between the low and the moderately contaminated with nickel.

Pollution load index (PLI): Table-5 showed the values of pollution load index ranged between 0.450-1.908. The lowest value was found in S_2 soil site, while the highest was in S_3 soil site, which are very low and close to number 1, except for some soils that showed values exceeding 1, thus can be considered as low values, so the level of pollution in the study soils ranged between not to very low.

TABLE-4
VALUE OF CONTAMINATION AND ENRICHMENT FACTORS OF METAL CONCENTRATIONS IN SOIL SAMPLES

Site No.	Contamination factor						Enrichment factor					
	May-16	Jun-16	Jul-16	Aug-16	Sep-16	Oct-16	May-16	Jun-16	Jul-16	Aug-16	Sep-16	Oct-16
	Cobalt						Cobalt					
S_1	0.800	1.769	1.214	0.813	1.059	0.917	0.335	1.643	1.135	0.776	0.035	0.550
S_3	0.933	1.462	1.214	1.125	0.706	0.917	0.607	2.200	1.135	0.950	0.015	1.375
S_4	0.733	1.846	0.643	0.938	0.765	1.000	0.308	1.899	0.601	1.181	0.072	1.000
S_5	0.733	0.923	1.043	1.000	0.765	1.250	0.433	0.060	0.975	1.154	0.765	0.625
	Zinc						Zinc					
S_1	2.000	0.750	1.500	1.000	0.327	7.000	0.839	0.696	1.403	0.955	0.011	4.200
S_3	0.125	2.833	0.840	1.000	1.038	1.000	0.081	4.604	0.785	0.845	0.023	1.500
S_4	1.250	1.333	2.000	1.000	0.133	10.000	0.524	1.926	1.870	1.260	0.013	10.000
S_5	2.500	1.000	0.500	1.000	0.519	1.000	1.477	0.065	0.468	1.154	0.519	0.500
	Cadmium						Cadmium					
S_1	8.462	1.038	1.000	0.333	1.000	2.500	3.548	0.964	0.935	0.318	0.033	1.500
S_3	1.538	1.077	1.000	1.389	0.400	2.000	1.000	1.750	0.935	1.173	0.009	3.000
S_4	4.000	1.031	0.155	1.389	0.160	2.250	1.677	1.489	0.145	1.750	0.015	2.250
S_5	4.462	1.108	0.100	0.722	1.000	2.500	2.636	0.072	0.094	0.833	1.000	1.250
	Lead						Lead					
S_1	0.750	0.836	1.000	1.333	0.800	0.250	0.315	0.776	0.935	1.273	0.027	0.150
S_3	0.950	0.707	0.547	1.333	1.000	0.500	0.618	1.149	0.511	1.126	0.022	0.750
S_4	1.625	0.871	1.781	1.667	0.600	1.125	0.681	1.259	1.665	2.375	0.057	1.125
S_5	1.875	1.214	2.031	1.333	1.000	0.875	1.108	0.079	1.899	1.538	1.000	0.438
	Nickel						Nickel					
S_1	1.207	2.246	1.200	0.783	1.000	0.698	0.506	2.086	1.122	0.747	0.033	0.419
S_3	0.109	1.036	0.600	0.348	7.000	0.349	0.071	1.683	0.561	0.294	0.152	0.523
S_4	1.696	1.214	0.400	0.870	1.900	1.000	0.711	1.754	0.374	1.096	0.179	1.000
S_5	1.413	1.286	1.000	0.348	2.200	0.744	0.835	0.084	0.935	0.401	2.563	0.372

TABLE-5
POLLUTION LOAD INDEX

Site No.	PLI-(Co, Zn, Cd, Pb, Ni)					
	May-16	Jun-16	Jul-16	Aug-16	Sep-16	Oct-16
S_1	1.651	1.209	1.169	0.777	0.774	1.228
S_3	0.450	1.267	0.803	0.938	1.155	0.796
S_4	1.588	1.218	0.676	1.135	0.450	1.908
S_5	1.850	1.098	0.638	0.804	0.973	1.153

Geoaccumulation index (I_{geo}): Table-6 showed that the values of I_{geo} of cobalt ranged between 1.222-0.300. The lowest and highest values were at S_3 soils and their values were within the second level. The soil ranged from uncontaminated to low pollution and there is no geological source to increase cobalt concentrations in those soils. The results showed that I_{geo} values of zinc ranged between 2.737-3.585, the lowest and highest values appeared at S_2 soils and all falling within the first and fourth levels (non-polluted to high polluted).The results showed that the I_{geo} values of cadmium ranged between 3.907-2.496 with the lowest S_1 site. Thus, these values were within the first and third levels which ranged from unpolluted to the high polluted by cadmium that come from the geological source, while the results showed that the values of I_{geo} of lead ranged between -2.585-0.437.The lowest value was found at S_1 site while the highest at S_4 site. The results showed that all values were within the first and second levels. Thus, the studied soil ranged from unpolluted to low pollution by lead. Results of I_{geo} values nickel ranged between -3.787-2.222, with the lowest and highest values at S_2 site. In general, the values of pollution index (EF, CF, I_{geo}) of heavy metals (Co, Zn, Cd, Pb, Ni) had the following order: Zn > Cd > Ni > Pb > Co.

Soils at S_3 site was one of the most heavily contaminated soils followed by S_2, S_4 and S_1 sites. This increase was mainly attributed to cadmium and zinc in all studied soils. According to Wu *et al*. [43], cadmium and zinc had the same chemical and environmental properties as they are present in the environment together with Zn/Cd (0.1-5 %). These high values of zinc are attributed to the use of fertilizers and pesticides in agriculture leading to contamination with zinc [44] or might increase in the surface layer of soil due to the retention of organic matter in the soil surface layer or by human additions [45]. Also, the main source of cadmium pollution and its levels in agricultural soils were due to sewage or the excess usage of phosphate fertilizers [46]. While the moderately values were for nickel in all studied soils could be attributed to the use of pesticides and chemical fertilizers or as a result of contamination of soils with the wastes of factories that are randomly dumped [47].

TABLE-6
GEOACCUMULATION INDEX

Site No.	May-16	Jun-16	Jul-16	Aug-16	Sep-16	Oct-16
	I_{geo}-Co					
S_1	-0.907	0.238	-0.305	-0.885	-0.503	-0.710
S_3	-0.684	-0.037	-0.305	-0.415	-1.087	-0.710
S_4	-1.032	0.300	-1.222	-0.678	-0.972	-0.585
S_5	-1.032	-0.700	-0.524	-0.585	-0.972	-0.263
	I_{geo}-Zn					
S_1	0.415	-1.000	0.000	-0.585	-2.198	2.222
S_3	-3.585	0.918	-0.837	-0.585	-0.531	-0.585
S_4	-0.263	-0.170	0.415	-0.585	-3.499	2.737
S_5	0.737	-0.585	-1.585	-0.585	-1.531	-0.585
	I_{geo}-Cd					
S_1	2.496	-0.531	-0.585	-2.170	-0.585	0.737
S_3	0.037	-0.478	-0.585	-0.111	-1.907	0.415
S_4	1.415	-0.541	-3.279	-0.111	-3.229	0.585
S_5	1.573	-0.437	-3.907	-1.054	-0.585	0.737
	I_{geo}-Pb					
S_1	-1.000	-0.844	-0.585	-0.170	-0.907	-2.585
S_3	-0.659	-1.085	-1.456	-0.170	-0.585	-1.585
S_4	0.115	-0.784	0.248	0.152	-1.322	-0.415
S_5	0.322	-0.305	0.437	-0.170	-0.585	-0.778
	I_{geo}-Ni					
S_1	-0.314	0.583	-0.322	-0.939	-0.585	-1.104
S_3	-3.787	-0.534	-1.322	-2.109	2.222	-2.104
S_4	0.177	-0.305	-1.907	-0.787	0.341	-0.585
S_5	-0.086	-0.222	-0.585	-2.109	0.553	-1.011

Lead and cobalt showed a decrement in their values in the studied soils, which can be attributed to the lack of means of transport and industrialization in those areas in addition to the presence of high trees and palms, which act as barriers for polluted air [48]. As well as that the calcareous soil containing carbonate rocks is a low concentration of lead the parent rocks are not the only source of lead, but there are other sources by human increasing their concentrations [41].

CONFLICT OF INTEREST

The authors declare that there is no conflict of interests regarding the publication of this article.

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