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New approach for calculation of pollution indices of the soils by heavy metals: case study for soils of Bahr El-Baqar Region, South of Manzala Lagoon, Egypt

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Abstract: Pollution of Bahr EL-Baqar soils are the case for comparison between the old pollution indices and the new pollution indices. The pollution indices are contamination factor, load pollution index, contamination degree and pollution rate. The heavy metals concentrations of Fe, Cu, Co, Ni, Zn, Pb, Cd and Cr from the soil samples of Bahr EL-Baqar region compared with many soil quality guidelines. New pollution indices used the Canadian soil quality guidelines (CSQGs) as background in the calculation of indices. Old (popular) pollution indices always used the background values reported by [1] and is based on element abundances in sedimentary rocks (shale).PR(CSQGs) = (Σ Mc) sample/(Σ Mc(CSQGs)) background, where PR is pollution rate, Mc is the concentration of metals in collected sample, Mc(CSQGs) concentration of metal in Canadian soil quality guidelines as background. The abundance of heavy metals measured in these soils decreases as follows: Fe > Zn > Cr > Cu> Co > Ni >Pb> Cd. The new methods of assessment are favorable and more accuracy than the ordinary methods, where using the Canadian soil quality guidelines (CSQGs) as background in the calculation of indices.

Key words : Pollution Indices- Ordinary- New - Guidelines- Bahr EL-Baqar- Soils

1. Introduction:

The pollution indices classified into two types: (i) single indices and (ii) integrated indices in an algorithm point of view[2]. The selected reference sample is usually an average crust or a local background sample [3], [4], [5]. The immobile element is often taken to be Al [3], [6], Li, Sc, Zr[5] or Ti, and sometimes Fe [7] or Mn[4] has been used. Al (for terrestrial sources) and Na (for oceanic sources) have been used for the purpose of comparing the chemical composition of atmospheric particulate material collected at the South Pole to the composition of the crust or the ocean [8].

[9] stated that the abundance of heavy metals measured in the soils of Bahr El-Baqar region decreases as follows: Cd > Cu > Zn > Cr > Ni > Pb. [10]reported that in soil of Bahr El-Baqar site irrigated with wastewater drain.[11]concluded that the heavy metal concentrations of Al, Cr, Cu, Fe, Mn, Sr and Zn in Bahr El-Baqar site were above the safe limits of EU standard [12]. The lower concentrations of Co, Ni and Mo than the safe limits might be due to the continuous removal of heavy metals by the food crops grown in this area and also due to leaching of heavy. Elevated levels of heavy metals in irrigation water led to significant increase of heavy metal contents in soil at Bahr El-Baqar site. In this study, the pollution of soils of Bahr EL-Baqarwere determined by ordinary and new methods. Calculation of pollution indices in the study area by two methods one, by shale

values of [1] as background or references, the other by using the Canadian soil quality guidelines (CSQG) as references or background in the equations of pollution indices.

2. New Approach for Pollution Indoces Calculations:

All authors used the background or reference metal values of the average shale estimated by [1]for calculation the pollution indices of the soils and sediments.

Using of average shale values of [1] in all studies in different sites in the world to calculate the single and integrated indices are not logically because of: 1- different sites in the world 2- different sources of sediments and soils 3- different methods used for the analysis of heavy metals (methods of digestions and type of instruments). Many of authorities and organizations study the permissible limits for each element and the toxic effect of such elements in the environment. These authorities and organizations were prepared many standards or guidelines for each element in different countries. The most famous guidelines are Canadian soil quality guidelines (CSQG) of [13], [12]and [14].

. These guidelines have been suggested a values for each elements depend on its effect on the human health. Where, these values considered as permissible for human health. These guideline values used in equations of indices calculations instead of the shale values of [1]. In this study, the values of each element of Canadian soil quality guidelines (CSQG) of [13] used as background or references in the equations of pollution indices. Where the equations become as following:

$CF_{(CSQGs)} = Mc/ Mc_{CSQGs}$

Where, CF (CSQGs) is contamination factor by using Canadian soil quality guidelines, Mc is concentration of metal in collected samples and Mc CSQGs is the Concentration of metal in CSQGs

The following terminologies are used to describe the contamination factor: CF<1, low contamination factor; $1 \le CF < 3$, moderate contamination factors; $3 \le CF < 6$, considerable contamination factors; and CF ≥ 6 , very high contamination factor.

PLI $_{(CSQGs)} = (CF_{1(CSQGs)} \times CF_{2(CSQGs)} \times CF_{3(CSQGs)} \times \cdots \times CF_{n(CSQGs)})^{1/n}$

PLI (CSQGs) is Pollution load index by using Canadian soil quality guidelines

The PLI value > 1 is polluted whereas PLI value < 1 indicates no pollution [15], [16].

$$Dc_{(CSQGs)} = \sum_{1}^{n} CF(CSQGs)$$

Where, **Dc**_(CSOGs) is Degree of Contamination

For the description of the degree of contamination in the study area the following terminologies have been used: Dc < 7 low degree of contamination; 7 < Dc < 14 moderate degree of contamination; $14 \le Dc < 28$ considerable degree of contamination; Dc > 28 very high degree of contamination. Where, n=7= the count of the studied heavy metals(after remove Fe metal)

Pollution Rate (PR_(CSQGs)):

$PR_{(CSQGs)} = (\sum Mc)_{sample} / (\sum Mc_{(CSQGs)})_{background}$

Mcis the concentration of metals in collected sample, $Mc_{(CSQGs)}$ concentration of metal in Canadian soil quality guidelines as background. If the PR is less than 1 the PR is very low Pollution Rate, If $1 \le PR < 2$ is low PR, If $PR \ge 2$ is high rate.

Comparison of the analyzed values of any area with any guidelines is the main method to evaluation the pollution of sediments and soils. The choice of any of guidelines depend on many reasons:- 1- The methods of analysis of the guideline and collected samples 2- The sources of sediments and soils 3- Resemble of the sites and the guideline values. Here, the guidelines values of [13] compared with the analyzed values of the study

area. As well as these guidelines values used in the equations of the pollution indices. The values of guidelines resulted due to a lot of studies by different methods in different sites. Using the values of guidelines in calculation of pollution indices is more logically than using of average shale values. The comparison of chemical concentrations with the values of any of these guidelines and use of guidelines values in equations of pollution indices is more suitable for assessment of the heavy metal pollution.

In this study, the pollution indices were estimated by usual or ordinary (normal) methods that used the average shale of [1] as references or backgrounds for calculation of pollution indices. Also the pollution indices were estimated by a new method and a new equation which using the Canadian soil quality guidelines (CSQGs) as a references or backgrounds. Where, the Canadian soil quality guidelines (CSQGs) Values of each metal used as reference value in many of equations instead of the average shale of [1].

3. Materials and Methods

3.1. Study area and sampling

The samples were collected from 12 sites (Fig. 1) in spring season 2013, representing the soils of Bahr El-Baqar region south of Manzala Lake. The sampling used topographic maps at a scale of 1:50,000, Landsat images and GPS instruments.



Fig. (1): Location map and sampling sites in the soils of Bahr EL-Baqar Region

2.2. Laboratory Analysis

The use of flame atomic absorption spectrometer is still regarded as the most convenient and appropriate technique for the purpose of heavy metal analysis in most cases. The soil samples were air dried,

and then sieved to separate the $<63\mu$ m fraction. This fraction is used by several workers to eliminate the effect of particle size and to obtain a more homogeneous grain distribution [17]. This fraction which consists of silt and clay is known to entrap most of the trace elements [18]. One gram of the powdered sample was digested with a mixture of .H₂O₂, HCl and HNO₃ according to the method described by [19]. Concentrations of Fe, Cu, Co, Ni, Zn, Pb, Cd and Cr were determined (Table 1) in the samples solutions using atomic absorption spectrophotometry ofPerkin Elmer, Model 2380.

4. Indices Calculation:

4.1. Pollution Indices Calculations (popular or oldcalculations) :

The most popularly used indices of pollution are the Contamination Factor, Pollution Load Index, Degree of Contamination, and Enrichment Factor. The averages of shale quoted by[1] is frequently used. The following is, however, short notes on the calculation of the indices:

4.1.1. Contamination factor (CF) and Pollution load index (PLI)

The level of contamination can be expressed by the contamination factor (CF); [20]. The CF is the ratio obtained by dividing the concentration of each metal in the sediment by the baseline or Background value. The background value corresponds to the baseline concentrations reported by [1] and is based on element abundances in sedimentary rocks (shale). The following terminologies are used to describe the contamination factor: CF<1, low contamination factor; $1 \le CF < 3$, moderate contamination factors; $3 \le CF < 6$, considerable contamination factors; and CF ≥ 6 , very high contamination factor.

CF of Fe indicate low contamination, CF of Cu indicate moderate contamination in all sample except sample 1 (very high contamination) and sample 2 (considerable contamination). CF of Co indicate considerable contamination factors in all samples. CF of Ni indicate low contamination as in samples 1,2,3,7,8,9 and 12 and moderate contamination as in samples 4,5,6,10 and 11. CFs of Zn, Pb and Cr indicate moderate contamination in all samples. CF of Cd indicate very high contamination in all samples (Table. 2).

The PLI proposed by [21] provide some understanding to the public of the area about the quantity of a component in the environment. The PLI of a single site is the nth root of n number of multiplied together Contamination factor (CF) values.

A PLI value of zero indicates perfection, a value of one indicates the presence of only baseline levels of pollutants, and values above one would indicate progressive deterioration of the site and estuarine quality [21]. The PLI value > 1 is polluted whereas PLI value < 1 indicates no pollution [15], [16].

$$PLI = (CF1 \times CF2 \times CF3 \times \cdots \times CF_n)^{1/n}$$

Where, n is the number of metals (seven in the present study) and CF is the contamination factor. The PLI value > 1 in all samples(Table. 2) indicate the pollution is occurred.

4.1.2. Degree of contamination (Dc)

Another index that can be derived from the CF values is the Degree of contamination (Dc) defined as the sum of all contamination factors for a given site [20]:

$$Dc = \frac{\prod_{n=1}^{n} CF}{1}$$

where CF is the single contamination factor, and n is the count of the elements present. Dc values less than n would indicate low degree of contamination; $n \le Dc \le 2n$, moderate degree of contamination; $2n \le Dc \le 4n$, considerable degree of contamination; and $Dc \ge 4n$, very high degree of contamination [2], [22].

For the description of the degree of contamination in the study area the following terminologies have been used: Dc < 8 low degree of contamination; 8 < Dc < 16 moderate degree of contamination; $16 \le Dc < 32$ considerable degree of contamination; Dc > 32 very high degree of contamination. Where, n=8= the count of

the studied heavy metals. In all collected samples (Table. 2) the degree of contamination is very high degree, where Dc > 32.

4.2. New Pollution Indices Calculations:

In these new methods, the values of Canadian soil quality guidelines (CSQGs) of [13] were used instead of average shale values [1] as a reference or background in the equations of pollution indices. The Contamination Factor, Pollution Load Index, Degree of Contamination, and Pollution Rate are estimated by new methods and equations. In these methods any metal not present in *CSQGs must be removed from the calculation such as Fe in this study, where Fe is not present in CSQGs*

4.2.1. Contamination factor (CF_(CSQGs)), *Pollution load index (PLI*_(CSQGs)) and Dgree of Contamination (Dc_(CSQGs)):

In these indices, the CSQGs were used as reference or background.

$$CF_{(CSQGs)} = Mc / Mc_{CSQGs}$$

Where, CF (CSQGs) is contamination factor by using Canadian soil quality guidelines, Mc is concentration of metal in collected samples and Mc (CSQGs) is the Concentration of metal in CSQGs

The following terminologies are used to describe the contamination factor: CF<1, low contamination factor; $1 \le CF < 3$, moderate contamination factors; $3 \le CF < 6$, considerable contamination factors; and CF ≥ 6 , very high contamination factor.

As given in Table. 3, CF of Cu indicate low contamination as in samples 6 and 10 (CF <1), indicate moderate contamination ($1 \le CF <3$) as in samples 3,4,5,7,8,9,11 and 12, and indicate considerable contamination ($3 \le CF <6$) as in samples 1 and 2. CFs of Co, Ni and Cr indicate moderate contamination ($1 \le CF <3$) as in all samples. CF of Zn and Pb is less than 1 indicate low contamination. CF of Cd is more than 6 which indicate very high contamination factor.

PLI $_{(CSQGs)} = (CF_{1(CSQGs)} \times CF_{2(CSQGs)} \times CF_{3(CSQGs)} \times \cdots \times CF_{n(CSQGs)})^{1/n}$

PLI (CSOGs) is Pollution load index by using Canadian soil quality guidelines

The PLI value > 1 is polluted whereas PLI value < 1 indicates no pollution ([15], [16]. All collected sample have values > 1 where pollution is present (Table3).

$$\mathbf{Dc}_{(CSQGs)} = \sum_{1}^{n} CF(CSQGs)$$

Where, **Dc**_(CSOGs) is Degree of Contamination

For the description of the degree of contamination in the study area the following terminologies have been used: Dc < 7 low degree of contamination; 7 < Dc < 14 moderate degree of contamination; $14 \le Dc < 28$ considerable degree of contamination; Dc > 28 very high degree of contamination. Where, n=7= the count of the studied heavy metals(after remove Fe metal). All samples in range $14 \le Dc < 28$ which indicate considerable degree of contamination except sample 7 indicate very high degree of contamination, where, Dc > 28 (Table. 3).

4.2.2. Pollution Rate (PR_(CSQGs))

$PR_{(CSQGs)} = (\sum Mc)_{sample} / (\sum Mc_{(CSQGs)})_{background}$

Mcis the concentration of metals in collected sample, $\mathbf{Mc}_{(CSQGs)}$ concentration of metal in Canadian soil quality guidelines as background. If the PR is less than 1 the PR is very low Pollution Rate, If $1 \le PR < 2$ is low PR, If $PR \ge 2$ is high rate. In these samples, the PR is very low pollution rate as in samples 7 and 12 and low PR as in others samples (Table 4)

Samples	Fe	Cu	Со	Ni	Zn	Pb	Cd	Cr
1	33567.43	270.20	76.96	54.29	144.55	52.56	14.44	108.88
2	22876.67	200.13	78.89	60.42	111.21	46.76	19.39	98.66
3	34234.25	129.66	74.6	59.22	211.22	43.83	13.94	119.98
4	31675.11	85.55	94.44	71.53	143.33	33.73	14.44	144.55
5	32453.54	85.26	94.88	70.88	142.43	34.34	13.93	142.56
6	11987.67	62.22	100.11	80.30	104.54	46.23	12.27	120.38
7	18985.24	66.66	83.74	67.37	95.13	45.92	12.37	104.56
8	19879.25	99.91	82.34	66.16	130.33	54.40	13.33	120.67
9	20300.89	99.38	83.00	67.17	141.11	53.33	13.32	119.99
10	18754.47	62.73	100.24	79.30	103.39	45.25	12.22	120.37
11	21342.90	99.88	106.44	78.86	123.33	40.70	13.32	124.39
12	19899.58	78.78	78.85	63.32	103.28	39.97	15.68	96.76
Average	35744.63	167.54	131.81	102.35	194.23	67.12	21.08	177.71
Average shale	47200	45	19	68	95	20	0.3	90
CSQG (Agricultural soil)	-	63	40	50	200	70	1.4	64
(EU, 2002)	-	140	-	75	300	300	3	150
Average upper earth crust	30890	14.3	11.6	18.6	52	17	0.1	35

Table. (1). Concentrations of heavy metals of the soil in Bahr EL-Baqar Region

- Average shale, after Turekian and Wedepohl (1961) - Average upper earth crust, after [23] -CSQG of Agricultural soil :[13], [12]:European Union Standards

Table. (2). Ordir	nary contamination	Factor, pollution	n Load Index	and D egree	e of Contamination	of Bahr
EL-Baqar Regio	n					

Samplag		рі і	DC							
Samples	Fe	Cu	Со	Ni	Zn	Pb	Cd	Cr	FLI	DC
1	0.71	6.00	4.05	0.79	1.52	2.62	48.13	1.20	2.74	65.05
2	0.48	4.44	4.15	0.88	1.17	2.33	64.63	1.09	2.5	79.21
3	0.72	2.88	3.92	0.87	2.22	2.19	46.46	1.33	2.61	60.61
4	0.67	1.90	4.97	1.05	1.50	1.68	48.13	1.60	2.45	61.52
5	0.68	1.89	4.99	1.04	1.49	1.71	46.43	1.58	2.44	59.85
6	0.25	1.38	5.26	1.18	1.10	2.31	40.9	1.33	2.04	53.73
7	0.40	1.48	4.40	0.99	1.00	2.29	41.23	1.161	2.02	52.97
8	0.42	2.22	4.33	0.97	1.37	2.72	44.43	1.34	2.33	57.81
9	0.43	2.20	4.36	0.98	1.48	2.66	44.4	1.33	2.35	57.87
10	0.39	1.39	5.27	1.16	1.08	2.26	40.73	1.33	2.15	53.65
11	0.45	2.21	5.60	1.15	1.29	2.03	44.4	1.38	2.38	58.54
12	0.42	1.75	4.15	0.93	1.08	1.99	52.26	1.075	2.07	63.68

complex	Ne	w Con	tamina	ation F	Factor (CF (CSQ	(Gs)	DC	DLI
samples	Cu	Co	Ni	Zn	Pb	Cd	Cr	DC _(CSQGs)	FLI (CSQGs)
1	4.28	1.92	1.08	0.72	0.75	10.31	1.70	20.78	1.88
2	3.17	1.97	1.20	0.55	0.668	13.85	1.54	22.97	1.78
3	2.05	1.86	1.18	1.05	0.62	9.95	1.87	18.62	1.77
4	1.35	2.36	1.43	0.71	0.48	10.31	2.25	18.92	1.66
5	1.35	2.37	1.41	0.71	0.49	9.95	2.22	18.52	1.65
6	0.98	2.50	1.60	0.52	0.66	8.76	1.88	16.92	1.55
7	1.05	2.09	1.34	0.47	0.656	40	1.63	47.26	1.79
8	1.58	2.05	1.32	0.65	0.77	9.52	1.88	17.80	1.68
9	1.57	2.07	1.34	0.70	0.76	9.51	1.87	17.85	1.7
10	0.99	2.50	1.58	0.51	0.64	8.72	1.88	16.86	1.54
11	1.58	2.66	1.57	0.61	0.58	9.51	1.94	18.47	1.71
12	1.25	1.97	1.26	0.51	0.571	11.2	1.51	18.28	1.47

Table. (3). New Contamination Factor ($CF_{(CSQGs)}$), Pollution load index (PLI (CSQGs)) and Dgree of Contamination ($Dc_{(CSQGs)}$) of Bahr EL-Baqar Region

Table. (4). Pollution Rate of Bahr EL-Baqar Region

samples	Cu	Со	Ni	Zn	Pb	Cd	Cr	Sum	PR
1	270.2	76.96	54.29	144.55	52.56	14.44	108.88	721.88	1.47
2	200.13	78.89	60.42	111.21	46.76	19.39	98.66	615.46	1.26
3	129.66	74.6	59.22	211.22	43.83	13.94	119.98	652.45	1.33
4	85.55	94.44	71.53	143.33	33.73	14.44	144.55	587.57	1.20
5	85.26	94.88	70.88	142.43	34.34	13.93	142.56	584.28	1.19
6	62.22	100.11	80.3	104.54	46.23	12.27	120.38	526.05	1.07
7	66.66	83.74	67.37	95.13	45.92	12.37	104.56	475.75	0.97
8	99.91	82.34	66.16	130.33	54.4	13.33	120.67	567.14	1.16
9	99.38	83	67.17	141.11	53.33	13.32	119.99	577.3	1.18
10	62.73	100.24	79.3	103.39	45.25	12.22	120.37	523.5	1.07
11	99.88	106.44	78.86	123.33	40.7	13.32	124.39	586.92	1.20
12	78.78	78.85	63.32	103.28	39.97	15.68	96.76	476.64	0.97
CSQGs	63	40	50	200	70	1.4	64	488.4	

5. Results and Discussion

5.1. Heavy metals distribution and pollution

Concentrations of heavy metals in the soils (agricultural soils) in Bahr EL-Baqar region are given in Table 1 and Figures 2 and 3.Heavy metal contents in the soils ranged from 11987.67 to 34234.25 mg/kg Fe; 62.22 to 270.20 mg/kg Cu; 74.60 to 106.44 mg/kg Co; 54.29 to 80.30 mg/kg Ni; 95.13 to 211.22 mg/kg Zn; 33.73 to 54.40 mg/kg Pb; 12.22 to 19.39 mg/kg Cd; 96.76 to 144.55 mg/kg Cr. The abundance of heavy metals measured in these soils decreases as follows:Fe>Zn >Cr > Cu>Co >Ni >Pb>Cd

The heavy metals concentrations of Fe, Cu, Co, Ni, Zn, Pb, Cd and Cr from the soil samples of Bahr EL-Baqar region (Table. 1 and Figs. 2,3) compared with Canadian soil quality guidelines (CSQG) of [13] and [12] as well as with average upper earth crust of [23] (Table. 1 and Fig 4). Fe concentrations in the study area less than the average upper earth crust values except in samples1,3,4 and 5 (Table.1). The typical iron concentrations in soils range from 0.2% to 55% (20,000 to 550,000 mg/kg) [24], and concentrations can vary

significantly, even within localized areas, due to soil types and the presence of other sources. Where, the iron in the range of [24]. Cu concentrations of the study area more than that CSQG Values except in samples 6 and 10, less than EU Values except in samples 1,2 and 3, and more than that of average upper earth crust of [23] (Table. 1).

Most copper compounds will settle and be bound to water, sediments or soil particles. The concentrations of copper are higher in some samples due to the irrigation of agricultural lands with untreated Bahr EL-Baqar water which led to the accumulation of Cu in soils. The Cu concentrations are lower due to the continuous removal of heavy metals by the food crops grown in this area and also due to leaching of heavy metals into the deeper layer of the soil and to the ground water.

Co concentrations of the study area are higher than that of CSQG, EU and average upper earth crust of [23] (Table.1). Cobalt usually occurs in association with other metals such as copper, nickel, manganese and arsenic. Small amounts are found in most rocks, soil, surface and underground water, plants and animals. Natural sources of cobalt in the environment are soil, dust, seawater, volcanic eruptions and forest fires. It is also released to the environment from burning coal and oil, from car, truck and airplane exhausts, and from industrial processes that use the metal or its compounds. The toxicity of cobalt is quite low compared to many other metals in soil. The concentrations of Cobalt are higher in the samples due to the irrigation of agricultural lands with untreated Bahr EL-Baqar water which led to the accumulation of Co in the soils.

Ni concentrations in the soil samples of the study area are higher than that of CSQG and average upper earth crust of [23] values, but the Nickel of samples are lower than EU values except in sample 6,10 and 11(Table. 1). Nickel occurs naturally in soils as a result of the weathering of the parent rock [25]. The underlying geology and soil-forming processes strongly influence the amount of nickel in soils with higher median concentrations reported in clays, silts, and fine grained loams relative to coarser grained loams, sandy and peaty soils [26], [25]. Agricultural fertilizers, especially phosphates, are also a significant source of nickel in soil but it is unlikely to build-up in soil in the long term from their use [25]. The irrigation by Bahr El-Baqar wastewater and uses of agricultural fertilizers led to the increasing the Ni concentrations.

Zn concentrations of the study area are lower than that of CSQG, EU except in sample 3 and the Zn concentrations are higher than the average upper earth crust values of [23] (Table.1). It is released to the environment from both natural and anthropogenic sources; however, releases from anthropogenic sources are greater than those from natural sources. The most important sources of anthropogenic zinc in soil come from discharges of smelter slags and wastes, mine tailings, coal and bottom fly ash, and the use of commercial products such as fertilizers and wood preservatives that contain zinc. Zinc does not volatilize from soil. Although zinc usually remains adsorbed to soil, leaching has been reported at waste disposal sites. The lower concentrations of the Zn than the safe limits of CSQG and EU at most sites might be due to the continuous removal of heavy metals by the food crops grown in this area and also due to leaching of heavy metals into the deeper layer of the soil and to the ground water.

Pb concentrations of the study area are lower than that of CSQG, EU and higher than the average upper earth crust values of [23] (Table.1). Lead particles are deposited in the soil from flaking lead paint, from incinerators (and similar sources), and from motor vehicles that use leaded gasoline. The concentrations of Lead is lower due to the study area has a little sources of Lead, where little vehicles and populations.

Cd concentrations of the study area are higher than that of CSQG, EU and average upper earth crust of [23] (Table.1). Cadmium (Cd) is regarded as one of the most toxic trace elements in the environment.

Cadmium occurs naturally in soils as a result of the weathering of the parent rock [27]. Although most natural soils contain less than 1 mg kg⁻¹ cadmium from the weathering of parent materials, those developed on black shales and those associated with mineralized deposits can have much higher levels [27]. Anthropogenic sources of cadmium are much more significant than natural emissions and account for its ubiquitous presence in soil [27], [28], [29]. Atmospheric deposition phosphatic fertilizers are important source of cadmium pollution [27], [28], [29]. Cadmium is much less mobile in soils than in air and water. The fact that highly weathered soils are somewhat depleted in Cd suggest that greater quantities of Cd are removed by Crops and leaching than are added through fertilization and atmospheric deposition. Surface soils commonly contain higher concentrations of Cd than subsurface horizons. The higher concentrations of Cd in surface horizons are probably due to the cycling of Cd from lower depths to the surface by plants [30]. Cadmium is higher in the

study area due to the uses of phosphatic fertilizers, irrigation by untreated wastewater of Bahr El-Baqar Darin and due to the soils of the study area are recent and derived from sediments (sand, silt and clay).

Cr concentrations of the study area are higher than that of CSQG, average upper earth crust of [23] and lower than EU values (Table.1). Chromium occurs naturally in the Earth's crust and can be detected in all environmental media. Chromium concentrations are higher in some sites due to irrigation by untreated wastewater of Bahr El-Baqar drain and the study area near from the waste incinerations and fugitive emissions from industrial sites in Port Said and around the Cairo Ismailia road. Chromium may be lower in some sites due to the continuous removal of heavy metals by the food crops grown in this area and also due to leaching of heavy metals into the deeper layer of the soil and to the ground water.



Fig. (2): showing the concentrations of Fe, Co, Ni and Zn



Fig. (3): showing the concentrations of Cu, Pb, Cd and Cr



Fig. (4): showing the standard values of the heavy metals concentrations

5.2. Assessment by Pollution indices

Another assessment methodswere applied using certain indices to assess the environmental impacts of the heavy metal pollution of the soils of Bahr El-Baqar Region. These indices include the Contamination Factor, Pollution Load Index Degree of Contamination and Pollution Rate.

When compare the data resulted from Ordinary and New pollution indices methods, the conclusions are as the following:

Both of ordinary and new contamination factors (CFs) were calculated, where, the ordinary CFs are more than new CFs (Table. 5). The new CFs is more accurate than ordinary CFs due to using CSQGs values, where these values are the permissible limits of heavy metals in soils as well as the removing of Fe values from the calculations, where Fe concentrations of Fe are very more than any other metals and not occurred in CSQGs. Using the values of CSQGs as backgrounds in calculation and remove the Fe from the comparison, give more accuracy contamination factors, where the CSQGs values resulted after many of studies and measurements to lead to more accurate permissible limits of the heavy metals. Removing of Fe from calculation due to its very more concentrations and it is not calculated by CSQGs. Occurrence of Fe in calculation related to the occurrence of Fe in used guidelines (used as background) and its concentration.

Both methods revealed that the sites of study area are polluted by heavy metals by using ordinary and new PLI (Table. 6 and Fig.5). The degree of contamination (Dc) calculated by ordinary method is very high degree of contamination in all sites, but Dc calculated by new method indicateconsiderable degree of contamination and very high degree of contamination (Fig.6). The new method of degree of contamination indicate that there are different degrees of contamination in the sitesaccording to concentrations of heavy metals and near the source of contamination. As well as the remove of Fe from the calculations of new method give more accuracy for results and let more light on the very important hazard metals.

Pollution rate (PR) is a new method instead of the ordinary PLI and Dc for determination the pollution in any site with more accuracy (Table. 6 and Fig. 7). The pollution rate calculated by guidelines or permissible limits of heavy metals (CSQGs were used in this study) to make a true comparison between the concentrations of metals of collected samples and the metals of CSQGs to more accuracy of results. The remove of Fe from the comparison give logic and more accuracy results about the pollution of each sites, where the concentration of Fe is very more than any other metals and the Fe is not occurred in CSQGs. New equation for calculate the pollution of any sites using direct comparison between the metals of the sites with the metals of CSQGs as following:

$PR_{(CSQGs)} = (\sum Mc)_{sample} / (\sum Mc_{(CSQGs)})_{background}$

Mc is the concentration of metals in collected sample, $Mc_{(CSQGs)}$ concentration of metal in Canadian soil quality guidelines as background

Table. (5).	Comparison	between the	results of Ordinar	y Pollution	Indices	(CF)andNew	Pollution Indic	es
(CF (CSQGs))							

		Ord	ion In	dices	New Pollution Indices									
Samples	Ordinary Contamination Factors (CF)						New Contamination Factors (CF (CSQGs))							
	Cu	Co	Ni	Zn	Pb	Cd	Cr	Cu	Co	Ni	Zn	Pb	Cd	Cr
1	VHC	CC	LC	MC	MC	VHC	MC	CC	MC	MC	LC	LC	VHC	MC
2	CC	CC	LC	MC	MC	VHC	MC	CC	MC	MC	LC	LC	VHC	MC
3	MC	CC	LC	MC	MC	VHC	MC	MC	MC	MC	LC	LC	VHC	MC
4	MC	CC	MC	MC	MC	VHC	MC	MC	MC	MC	LC	LC	VHC	MC
5	MC	CC	MC	MC	MC	VHC	MC	MC	MC	MC	LC	LC	VHC	MC
6	MC	CC	MC	MC	MC	VHC	MC	LC	MC	MC	LC	LC	VHC	MC
7	MC	CC	LC	MC	MC	VHC	MC	MC	MC	MC	LC	LC	VHC	MC
8	MC	CC	LC	MC	MC	VHC	MC	MC	MC	MC	LC	LC	VHC	MC
9	MC	CC	LC	MC	MC	VHC	MC	MC	MC	MC	LC	LC	VHC	MC
10	MC	CC	MC	MC	MC	VHC	MC	LC	MC	MC	LC	LC	VHC	MC
11	MC	CC	MC	MC	MC	VHC	MC	MC	MC	MC	LC	LC	VHC	MC
12	MC	CC	LC	MC	MC	VHC	MC	MC	MC	MC	LC	LC	VHC	MC

LC= low contamination MC=moderate contamination CC=considerable contaminationVHC=very high contamination

Table. (6). Comparison between the results of Ordinary Pollution Indices (PLI and Dc)andNew Pollution Indices ((PLI_(CSQGs))) and (Dc_(CSQGs))) and Pollution Rate (PR)

Samplas	Ordinary Poll	ution Indices	New Polluti	ion Indices	Pollution Rate (PR)	
Samples	PLI	Dc	(PLI _(CSQGs))	(Dc _(CSQGs))	ronution Rate (rR)	
1	Polluted	VHDC	Polluted	CDC	LPR	
2	Polluted	VHDC	Polluted	CDC	LPR	
3	Polluted	VHDC	Polluted	CDC	LPR	
4	Polluted	VHDC	Polluted	CDC	LPR	
5	Polluted	VHDC	Polluted	CDC	LPR	
6	Polluted	VHDC	Polluted	CDC	LPR	
7	Polluted	VHDC	Polluted	VHDC	VLPR	
8	Polluted	VHDC	Polluted	CDC	LPR	
9	Polluted	VHDC	Polluted	CDC	LPR	
10	Polluted	VHDC	Polluted	CDC	LPR	
11	Polluted	VHDC	Polluted	CDC	LPR	
12	Polluted	VHDC	Polluted	CDC	VLPR	

Polluted = PLI >1, CDC= considerable degree of contamination, VHDC= very high degree of contaminationVLPR= very low pollution rate LPR= low pollution rate HPR= high pollution rate



Fig. (5) Ordinary and new pollution load index (PLI)



Fig. (6). Ordinary and New Degree of Contamination



Fig.(7). Pollution rate of the soils of Bahr EL-Baqar Region

6. Conclusions

This study reveal that the soils of Bahr El-Baqar region is polluted by heavy metals in all sites of sampling. The abundance of heavy metals measured in these soils decreases as follows: Fe > Zn > Cr > Cu > Co > Ni > Pb > Cd

Fe concentrations in the study area less than the average upper earth crust values except in samples 1,3,4 and 5. Cu concentrations of the study area more than that CSQG Values except in samples 6 and 10, less than EU Values except in samples 1,2 and 3, and more than that of average upper earth crust of [23]. Co concentrations of the study area are higher than that of CSQG, EU and average upper earth crust of [23]. Cobalt usually occurs in association with other metals such as copper, nickel, manganese and arsenic. Ni concentrations in the soil samples of the study area are higher than that of CSQG and average upper earth crust of [23] values, but the Nickel of samples are lower than EU values except in sample 6,10 and 11. Zn concentrations of the study area are lower than that of CSQG, EU except in sample 3 and the Zn concentrations are higher than the average upper earth crust values of [23]. It is released to the environment from both natural and anthropogenic sources; however, releases. Pb concentrations of the study area are lower than that of CSQG,

EU and higher than the average upper earth crust values of [23]. Cd concentrations of the study area are higher than that of CSQG, EU and average upper earth crust of [23].Cadmium (Cd) is regarded as one of the most toxic trace elements in the environment. Cadmium occurs naturally in soils as a result of the weathering of the parent rock [27]. Cr concentrations of the study area are higher than that of CSQG and average upper earth crust of [23] and lower than EU values.

Both of ordinary and new contamination factors (CFs) were calculated, where, the ordinary CFs are more than new CFs. The new CFs is more accurate than ordinary CFs due to using CSQGs values, where these values are the permissible limits of heavy metals in soils as well as the removing of Fe values from the calculations, where Fe concentrations of Fe are very more than any other metals and not occurred in CSQGs. Using the values of CSQGs as backgrounds in calculation and remove the Fe from the comparison, give more accuracy contamination factors, where the CSQGs values resulted after many of studies and measurements to lead to more accurate permissible limits of the heavy metals. Both methods revealed that the sites of study area are polluted by heavy metals by using ordinary and new PLI. The new method of degree of contamination indicate that there are different degrees of contamination in the sites according to concentrations of heavy metals and near the source of contamination. As well as the remove of Fe from the calculations of new method give more accuracy for results and let more light on the very important hazard metals.

Pollution rate (PR) is a new method instead of the ordinary PLI and Dc for determination the pollution in any site with more accuracy. The pollution rate calculated by guidelines or permissible limits of heavy metals (CSQGs were used in this study) to make a true comparison between the concentrations of metals of collected samples and the metals of CSQGs to more accuracy of results.

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