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Heavy metals contamination in the coastal area between Burg EL-Burullus and Baltim, Northern Nile Delta, Egypt

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Abstract : The present work for study the pollution of the coastal area between Burg EL-Burullus and Baltim. Where, the heavy metals pollution determined for the beaches and sand dunes sediments. Sr, Zn, Pb, Mn, As, Ce, Ni, Cr, Zr, Mn, Cu, Ga, Y, Nb, Rb, Hf, W and Co analyses by X-ray fluorescence (XRF). The degree of contamination, modified degree of contamination and ecological potential risk factor indicated that the shorelines and backshore are high polluted than the sand dunes.
Keywords: Heavy metals, coastal area, Burg EL-Burullus, Baltim, Northern Nile Delta, Egypt.

1. Introduction:

Metals enter to the aquatic system due to rocks and soils weathering and from many of human activities. According to (El-Sorogy et al[1], El-Sorogy et al[2], El-Sorogy et al[3]) the metals can occur in the aquatic system as a results of uses the metal and substances that containing metal contaminants in many activities. Where, the sediments is carriers for contaminants in aquatic system.

Determination of contaminants in the water column only are not accuracy and conclusive due to water discharge fluctuations and low residence time. Evaluation of heavy metals in sediments plays an important role as they have a long residence time. Therefore, the analysis of estuarine and coastal sediments is a useful method to study the metal pollution in these areas (Diop et al[4]).

According to Dabbour[5] and Dawod and Abdelnaby[6], the black sands of Egypt are derived from the metamorphic and igneous rocks due to disintegration of them. These disintegration materials comprise large reserves of most common economic heavy minerals such as magnetite, ilmenite, zircon, garnet, rutile andmonazite (El-Askary and Frihy[7], Hedrick[8]). Where, the beaches are consists of fine sands with heavy minerals. The heavy minerals of the beach black sands comprisilmenite, magnetite, zircon, garnet, rutile, and monazite. According to Hammoud [9], the beach black sands contain traces of gold, cassiterite, beryl, chromite, corundum, apatite, collophane, uranothorite and gangue minerals. The latter include hornblend, actinolite, augite, hedenbergite, hyperthene, enstatite and minor amounts of biotite, epidote, sturolite, sphene, tourmaline, sillimanite and olivine (Hammoud[9]).

According to El-Sorogy and Attiah[10], Pb, As, Zn and Ni values of Mediterranean coastal sediments are higher than those recorded in coastal sediments of the Gulf of Aqaba, the Red Sea coast, the Arabian Gulf and backgrounds of shale and continental crust (Turekian and Wedepohl[11], Taylor[12]). The Mediterranean coastal have higher concentrations in certain heavy metals like Fe, Pb, As, Zn and Nithan that in the Arabian Gulf, Red Sea coasts. The study of pollution of the coastal sediments between Burg EL-Burullus and Baltim were studies in this manuscript.

2. Materials and Methods

The study area is the coastal area between Burg EL-Burullus and Baltim, which including the beaches and coastal sand dunes (Fig. 1). About 11 sedimentary samples were collected from this area (Table. 1). The study area is characterized by a low relief mainly below 2 m above sea level, and slope gently from south to north. Geomorphologically, it is represented by a flat coastal plain and by belts of sand dunes. Samples were analyzed in the XRF unit in National Research Center (NRC) to get the values of major contents, heavy and trace elements for each sample, where XRF is used to calculation the concentration of heavy and trace elements (Table.2).

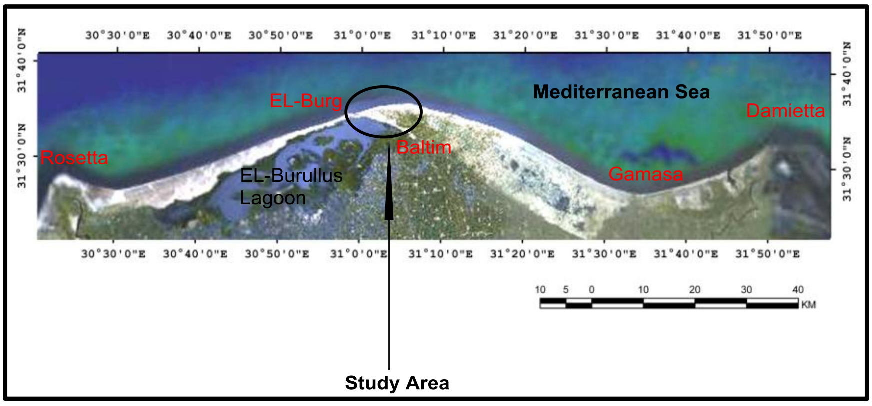

Fig. (1): Location map for the area between Burg EL-Burullus and Baltim

Table.(1): Locations of samples in the study area

Samples	Location	Samples	Location
1	Shoreline EL-Burg	**7**	Lee side middle dune
2	Backshore, after the first sample by 50 m	**8**	Right side of international road toward Baltim
3	On the bottom of dune	**9**	Shoreline, east of Baltim resort
4	Top of dune	**10**	Backshore, east Baltim resort
5	Stoss side bottom dune	**11**	Lift side of international road toward Gamasa
6	Lee side bottom dune		

Table (2) Heavy metals in the study coastal area between Burg EL-Burullus and Balim

Heavy metals	Samples											Means	AS	Tr	EC
	1	2	3	4	5	6	7	8	9	10	11				
As					14		8					2	13	10	1.8
Mn	465	837	1292	1061	1291	1258	448	558	1632	343	529	883	850		850
Ni	85	74	44	52	71	69	61	37	80	44	37	59.5	68	5	75
Cu	31	20	30	36	26	38		30	44	22	32	28	45	5	55
Zn	45	34	62	37	62	55	28	36	67	21	32	43.5	95	1	70
Pb	21	42	37		25	28	11			23		17	20	5	12.5
Sr	255	187	169	155	182	187	146	1416	230	149	136	292	300		375
Cr	126	243	530	297	494	477	205	252	731	169	251	343.2	90	2	100
Ga	10				11			157				16.2	19		15
Y	20	44	61	33	48	57	20	22	67		33	36.8	26		33
Nb			35	20	31	33	10	22	54		20	20.5	11		20
Rb	28	24	11		18		12	15		18	18	13	140		90
Ce	268		226		199				260			86.6	59		60
Hf	107	159	327		187	237		77	242	64	146	140.5	2.8		3
Zr	3140	5060	6796	1028	4820	6071	1735	3932	5117	4670	3627	4181.5	160		165
W	229				65			65				32.6	1.8		1.5
Co	91	70	86		88				88	66		44.5	19	5	25

EC, earth crust proposed by Taylor [12]. AV, average shale proposed by Turekian and Wedepohl [11]; Tr, Toxic response suggested by Håkanson [13] and Swarnalatha et al [14]

2.1. Indices Calculations

In this manuscript, the used pollution indices classified into two types: (i) single indices and (ii) integrated indices in an algorithm point of view. Single indices are indicators used to calculate only one metal contamination, which include contamination factor and ecological risk factor. Integrated indices are indicators used to calculate more than one metal contamination, which were based on the single indices. Each kind of integrated index might be composed by the single indices separately.

Contamination indices and ecological risk indices were analyzed to assess heavy metal contamination of bottom sediments of northern lagoons using single and integrated indices. In this study, contamination factor (CF) and ecological risk factor (Er) as single indices, the degree of contamination (DC), modified degree of contamination and the potential ecological risk index (RI), as integrated indices, were calculated.

2.1.1. Contamination factor (CF) and Degree of contamination (Dc)

The level of contamination can be expressed by the contamination factor (CF), (Håkanson [13]). 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 Turekian and Wedepohl [11] 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≤ CF <3, moderate contamination factors; 3≤ CF <6, considerable contamination factors; and CF ≥6, very high contamination factor.

2.1.2. 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 (Håkanson [13]):

$$Dc = \sum_{1}^{n} CF$$

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≤Dc<2n, moderate degree of contamination; 2n≤Dc<4n, considerable degree of contamination; and Dc>4n, very high degree of contamination (Caeiro et al [15], Pekey et al [16]).

For the description of the degree of contamination in the study area the following terminologies have been used: Dc <17 low degree of contamination; 17<Dc<34 moderate degree of contamination; 34≤Dc<68 considerable degree of contamination; Dc >68 very high degree of contamination. Where, n=17= the count of the studied heavy metals.

2.1.3. Modified degree of contamination (mDc)

Also another index can be derived from contamination factor is modified degree of contamination (mDc). Abrahim [17] presented a modified and generalized form of the (Håkanson [13]) equation for the calculation of the overall degree of contamination at a given sampling site. The modified equation for a generalized approach to calculating the degree of contamination is given below:

$$\mathbf{mDc} = \left(\sum_{i=1}^{i=n} Dc\right)/n$$

Where n = number of analyzed elements and i = ith element (or pollutant) and CF = Contamination factor. Using this generalized formula to calculate the mDcallows the incorporation of as many metals as the study may analyze with no upper limit. For the classification and description of the modified degree of contamination (mDc), the following gradations have been given below (Table. 3).

Table. (3): Grading of modified degree of contaminations

Modified degree of contamination (mDc)	According to [18]
mDC< 1.5	Nil to very low degree of contamination
1.5 <mDC< 2	Low degree of contamination
2<mDC< 4	Moderate degree of contamination
4 <mDC< 8	High degree of contamination
8<mdC< 16	Very high degree of contamination
16 <mDC< 32	Extremely high degree of contamination
mdC>32	Ultra high degree of contamination

2.1.4. Ecological risk factor (Er) and potential ecological risk index(RI)

An ecological risk factor (Eri) to quantitatively express the potential ecological risk of a given contaminant also suggested by Håkanson [13]

Er =Tr × CF

Where Tr is the toxic-response factor for a given substance, and CF is the contamination factor. The Tr values of heavy metals suggested by Håkanson [13], wherePb=Cu=5, Cd= 30, Cr=2, Zn=1, As=10, Hg=40 and (Swarnalatha et al 14), where Ni=Co=5. The following terminologies are used to describe the risk factor: Er<40, low potential ecological risk; 40≤Er<80, moderate potential ecological risk; 80≤Er<160, considerable potential ecological risk; 160≤Er<320, high potential ecological risk; and Er≥320, very high ecological risk.

The potential ecological risk (RI) of the heavy metals is quantitatively evaluated by the potential ecological risk index (Er) (Håkanson [13], Zhu et al [19]), which takes into account both contamination factor (CF), and the “toxic-response” factor.

The potential ecological risk values obtained were compared with categories grade of Er and RI of metal pollution risk on the environment suggested by (Håkanson [13], Shi et al [20]). The potential ecological risk index (RI) was in the same manner as degree of contamination defined as the sum of the risk factors.

$$\mathbf{RI} = \sum_{1}^{n} \mathbf{Er}$$

Where, Er is the single index of ecological risk factor, and n is the count of the heavy metal species. The following terminology was used for the potential ecological risk index: RI<150, low ecological risk; 150≤RI<300, moderate ecological risk; 300≤RI<600, considerable ecological risk; and RI>600, very high ecological risk (Håkanson[13], Shi et al[20]). Where, Er and RI denote the potential ecological risk factor of individual and multiple metals, respectively.

3. Results and Discussions

3.1. Heavy Metals Distribution:

Distribution of heavy metals in the sediments of the coastal area between Burg EL-Burullus and Baltim are given in Tables 2. The means of heavy metal contents (Table. 2) are 2, 883, 59.5, 28, 43.5, 17, 292, 343.2, 16.2, 36.8, 20.5, 13, 86.6,140.5, 4181.5,32.6, 44.5, As, Mn, Ni, Cu, Zn, Pb, Sr, Cr, Ga, Y, Nb, Rb, Ce, Hf, Zr, W, and Co respectively. The mean concentrations of heavy metals in the coastal sediments of beaches and sand dune are in the following order: Zr>Mn> Cr >Sr>Hf>Ce>Ni >Co >Zn>Y> W> Cu >Nb>Pb>Ga>Rb> As.

3.2. Possible Biological Effects

Heavy metals are regard as serious pollution of aquatic ecosystem because of their environmental persistence, toxicity effects on living organisms. To estimate the biological effects of metals, ERL (Effects-Range Low) and ERM (Effects-Range Median) reported by Long and Morgan [21] and Long et al [22] were used. Also, TEL (threshold effect level); LEL (lowest effect level); MET (minimal effect threshold); PEL (probable effects level); TET (toxic effect threshold); SEL (severe effect level); TRV, (Toxicity reference value); AV, (average shale); EC, (earth crust) were used (MacDonald et al [23], Smith et al[24], Persuad et al[25], Environment Canada and Ministere de l'Envionnement du Quebec[26], US EPA [27]) (Tables 2,4).

Several sediment quality guidelines have been proposed by different countries and organizations. However, it has been rather difficult to establish internationally accepted guidelines. Table 4 list some of the common guidelines for Cu, Cr, Pb, Ni, Zn, As and Hg. Comparing the concentration of these metals in the sediments of the coastal area between Burg EL-Burullus and Baltim (Tables 2) with the guidelines given in Table 9. Some guidelines (ERL and ERM of (Long et al [22]), TET and SEL of (MacDonald et al [23], Smith et al [24], Persuad et al [25], Environment Canada and Ministere de l'Envionnement du Quebec [26]) were compared with the concentrations of heavy metals in each station or site in the beaches and sand dunes and the others guidelines (LEL and SEL of (MacDonald et al[23]), TRV, AS and EC) (Table 5) compared with the means concentrations of each metals in the coastal area between Burg El-Burullus and Baltim.

It appears that As<ERL and ERM (MacDonald et al[23], Smith et al[24]) in all samples and it less than SEL and more than LEL. Cr of the study area > ERL, LEL, SEL in all samples, and it > ERM (MacDonald et al [23], Smith et al [24]) except in sample 1 (Table 2,4).Pb< ERL, ERM, LEL, SEL in all samples. Cu < ERL, ERM , SEL and more than LEL. Ni **>** ERL and LEL, while it more than ERM except in samples 3,8,10 and 1. Ni more than SEL except in samples 3,4,8,10 and 1. Zn < ERL, ERM, TET and SEL (Table. 2, 4).

Here, another comparison between the mean concentrations of the heavy metals in the coastal area compared with LEL, SEL, TRV, AV and EC as in Table 10.

AS (Average Shale) > As, Ni, Cu, Zn,Pb,Sr, Ga,Rb while it <Mn, Cr, Y,Nb, Ce, Hf,Zr,W,Co. EC (Earth Crust) > Ni, Cu, Zn, Sr,Ce while it < As, Mn, Pb, Ga, Cr, Y, Nb, Rb, Hf, Zr, W, Co. TRV (Toxicity reference value) >As,Zn, Pb while it <Ni,Cu, Cr. SEL >As,Zn, Ni,Cu, Pb while it < Cr. LEL > As, Zn, Pb while it < Ni, Cu, Cr. (Table. 5).

Table. (4): Sediment quality guidelines according to (Long ER and Morgan [21], Long et al 22, MacDonald et al [23], Smith et al [24], Persuad et al [25], Environment Canada and Ministere de l'Envionnement du Quebec [26], US EPA [27])

SQG	Mn	Cd (ppm)	Cr (ppm)	Cu (ppm)	Pb (ppm)	Ni (ppm)	Zn (ppm)	As (ppm)	Hg (ppm)	References
TEL[1]		0.6	37.3	35.7	35	18	123	5.9	0.17	a
ERL		5	80	70	35	30	120	33	0.15	a,b,e
		1.2	81	34	46.7	20.9	150	8.2	0.15	f
LEL[2]		0.6	26	16	31	16	120	6	0.2	a
MET[3]		0.9	55	28	42	35	150	7	0.2	a
PEL[1]		3.53	90	197	91.3	36	315	17	0.48	a
ERM		9	145	390	110	50	270	85	1.3	a.b.c.d.e
		9.6	370	270	218	51.6	410	70	0.71	f
TET		3	100	86	170	61	540	17	1	a,b,c,d
SEL[1]		10	110	110	250	75	820	33	2	a,b,c,d
TRV		0.6	26	16	31	16	110	6	0.2	g
AS	٨٥٠	0.3	90	45	20	68	95	13	0.4	h
EC	850	0.15	100	55	12.5	75	70	1.8	0.08	i
Means	883		343.2	28	17	59.5	43.5	2		

SQG, Sediment quality guideline; TEL, threshold effect level; ERL, effects range low; LEL, lowest effect level; MET, minimal effect threshold; PEL, probable effects level; ERM, effect range median; TET, toxic effect threshold; SEL, severe effect level; TRV,Toxicity reference value proposed by US EPA [27]; AV, average shale proposed by (Turekian and Wedepohl [11]); EC, earth crust proposed by (Taylor [12]).

1Same as Canadian Freshwater Sediment Guidelinesb; 2Same as Ontario Ministry of Environment Screening Level Guidelines; 3Same as MEL in SQAVsc (SQAV, Sediment Quality Advisory Value) a (MacDonald et al [23]); b (Smith et al [24]); c (Persuad et al [25]); d (Environment Canada and Ministere de l'Envionnement du Quebec [26]); e(Long and Morgan [21]); f (Long et al [22]); g (US EPA [27]); h (Turekian and Wedepohl [11]); i (Taylor [12]). 1 mg/kg =1ug/g

3.3. Heavy metal pollution indices:

The pollution in the sediments of the coastal area between Burg EL-Burullus and Baltim can be assessed by determining some of indices such as the contamination factors (CF), degree of contaminations (Dc), modified degree of contaminations (mDc) and ecological risk index (RI) (Table. 6). Potential ecological risk index (RI) depends on the potential ecological risk factor (Er), the toxic-response factor (Tr) and the contamination factors (CF). The evaluation of the pollution degree of the coastal sediments depend on many indices (Table 6 and Fig.2).

Table. (5) Comparison between mean concentrations of heavy metals of the coastal area with the LEL, SEL, TRV, AV and EC values of many guidelines.

Heavy metals	Means	AS		EC		TRV		SEL		LEL	
As	2	13	>	1.8	<	6	>	33	>	6	>
Mn	883	850	<	850	<						
Ni	59.5	68	>	75	>	16	<	75	>	16	<
Cu	28	45	>	55	>	16	<	110	>	16	<
Zn	43.5	95	>	70	>	110	>	820	>	120	>
Pb	17	20	>	12.5	<	31	>	250	>	31	>
Sr	292	300	>	375	>						
Cr	343.2	90	<	100	<	26	<	110	<	26	<
Ga	16.2	19	>	15	<						
Y	36.8	26	<	33	<						
Nb	20.5	11	<	20	<						
Rb	13	140	>	90	<						
Ce	86.6	59	<	60	>						
Hf	140.5	2.8	<	3	<						
Zr	4181.5	160	<	165	<						
W	32.6	1.8	<	1.5	<						
Co	44.5	19	<	25	<						

EC, earth crust proposed by (Taylor [12]). AV, average shale proposed by(Turekian and Wedepohl [11]);; TRV, Toxicity reference value proposed by (US EPA [27]); Tr, Toxic response. LEL- Lowest effect level; SEL- Severe effect level according to (MacDonald et al [23]); b (Smith et al [24]); c (Persuad et al [25]) mg/kg =1ug/g

In the study area, degree of contamination (Dc) was very high degree of contamination in all samples except sample 4 (Low degree contamination), sample 7 (Moderate degree contamination), sample 10 (considerable degree contamination).

Modified degree of contamination (mDc) are very high degree of contamination (VHDC) in samples 1,3,5,6 and 9, high degree contamination (HDC) in samples 2,8 and 11, very low degree of contamination (VLDC) in samples 4 and 7, moderate degree of contamination (MDC) as in sample 10. The potential ecological risk index (RI) are Low ecological risk (LER) in all samples (Table 6 and Fig.2).

The average degree of contamination of the beaches and sand dunesare in the following order: Shoreline = Backshore = Bottom stoss side of sand dune = Bottom lee side of sand dune > Crest of sand dunes< Right side of international road.

Also, the average modified degree of contamination of the beaches and sand dunes are in the following order: Shoreline >Backshore < Bottom stoss side of sand dune = Bottom lee side of sand dune > Crest of sand dunes< Right side of international road (Table 6).

Table (6):Contamination factor (CF), Degree of contamination (Dc), Modified degree of contamination (mDc) and potential ecological risk index(RI)

Heavy Minerals	Contamination factor (CF)										
	1	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**	**10**	**11**
As	0	0	0	0	1.07	0	0.61	0	0	0	0
Mn	0.54	0.98	1.52	1.24	1.51	1.48	0.52	0.65	1.92	0.40	0.62
Ni	1.25	1.08	0.64	0.76	1.04	1.01	0.89	0.54	1.17	0.64	0.54
Cu	0.68	0.44	0.66	0.8	0.57	0.84	0	0.66	0.97	0.48	0.71
Zn	0.47	0.35	0.65	0.38	0.65	0.57	0.29	0.37	0.70	0.22	0.33
Pb	1.05	2.1	1.85	0	1.25	1.4	0.55	0	0	1.15	0
Sr	0.85	0.62	0.56	0.51	0.60	0.62	0.48	4.72	0.76	0.49	0.45
Cr	1.4	2.7	5.88	3.3	5.48	5.3	2.27	2.8	8.12	1.87	2.78
Ga	0.52	0	0	0	0.57	0	0	8.26	0	0	0
Y	0.76	1.69	2.34	1.26	1.84	2.19	0.76	0.84	2.57	0	1.26
Nb	0	0	3.18	1.81	2.81	3	0.90	2	4.90	0	1.81
Rb	0.2	0.17	0.07	0	0.12	0	0.08	0.10	0	0.12	0.12
Ce	4.54	0	3.83	0	3.37	0	0	0	4.40	0	0
Hf	38.21	56.78	116.7	0	66.78	84.64	0	27.5	86.42	22.8	52.4
Zr	19.62	31.62	42.47	6.42	30.12	37.94	10.8	24.57	31.98	29.5	22.6
W	127.2	0	0	0	36.11	0	0	36.11	0	0	0
Co	4.78	3.68	4.52	0	4.63	0	0	0	4.63	3.47	0
Dc	202.1	102.2	185.01	16.5	158.6	139.02	18.2	109.13	148.61	60.93	83.48
	VHD	VHD	VHD	LD	VHD	VHD	MD	VHD	VHD	CD	VHD
mDc	11.89	6.01	10.88	0.97	9.33	8.17	1.07	6.42	8.74	3.58	4.91
	VHDC	HDC	VHDC	VLD	VHDC	VHDC	VLDC	HDC	VHDC	MDC	HDC
RI	42.16	42.34	50.88	14.8	59.91	27.47	18.23	12.03	12.03	32.77	12.19
	LER	LER	LER	LER	LER	LER	LER	LER	LER	LER	LER

LD, low degree of contamination; MD, moderate degree of contamination; CD, considerable degree of contamination; VHD, very high degree of contamination; VLD, very low degree of contamination; MDC, Moderate degree of contamination; HDC, High degree of contamination; VHDC, Very high degree of contamination; LER, low ecological risk

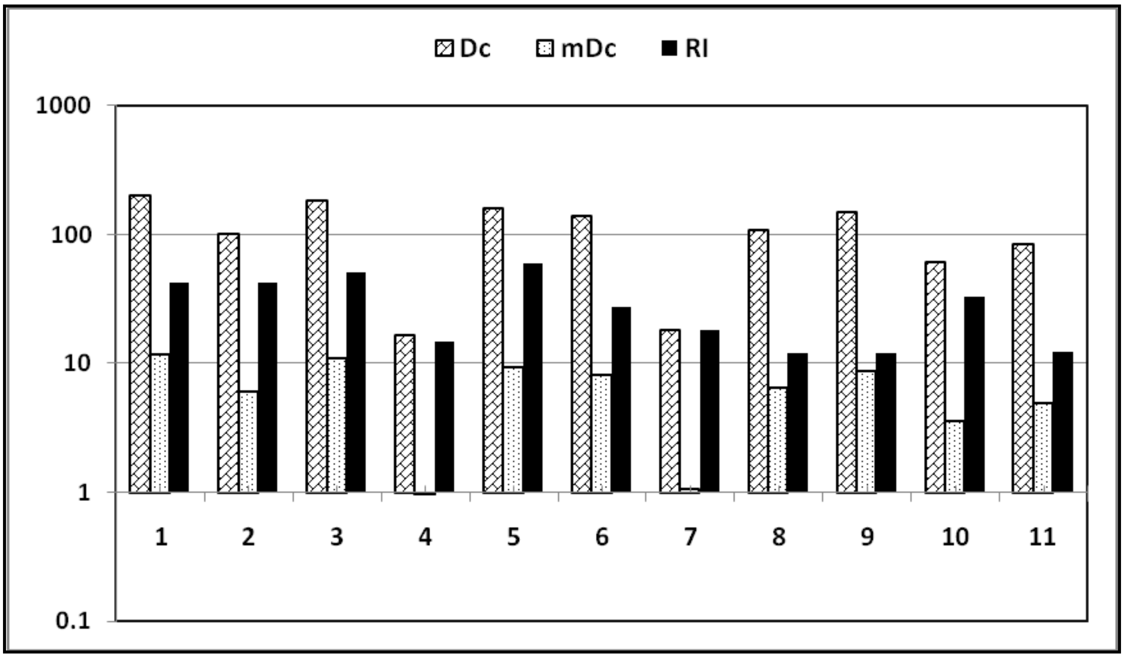

Fig. (2): Degree of contamination (Dc), Modified degree of contamination (mDc) and potential ecological risk index(RI)

4. Conclusions

The average degree of contamination of the shoreline and backshore are more than that in the crest of coastal sand dunes. The potential ecological risk index (RI) are low ecological risk (LER) in shoreline, backshore, bottom stoss, lee side and crest of dunes as well as in the right and lift sides of the international road sites.

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