Australian Journal of Basic and Applied Sciences, 6(6): 44-58, 2012
ISSN 1991-8178

Assessment of Heavy Metals Contamination in Surface Sediments of the Egyptian Red Sea Coasts

[1]Mamdouh S. Masoud, [2]Tarek O. Said [2]Gehan El Zokm And [2]Mohamed A. Shreadah

[1]Chemistry Department, Faculty of Science, University of Alexandria, Egypt.
[2]National Institute of Oceanography and Fisheries, Kayet Bay, Alexandria, Egypt.

Abstract: Five approaches were employed to evaluate degree of sediment pollution along Egyptian Red Sea coasts based on one step digestion of eight metals (Fe-Mn-Zn-Pb-Cd-Cu-Cr-Ni): 1) Comparison with the background value, (2) Toxicity guidelines of heavy metals, (3) Metal Pollution Index (MPI), (4) Enrichment Factor and (5) Sediment Quality Index (SQI). The results declared that sediments of the Egyptian Red Sea coasts were highly enriched with Cd and scientifically enriched with Pb. Principal component analysis (PCA) was applied to discuss metal correlations and sources also to evaluate hot spots. Another important approach identifying different forms of metals is speciation; two sequential extraction schemes were applied for Pb and Cd speciation. The recoveries of both schemes were calculated to recommend the scheme with the high recovery to make comparison among Gulf of Suez, Gulf of Aqaba and Red Sea proper to identify the state of pollution. Scheme I is recommended for studying speciation of Pb and Cd. The data declared that fractionation pattern of Pb was different in Gulf of Suez than from both Gulf of Aqaba and Red Sea proper that for Gulf of Suez Pb content in the non-residual fractions was more than in the residual one, indicating that in Gulf of Suez Pb has anthropogenic origin due to man activities. High % of Cd was recorded as Fe and Mn oxides fraction in the area of investigation. PCA for metal speciation of Pb and Cd revealed that organic matter played an important role in fractionation pattern of each metal.

Key words: heavy metals, assessment, contamination, speciation, sediment, Red Sea,

INTRODUCTION

Natural weathering of rocks and soil can break down and release heavy metals into aquatic environment, volcanic activities play a noticeable role in enriching the water reservoirs with heavy metals. In addition to the geological weathering, human activities have also introduced large quantities of metals to the localized area of water bodies (Nriagu 1990 and Meherm 2002). Sediments are the main reservoir and source of heavy metals in marine environment. They play an important role in the transport and storage of potentially hazardous metals. Strong acid digestion has been widely applied for the determination of total heavy metals in sediments. This approach can be misleading when assessing environmental effects due to the potential for an overestimation of exposure risk. It provides no information regarding the chemical nature or potential mobility and bioavailability of particular element (Ford et al. 2001; Han et al. 2001; Vijver et al. 2004; Jin et al. 2005; Powell et al. 2005).

The present study is aimed to: 1) Measure the degree of pollution of sediment with heavy metals applying different scales, (2) Evaluate the hot spots along the area of investigation and the pollution sources, (3) Identify of specific fractions of Pb and Cd in sediment samples collected from the shoreline of the Red Sea applying two schemes for speciation to recommend the scheme with high recovery, (4) Use the scheme with the high recovery to make comparison among Gulf of Suez, Gulf of Aqaba and Red Sea proper to identify the state of pollution in the three regions. (5) Apply principal component analysis to get clear image revealed metals distributions, correlations, associations and sources, (6) Use risk assessment code (RAC) of the metals in the sediments to give a clear indication of sediment reactivity, which assess the risk connected with the presence of metals in aquatic environment.

MATERIALS AND METHODS

2.1 Sampling:

Surface sediment samples were collected from 24 stations using a Hydro-Bios stainless-steel grab sampler during winter 2006, stored in plastic bags and kept frozen at -20^{0}C, until analysis. The samples were left to dry in Petri-dishes at room temperature. Samples are distributed along the Egyptian Red Sea coasts: 9 samples from Gulf of Suez, 6 samples from Gulf of Aqaba and 9 samples from the Red Sea proper (Figure 1 and Table 1).

2.2 Quality Assurance And Quality Control For Heavy Metals Measurements:

The aim is to control accuracy and to determine the uncertainty of heavy metal determination. The method aimed to document successful implementation of the method for measurements in sediment according to

Corresponding Author: Mamdouh s. Masoud, Chemistry Department, Faculty of Science, University of Alexandria, Egypt.

standard operating procedures for trace metals (UNEP/IAEA, 1986). An exact weight (0.5g) of dry sample (drying at room temperature) of sediment was completely digested in Teflon vessels using a mixture of HNO_3, HF and $HClO_4$ (3:2:1) at 70°C (UNEP/IAEA 1986 and Ajay and Van Loon 1989). The final solution was diluted to 25 ml with double deionized distilled water. All digested solutions were analyzed in duplicate using the atomic absorption spectrophotometer (AAS Varian Techtron-Model 1250 equipped with a hydride vapor system) and the results were expressed in µg/g; dry weight. The detection limits and the recovery % of reference material (SD-M-2/TM) obtained for different metals applying AAS instrument were represented in Table (2).

All reagents used were of analytical grade (Merck), a replicate analysis for samples showed a good accuracy. To prevent contamination, all used plastic vessels were previously washed in diluted nitric acid and deionized water. Blanks were treated identically, using the same reagents for testing the precision. Two schemes (I and II) are used for optimization Tables (2 and 3).

Table 1: List of names, sites codes and different sampling locations for the area of investigation during 2006

Name	Site Code	Latitude	Longitude
Gulf of Suez			
1- Port Tawfiq	SU-1	29° 57' 0"	32° 32' 24"
2- Rex Beach	SU-2	29° 56' 50"	32° 30' 48"
3-Kabanon Beach	SU-3	29° 56' 46"	32°29' 36"
4-Suez Middle (NIOF)	SU-4	29° 55' 12"	32° 28' 48"
5-Ain Sukhna (SUMED)	SU-5	29° 20' 24"	32° 36' 36"
6-Ain Sukhna(Porto Hotel)	SU-6	28° 55' 25"	32° 51' 17"
7- Ras Gharib	SU-7	28° 22' 12"	33° 4' 48"
8- Ras Shukeir	SU-8	28° 8' 24"	33° 16' 48"
9- El-Tur	SU-9	28° 14' 24"	33° 36' 36"
Gulf of Aqaba			
10-Ras Mohamed	AQ-1	27° 47' 40"	34° 12' 51"
11- Marina Sharm	AQ-2	27° 51' 23"	34° 16' 50"
12-Sharm El Sheikh (Nama Bay)	AQ-3	27° 54 ' 39"	34° 19' 47"
13- Dahab	AQ-4	28° 28' 39"	34° 30' 44"
14-Nuweiba Harbor(El-Saideen)	AQ-5	28° 58 ' 15"	34° 39' 12"
15- Taba	AQ-6	29° 29 ' 17"	34°53' 34"
Red Sea proper			
16-Hurghada (Sheraton Hotel)	RE-1	27° 1' 37.5"	33°50' 48.4"
17- Safaga North (Suma Bay)	RE-2	26° 47' 34.9"	33° 56' 12.5"
18- Safaga Middle	RE-3	26° 30' 20"	34° 0' 20"
19- El Hamarawein	RE-4	26° 15' 9"	34° 12' 5"
20- Movenpick	RE-5	26° 12' 15"	34° 3' 15"
21- Qusier Middle	RE-6	26° 8' 30"	34° 14' 30"
22- Qusier South	RE-7	25° 55' 48"	34° 36' 36"
23- Marsa Alam	RE-8	25° 4 ' 6.1"	34° 45' 0 .4"
24- Bir Shalatin	RE-9	23° 9' 9.9"	35° 36' 48.3"

Table 2: Results of validation study for Pb and Cd concentrations (µg/g) in reference material (SD-M-2/TM) analyzed together with the sediments of the study area

Element	LOD	Certified values	Found values	Recovery %
Fe	0.007	27.1	25.46	93.9
Mn	0.006	12.0	10.9	90.8
Zn	0.004	74.8	70	93.6
Pb	0.008	22.8	21	92.1
Cd	0.009	0.11	0.099	90.0
Cu	0.007	32.7	30.1	92.1
Cr	0.009	77.2	74.9	97.0
Ni	0.009	56.1	53.2	94.8

LOD: Limit of detection

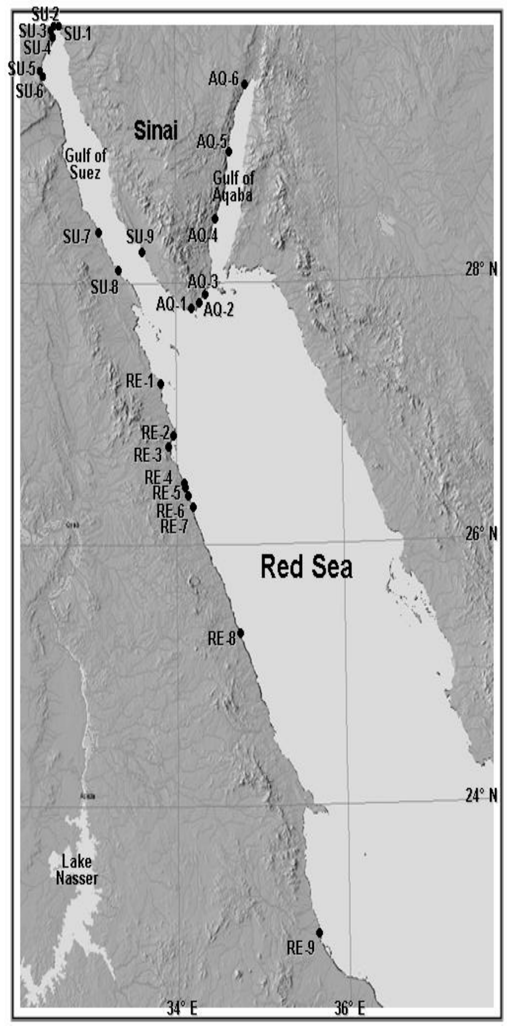

Fig. 1: Location of sampling sites along the area of investigation during 2006

2.3 Measurement of the degree of pollution of sediment with heavy metals (One step digestion):

2.3.1 Metal Pollution Index (MPI):

MPI is calculated according to the following formula:

$MPI = (M_1 \times M_2 \times M_3 \times \cdots \times M_n)^{1/n}$,

Where M_n is the concentration of metal expressed in μg/g of dry weight, n number of metals (Usero et al. 1996; Masoud et al. 2007).

2.3.2 Estimation of enrichment factor:

The metal enrichment factor (EF) is defined as follows:

$$EF = \frac{(M/Fe)sample}{(M/Fe)crust}$$

Where EF is the enrichment factor, $(M/Fe)_{sample}$ is the ratio of metal and Fe concentration of the sample, and $(M/Fe)_{crust}$ is the ratio of metal and Fe concentration in the crust (Schiff and Weisberg 1999; Baptista et al. 2000; Mucha et al. 2003).

2.3.3 Statistical analysis for assessment of metal pollution:

Principal component analysis (PCA) a multivariate statistical technique, is generally employed to reduce the dimensionally of dataset while attempting to preserve the relationships present in the original data. The PCA enables a reduction of data and description of a given multi dimensional system (Liu et al. 2003; Loska and

Wiechula 2003). The PCA was applied on the multivariate data derived from the geochemical analysis of 24 stations in the study area. Data analysis including (PCA) was done on the correlation matrix using SPSS-15

2.3.3.1 Sediment Quality Index (SQI):

It is calculated according to the following formula:

SQI= $(\lambda 1/\Sigma\lambda)$ **PC1** + $(\lambda 2/\Sigma\lambda)$ **PC2** + $(\lambda 3/\Sigma\lambda)$ **PC3**

For PC Assessment Model where $\lambda 1$, $\lambda 2$ and $\lambda 3$ are the first, second and third largest Eigen values, and PC1, PC2 and PC3 are the principal component factor scores (Davis 1986; El- Iskandarani et al. 2004).

2.4 Schemes used for speciation:

Two schemes (I and II) were used for sequential chemical extraction in order to get the best recovery for heavy metal extracted in sediment samples collected from the area of investigation (Tables 3 and 4). The difference between the two schemes is dependent on the stages of extractions specially the forms of Fe and Mn.

2.4.1 The recovery of the two schemes:

The efficiency of the sequential extractions can be evaluated from the recovery for each element, defined as the sum of the concentrations of each leaching step, divided by the total concentration determined by one step digestion (Rutten et al. 2003; Cuong and Obbard (2006); Zemberyova et al. 2006; Long et al.2009).

Recovery= (sum of the concentrations of each leaching step / total digestion)

Table 3: Sequential chemical extraction procedure used for metal speciation applying scheme I

Fraction	Reagents of extraction	Volume of extraction (ml)	Conditions
F1 Exchangeable	1M KNO_3 natural soil pH	8	1h room temperature shaking continuously
F2 Carbonate	1M NaOAc, pH 5	8	5h room temperature continuously agitated
F3 Fe and Mn oxides	0.04M $NH_2OH.HCl$ in 25%(v/v) HOAc at pH 2	20	96 ± 3 ^oC 6h agitated occasionally
F4 Organic matter	1- 3 ml of 0.02M HNO_3+5ml (30%) H_2O_2 , pH 2 with HNO_3	20	85±2^oC 2h agitated occasionally
	2- 3ml of(30%)H_2O_2 at pH=2 with HNO_3		85±2^oC 3h agitated occasionally
	3- 5ml of 3.2M NH_4OAc in 20%(v/v) HNO_3, diluted to 20ml		30min, room temperature agitated occasionally
F5 Residual	HNO_3/ /HF/ $HClO_4$ digestion	25	70 ^oC

Table 4: Sequential chemical extraction procedure used for metal speciation applying scheme II

Fraction	Reagents of extraction	Volume of extraction (ml)	Conditions
F1 Exchangeable	0.1M $CaCl_2$	15	2h
F2 Surface adsorbed	1M NaOAc, pH 5	30	5h
F3 Organic matter	NaOCl, pH 8.5	5	30min; 90-95^oC
F4 Mn oxides	0.05M $NH_2OH.HCl$, pH 2	30	30min, room temperature
F5 Poor crystalline Fe oxides	0.2M Oxalic acid + 0.2 M NH_4 oxalate, pH3	30	2h dark
F6 Crystalline Fe oxides	6M HCl	40	24h, room temperature
F7 Residual	HNO_3 /HF /$HClO_4$ digestion	25	70 ^oC

Scheme I is based on Tessier et al. (1979) as modified by Ajay and Van Loon (1989); Yong and Phandungchewit (1993). Scheme II is based on Silveira et al. (2006).

RESULTS AND DISCUSSION

3.1 Assessment of sediment contaminations:

It is difficult to make an overall assessment of the degree of metal contamination in marine sediments (Rubio et al. 2000), due to variation in analytical procedures between studies and the presence of an unknown natural background in the sediment. In the present study, five approaches were employed to evaluate sediment pollution: 1) Comparison with the background value, (2) Toxicity guidelines of heavy metals, (3) Metal Pollution Index (MPI). (4) Enrichment Factor (EF) and (5) Sediment Quality Index (SQI).

3.1.1 Comparison with the background value:

The background values of different metals were defined according to international standard: Zn, Pb, Cd, Cu and Cr (Ruiz et al. 1998; Bervoets and Blust 2003) and Fe, Mn and Ni (Fifield and Haines 2000), which are shown in Table (5). For Cd and Pb the concentrations were exceeded the background values in all stations except Kabanon Beach.

3.1.2 Toxicity guidelines of heavy metals:

Some toxicity guidelines of heavy metals are given in Table (5). The incidence of effects increased from 20% to 30% for most trace metals when concentrations exceeded ERL value but were lower than the ERM values. When concentrations exceeded the ERM values, the incidence of adverse effects increased from 60% to 90% for most trace metals. Concentrations below the TEL value represent concentrations, which are not expected to cause any adverse biological effects. Theconcentrations $\geq$ TEL, but below the PEL probable-effect level represent a range of concentrations within which effects may occasionally occur on sensitive organisms, but there is only a slight risk. Concentrations $\geq$ PEL value represent a probable-effects range within which adverse biological effects would frequently occur (Long et al. 1995; Pekey 2004; Saleh 2006; Bakon and Ozkoc 2007).

According to scales of pollution presented in Table (5), the stations with bold number may be suffered from pollution. The total concentrations (one step digestion) of eight heavy metals in the study area are given in Table (5). For Gulf of Suez and Red Sea proper, the mean concentrations of heavy metals represented the decreasing order Fe > Mn > Zn > Pb > Cr >Ni >Cu > Cd but for Gulf of Aqaba the order is Fe > Mn > Zn > Pb >Ni > Cu > Cr > Cd.

3.1.3 Metal Pollution Index (MPI):

MPI is calculated according to the following formula:

$$MPI = (M_{Fe} \times M_{Mn} \times M_{Zn} \times M_{Pb} \times M_{Cd} \times M_{Cu} \times M_{Cr} \times M_{Ni})^{1/8}$$

It is used to estimate the degree of pollution. According to the calculated values, Table (5), it can be indicated that MPI values recorded at stations 19 (El-Hamrawein), 23 (Marsa Alam) and 8 (Ras Shukeir) were 110.93 105.93 and 82.34, respectively due to the presence of El- Nasr Phosphate Company at El- Hamrawein, Heavily tourist activities at Marsa Alam. Gulf Petroleum Company and ships (oil loading and unloading, discharge of oil ballast) at Ras Shukeir.

3.1.4 Estimation of enrichment factor (EF):

In the present study the enrichment factor was used to assess the level of contamination and the possible anthropogenic impact in sediments of Egyptian Red Sea Coasts. To identify anomalous metal concentration, geochemical normalization of the heavy metals data to a conservative element, such as Fe was employed. (Schiff and Weisberg 1999; Baptista et al. 2000; Mucha et al. 2003). In this study iron has also used as a conservative tracer to differentiate natural from anthropogenic components. According to Ergin et al. (1991) the metal enrichment factor (EF) value is defined following to Ergin et al. (1991) concept as follows:

$$\frac{(M/Fe)sample}{(M/Fe)crust}$$

$(M/Fe)_{sample}$ is the ratio of metal and Fe concentrations of the sample, and $(M/Fe)_{crust}$ is the ratio of metal and Fe concentrations of a background. The values for the surficial earth crust of Mn, Zn, Pb, Cd, Cu, Cr and Ni were taken from Martin and Meybeck (1979) and represent the average composition of the surficial rocks exposed to weathering. Because of natural mineralogical differences of sediment and analytical uncertainty, only sediments with an EF > 2 were considered to be as enriched as stated by Angelidis and Aloupi (1997) and Liaghati et al. (2003).

Table (6) gives EF values of Mn, Zn, Pb, Cd, Cu, Cr and Ni in Egyptian Red Sea coasts sediments along with the background concentrations of these metals. The EF values were < 2 indicate that the metal is entirely from crustal materials or natural processes; whereas EF values > 2 suggest that the sources are more likely to be anthropogenic. Cd has the highest average EF of 248.0, 208.33 and 231.1 for Gulf of Suez, Gulf of Aqaba and Red Sea proper, respectively. EF_{Cd} ranged from 111.2 at Quseir South to 556.68 at Ain Sukhna Porto Hotel. Lead recorded the second highest average EF of 47.881, 39.14 and 37.84 for Gulf of Suez, Gulf of Aqaba and Red Sea proper, respectively. With a range of 14.43 at Hurghada Hotel to 80.0 at Rex Beach. Zn has the third highest average EF of 10.8, 9.0 and 8.3 with a range of 2.18 at SUMED to 18.4 at Ras Gharib.

For Gulf of Suez EF mean values (Mn, Cu, Cr and Ni) have the order $EF_{Mn} > EF_{Cr} > EF_{Ni}$ EF_{Cu} >. For Gulf of Aqaba, EF mean values have the order of $EF_{Mn} \geq EF_{Ni} > EF_{Cr} > EF_{Cu}$. For Red Sea proper EF mean values have the order of $EF_{Ni} > EF_{Mn} > EF_{Cu} > EF_{Cr}$. The difference in EF values may be due to the difference in the magnitude of input for each metal in the sediment and/or the difference in the removal rate of each metal from the sediments. The results of the present study showed that Egyptian Red Sea coasts sediments were highly enriched in Cd and significantly enriched in Lead .These results are in harmony with El- Sikaily et al. 2005 at Gulf of Suez. Enrichment factors for Mn, Cu, Cr and Ni in most stations show anthropogenic impact of these metals.

Table 5: Heavy metals concentrations (µg/g: dry wt.) and MPI in sediments along study area 2006

St.	Fe	Mn	Zn	Pb	Cd	Cu	Cr	Ni	MPI
Gulf of Suez									
1	2300.131	82.76	51.05	47.69	3.035	4.96	6.16	8.01	27.68
2	1032.6	130.92	58.78	36.81	1.175	4.12	16.64	8.525	25.87
3	2662.4	358.77	98.88	70.37	2.015	4.21	11.33	9.405	39.57
4	2445.3	814.2	163.55	46.41	2.39	6.15	22.305	16.045	54.64
5	2915.5	182.92	22.23	51.5	3.845	5.94	22.745	16.935	39.02
6	2100.11	54.91	99.87	65.16	6.43	3.79	8.77	13.82	34.93
7	2011.05	601.6	129.81	39.37	3.115	8.44	34.115	12.155	53.53
8	4329.75	966.39	108.15	31.08	3.615	20.14	67.135	30.43	82.24
9	2811	253.23	35.22	41.56	3.715	11.61	27.815	18.265	46.75
Mean	2511.982	382.86	85.28	47.77	3.259	7.707	24.113	14.843	49.36
Gulf of Aqaba									
10	3564.2	343.81	75.84	29.46	2.285	10.57	11.77	16.29	43.44
11	3389.95	724	28.1	29.49	3.145	11.83	1.585	13.56	33.60
12	3132.5	453.15	112.62	34.74	2.705	5.08	1.78	11.635	33.48
13	2664.7	126.12	32.92	32.57	1.735	4.49	0.55	9.075	18.55
14	2449.4	169.89	72.11	29.01	2.39	4.78	1.485	12.42	25.58
15	3700.7	1095.4	35.36	32.1	2.34	16.43	17.48	15.21	51.17
Mean	3150.242	485.395	58.23	31.23	2.433	8.863	5.775	13.032	38.18
Red Sea proper									
16	1676.8	82.76	78.11	50.26	3.005	6.07	4.49	9.465	28.39
17	2237.2	130.92	30.11	10.78	2.695	5.12	7.44	12.85	24.39
18	2502.45	311.77	58.156	46.91	5.19	15.63	17.185	15.66	51.10
19	4988.65	814.2	81.9	40.11	8.135	48.87	68.22	63.35	110.93
20	1549.75	54.91	99.55	46.53	3.08	5.36	1.39	18.16	25.23
21	2781.45	182.92	99.8	53.3	6.795	8.02	13.74	12.47	47.35
22	4161.6	601.6	55.23	47.06	2.545	16.27	47.45	33.92	67.55
23	4729.75	966.39	45.01	70.37	4.735	45.8	75.305	67.035	105.93
24	3026.5	253.23	68.77	34.15	2.48	10.13	33.87	27.485	50.47
Mean	3072.683	377.633	75.04	44.38	4.296	17.919	29.899	28.933	63.29
B.G	5%	450	67	14	0.38	8	17	20	
ERL	NM	NM	150	46.7	1.2	34	81	20.9	
ERM	NM	NM	410	218	9.6	270	370	51.6	
TEL	NM	NM	124	30.2	0.68	18.7	52.3	15.5	
NOEL	NM	NM	68	21	-	28	33	-	
AET	NM	NM	340	150	-	310	2600	>140	
PEL	NM	NM	270	110	4.2	110	160	43	

Wt: weigh TEL: Threshold Effects Level, NOEL: No Observed Effects Level, ERL: Effects Range-Low, ERM: Effects Range-Median; (Long et al. 1995; Pekey 2004). AET: Apparent Effects Threshold (Saleh 2006). PEL: Probable Effect Level (Bakon and Ozkoc 2007).Bold number: (pollution effect according to ERL and ERM).

Table 6 Enrichment factors for seven heavy metals along the area of investigation during 2006

St.	EF_{Mn}	EF_{Zn}	EF_{Pb}	EF_{Cd}	EF_{Cu}	EF_{Cr}	EF_{Ni}
Gulf of Suez							
1	1.241	6.341	46.530	239.907	2.419	1.354	2.551
2	4.372	16.264	80.000	206.892	4.477	8.148	6.049
3	4.647	10.611	59.316	137.607	1.774	2.152	2.588
4	11.482	19.110	42.593	177.706	2.822	4.612	4.807
5	2.163	2.179	39.641	239.784	2.286	3.945	4.256
6	0.902	13.587	69.630	556.681	2.025	2.112	4.821
7	10.315	18.442	43.934	281.626	4.709	8.577	4.428
8	7.696	7.137	16.109	151.804	5.219	7.840	5.149
9	3.106	3.580	33.179	240.290	4.634	5.003	4.761
Mean	5.103	10.806	47.881	248.033	3.374	4.860	4.379
Gulf of Aqaba							
10	3.326	6.080	18.549	116.563	3.327	1.670	3.349
11	7.365	2.368	19.523	168.680	3.915	0.236	2.931

12	4.988	10.272	24.888	157.005	1.819	0.287	2.721
13	1.632	3.530	27.430	118.383	1.890	0.104	2.495
14	2.392	8.411	26.579	177.409	2.189	0.307	3.715
15	0.771	6.031	30.478	114.966	4.981	2.388	3.011
Mean	4.469	9.047	39.141	208.333	3.241	3.350	3.876
Red Sea proper							
16	2.692	5.131	14.428	325.837	4.061	1.354	4.136
17	4.805	7.427	47.056	219.024	2.568	1.682	4.208
18	11.219	9.351	35.970	377.085	7.008	3.472	4.585
19	0.380	5.702	20.932	296.491	10.991	6.915	9.304
20	4.070	18.399	77.183	361.349	3.880	0.454	8.585
21	7.458	5.673	37.970	444.176	3.235	2.498	3.285
22	8.007	3.090	37.947	111.190	4.386	5.765	5.972
23	1.846	4.154	16.203	182.020	10.864	8.050	10.384
24	2.885	3.325	30.813	148.987	3.755	5.659	6.654
Mean	4.590	8.309	37.842	231.070	4.071	3.569	4.731

3.1.5 Applications of PCA for assessment of metals pollution:

PCA is applied for multivariate data derived from the geochemical analysis of 24 sediments samples of the area of investigation. The data contains11 variables: Fe, Mn, Zn, Pb, Cd, Cu, Cr, Ni , TC, TOM and Si (Bakac 2000; Kumru and Bakac 2003; Loska and Wiechula 2003; Pardo et al. 2004; El- Iskandarani et al. 2004; Saleh 2006; Mil-Homens et al. 2009).

The Eigen values obtained from the PCA of the data matrix are selected with a minimum acceptable Eigen value greater than one. The output data revealed that three factors (PC1-PC3) affected on metals distribution, association and sources, with cumulative covariance of 74.95%. Varimax rotated components matrix is given in Table 7 to give an overview on the nature of loading among the parameters.

PC1, PC2 and PC3 have Eigen values of 4.4, 2.39 and 1.45 representing covariance of 40.0%, 21.746% and 13.2%, respectively. PC1 represented loading for Fe 0.877, Mn 0.772, Cu 0.973, Cr 0.848 and Ni 0.949. Most these metals are known to be associated with hydrothermal processes and probably come from the same source. This may be considered as lithogenic factor. PC2 represented loading for Pb = 0.701, total carbonate = 0.831 and a high negative loading of silicon content = -0.926. This factor mainly related to carbonate content, the positive correlation between Pb concentration and carbonate content results from Pb^{+2} makes substitution with Ca^{+2} in $CaCO_3$ since Pb and Ca have similar ionic radius. PC3 represented loading for Zn = 0.843 and organic matter = 0.881, probably due to anthropogenic factor like fertilizers industry sewage sludge and so on. The combination between Zn and TOM may be indicated that Zn organic complexes played an important role in this factor. The higher the loading value the higher the contribution of this factor.

3.1.6 Evaluation of SQI:

It is proposed as given by the following formula (Davis 1986; El- Iskandarani et al. 2004; Saleh 2006):

$$\mathbf{SQI} = (\lambda1/\Sigma\lambda)\,\mathbf{PC1} + (\lambda2/\Sigma\lambda)\,\mathbf{PC2} + (\lambda3/\Sigma\lambda)\,\mathbf{PC3}$$

For PC assessment model where λ1, λ2 and λ3 are the first, second and third largest Eigen values, Σλ sum of the Eigen values and PC1, PC2 and PC3 are the principal component scores. The values at each station given in Table (9) displaying that the highest sediment quality index are 1.19 at El-Hamrawein station probably to the presence of El-Nasr Phosphate Company and 1.1 at Marsa Alam probably due to ships activities.

Table 7: Varimax rotated component matrix (Fe, Mn, Zn, Pb, Cd, Cu, Cr, Ni, TC, TOM and Si)

Variable	PC1	PC2	PC3
Fe	0.877	-0.099	-0.114
Mn	0.772	-0.317	0.281
Zn	-0.079	0.166	0.843
Pb	0.199	0.701	0.148
Cd	0.544	0.418	0.024
Cu	0.973	-0.058	0.005
Cr	0.849	0.113	0.132
Ni	0.949	0.082	0.024
TC	-0.323	0.831	-0.209
TOM	0.141	0.12	0.749
Si	0.036	*-0.926*	-0.07
Variance	40.0	21.746	13.2
CV (%)	40.0	61.75	74.95

PC: Principal Component, TC: total carbonate, TOM: total organic matter, Si: silicon content, CV: cumulative variance: [TC: total carbonate and TOM: total organic matter (Cited from Shredeah et al. 2008)]. Bold numbers indicate positive correlation; negative italic values indicate negative correlation.

3.1.7 Evaluation of Hot Spots:

Principal component scores corresponding to each station must be evaluated in Table (8). Where the high values pointed to that this station is from hot spots. The corresponding concentrations of metals and organic matter must emphasize the evaluated results from Table (9). According to PCA data, Kabanon Beach, NIOF, Ain Sukhna (SUMED), Ain Sukhna (Porto Hotel), Ras Shukeir, El Hamrawein, Movenpick, Qusier Middle and Marsa Alam could be considered as hot spots.

Table 8: Principal component factor scores and sediment quality index (SQI) of sediments in Gulf of Suez, Gulf of Aqaba and Red Sea proper

Name	PC1	PC 2	PC 3	SQI
1- Port Tawfiq	-0.74	0.94	0.37	-0.04
2- Rex Beach	-0.97	-1.02	-0.25	-0.64
3- Kabanon Beach	-0.56	1.13	1.19	0.18
4- Suez Middle (NIOF)	-0.30	-0.05	1.87	0.12
5- Ain Sukhna (SUMED)	-0.19	1.57	-1.51	0.06
6- Ain Sukhna Porto Hotel	-0.49	2.05	0.03	0.25
7- Ras Gharib	-0.26	-0.65	2.84	0.13
8- Ras Shukeir	1.11	0.62	0.58	0.66
9- El- Tur	0.03	0.12	-1.03	-0.10
10- Ras Mohamed	-0.15	-1.04	-0.13	-0.30
11- Marina Sharm	-0.02	-0.88	-0.81	-0.30
12- Sharm El-Sheikh (Nama Bay)	-0.46	-1.08	0.42	-0.36
13-Dahab	-0.75	-0.25	-1.01	-0.49
14- Nuweiba Harbor (El-Saideen)	-0.70	-1.35	-0.23	-0.60
15-Taba	0.45	-1.72	-0.18	-0.22
16- Hurghada (Sheraton Hotel)	-0.81	0.06	0.10	-0.30
17- Safaga North (Suma Bay)	-0.71	-1.00	-1.08	-0.64
18- Safaga Middle	0.08	-0.19	-0.65	-0.09
19- El Hamarawein	2.78	-0.29	1.05	1.19
20- Movenpick	-0.88	1.13	0.47	-0.04
21- Qusier Middle	-0.13	1.12	-0.23	0.16
22- Qusier South	0.88	-0.37	-0.67	0.18
23- Marsa Alam	2.75	0.49	-0.78	1.10
24- Bir Shalatin	0.01	0.65	-0.38	0.09

PC1, PC 2 and PC 3: principal component factor scores, SQI: sediment quality index, Bold number: high effect of factor scores.

Table 9: Evaluation of Hot Spots in the Area of Investigation based on factor scores calculations.

Hot Spots	Name	PC1	PC 2	PC 3	Parameters
1	Kabanon Beach	-0.56	1.13	1.19	PC2 (Pb: 70.37), TC: 54.00%) and PC3 Zn: 98.88), (TOM: 1.96)
2	NIOF	-0.30	-0.05	1.87	PC3(Zn :163.55),(TOM: 0.71).
3	Ain Sukhna (SUMED)	-0.19	1.57	-1.51	PC2 (TC: 60%)and (Pb: 51.5)
4	Ain Sukhna Porto Hotel	-0.49	2.05	0.03	PC2 (TC: 66% and Pb: 65.16)
5	Ras Shukeir	1.11	0.62	0.58	PC1(Fe: 4329.75),(Mn: 966.39), (Cu:20.14),(Cr:67.135) and Ni (30:43).
6	El Hamrawein	2.78	-0.29	1.05	PC1(Fe: 4988.65),(Mn: 814.2), (Cu:48.87),(Cr:68.22) and Ni (63.35).PC3 (Zn: 81.9), (TOM: 2.67)
7	Movenpick	0.20	-0.88	1.13	PC3 (TOM: 1.17) and (Zn: 99.55).
8	Qusier Middle	-0.13	1.12	-0.23	PC2(Pb: 53.3) and (TC: 38.00)
9	Marsa Alam	2.75	0.49	-0.78	PC1 (Fe: 4729.75.), (Mn: 966.39), (Cu: 45.8), (Cr: 75.3) and(Ni : 67.0)

3.2 Speciation of Lead and Cadmium:

Pb is oxidized by the joint action of oxygen and water to give Pb (II).

The metal dissolves as follow:

$Pb_{(s)} \rightarrow Pb^{2+}_{(aq)} + 2e^-$

The electrons are consumed in the reaction:

$$\frac{1}{2} O_{2\,(aq)} + H_2O + 2e^- \rightarrow 2OH^-_{(aq)}$$

Pb (II) salts in general have low water solubility and can act as protective layers.

Lead has a tendency to form compounds with anions having low solubility, such as hydroxides, carbonates, and phosphate. The amount of pb remaining in solution of surface waters (also dependent on pH and salinity) is often low. In soils and sediments, the fate of Pb is affected by different chemical processes. Cd is a nonconservative element, exchanges between particulate and dissolved phases must be taken into account for studying Cd in the environment. Cd is an oxyphilic element; it undergoes multiple hydrolysis at pH values encountered in the environment.

Speciation of Pb and Cd given in Table (10) is achieved by applying scheme I, however, Table (11) by applying scheme II. The fractionation pattern of Pb was different in Gulf of Suez than from both Gulf of Aqaba and Red Sea proper, The difference was that for Gulf of Suez Pb content in the non-residual fractions was more than in the residual one, indicating that in Gulf of Suez Pb has anthropogenic origin due to man activities in this region such as oil refineries in Suez City, Ain Sukhna houses the oil terminal for SUMED pipeline for transmission of oil across the Mediterranean Sea. In addition, the most extensive oil fields activity in Egypt are centered at Ras Gharib and Ras Shukheir, which comprise the Gulf of Suez Petroleum Company (GUPCO) facility and offshore oil production platforms. Many stations do not have Pb in the organic fraction. High % of Pb in the exchangeable fraction was recorded in most stations indicating that Pb has anthropogenic origin via human activities Tables (10 and 11).

High % of Cd was recorded as Fe and Mn oxides fraction. The relatively high content of Cd bounds to Fe and Mn oxides fraction is in agreement with that recorded (Garcia-Miragya and Page 1978; Szakova et al. 1999) they reported that Fe oxides have a higher affinity for trace amounts of Cd than clay layer silicate, particularly at pH levels between 6 and 7. While, hydrous Fe oxides are typically more abundant in soils than those of Mn (Alloway 1995).

The recoveries for each scheme are given in Table (12). Mean recoveries values recorded 89.32%, 87.51% and 90.96% for Pb and 95.33%, 98.41% and 104.13% for Cd in Gulf of Suez, Gulf of Aqaba and the Red Sea proper, respectively. However, on applying scheme II the mean recoveries values for Pb recorded 113.0%, 115.66% and 114.6 for Pb and 113.92%, 111.41% and 108.0% for Cd in Gulf of Suez, Gulf of Aqaba and Red Sea proper, respectively. From such data, scheme I is fairly recommended for discussing Pb and Cd speciation.

3.2.1 Comparison of Pb and Cd fractionation patterns between the areas of investigation with other worldwide records:

Table (14) indicated that the most abundant fraction of Pb was the oxide form (Fe and Mn oxide), and clearly recorded in Gulf of Suez area with 47.63% of the total Pb. However in both Gulf of Aqaba and Red Sea proper, the most dominant was the residual fraction with 55.33% and 51.36% of total Pb. This indicated that Gulf of Suez area is subjected to heavy industrial activities especially SUMED pipelines, Oil fields (centered at Ras Gharib and Ras Shukeir) in addition to oil refiners located at the northern part at Gulf of Suez. Comparing the results of the present study with the previously recorded in the same area, the residual fraction was the most dominant (Hamed 2004). Data recorded during 2003-2006, indicated that Gulf of Suez was suffering from increasing industrial activities.

On the other hand Abd El-Azim and Moselhy (2005) reported that for Suez Canal the oxide form was the most abundant during 1998 with 49.2% of total Pb. Okbah et al. (2005) recorded high Pb% at carbonate with 30% of the total Pb for mangrove sediments collected from Red Sea. Abu Kir Bay and Western Harbour areas were investigated by Mahmoud 1994 and Ahdy 1999. They reported that high Pb% was at residual fraction with 51.2% and 45.99%, respectively. Saad and Ahdy (2006) recorded high Pb% at oxide fraction with 46.79% of the Pb content for Brackish water (Lake Mariut). While Saleh (2006) recorded high Pb% at residual fraction with 56.89% of total Pb for Arabian area, Aden Gulf.

Table (14) represented that the most abundant fraction of Cd was the oxide fraction (Fe and Mn oxide), and recorded 30.2% of total Cd in Gulf of Suez area. However, in both Gulf of Aqaba and Red Sea proper, the most abundant fractions were residual and oxide with 30.22 % and 27% for Gulf of Aqaba and 37.90% and 23.35 % of total Pb for Red Sea proper. However for different stations in Red Sea area, during 2003, the major Cd component was represented as carbonate and oxide fractions (Hamed 2004). This indicated that Gulf of Suez area is subjected to heavy industrial activities especially SUMED pipelines, oil fields (centered at Ras Gharib and Ras Shukeir) in addition to oil refiners located at the northern part at Gulf of Suez.

On the other side Abd El-Azim and Moselhy (2005) reported that for Suez Canal, during 1998 high Cd% was found as a residual fraction with 43.1% of total Cd. Okbah et al. (2005) recorded high Cd % for Red Sea (mangrove sediment), as carbonate with 34.5% of total Cd. Abu Kir Bay and El Mex Bay recorded high Cd % as carbonate with 100% (Ahdy 1999) and oxide with 39% (Abdallah 2007). For Lake Mariut (Brackish water), high Cd % was found as carbonate 54% (Saad and Ahdy 2005). As a literary concept published data given in Table (14) showed that Pb and Cd had different fractionation patterns depended on the nature of the region (Tessier et al. 1979; Giordano et al. 1992; Marin et al. 1997; Takarina et al. 2004; Cuong and Obbard 2006; Zemberyova et al. 2006; Arias et al 2008).

3.2.2 Risk Assessment Code (RAC):

This classification is based on the strength of the bond between metals and the different geochemical fractions in sediments or soils and the ability of metals to be released and enter into the food chain. Although the

RAC does not take into account the total metal concentration, this code may be useful to assess the environmental risk using sequential extraction as a characterization method (Rodrıguez et al. 2009). Risk Assessment Code (RAC) assesses the availability of metals in solution by applying a scale of the relative percentages in the exchangeable and carbonates fractions (%Σ F1 +F2). This classification is 1-10% (low risk), 11-30% (medium risk), 31-50% (high risk) and >50% (very huge risk) (Singh et al. 2005).

Risk Assessment Code (%Σ F1 +F2) for Fe, Mn and Zn in study area are given in Table (13). The data revealed that RAC were within high risk for Cd in stations (1, 4, 15 and 19) Port Tawfiq, NIOF, Taba and El-Hamrawein, respectively and very huge risk at Rex Beach. For Pb was within huge risk at Rex Beach and were within high risk in stations (9, 10, 13, 14 and 16), El-Tur, Ras Mohamed, Dahab, Nuweiba Harbour and Hurghada, respectively. For Zn and Mn, RAC recorded high values at NIOF and Rex Beach stations.

Table 10: Distribution of different fractions of Pb and Cd (µg/g: dry wt.) applying scheme I

St.	F1%		F2%		F3%		F4%		F5%	
	Pb	Cd	Pb	Cd	Pb	Cd	Pb	Cd	Pb	Cd
Gulf of Suez										
1	5.01	16.30	18.56	14.04	52.18	45.38	14.06	2.04	10.18	22.24
2	31.79	25.18	29.21	41.20	6.02	0.86	16.05	17.79	16.93	14.97
3	9.55	10.87	13.32	15.06	56.94	60.80	2.32	8.45	17.86	4.82
4	9.47	21.07	16.21	15.34	63.59	31.34	7.93	3.97	2.81	28.28
5	5.33	6.04	16.18	13.33	68.42	57.40	5.24	16.52	4.82	6.71
6	12.04	13.11	8.78	2.03	55.63	17.64	8.45	11.51	15.11	55.71
7	5.36	6.93	16.99	4.25	30.96	16.66	5.54	28.81	41.16	43.34
8	5.17	5.64	9.72	8.62	57.99	56.89	2.89	20.80	24.22	8.05
9	14.39	4.96	25.83	9.33	36.97	49.76	N.D	17.55	22.81	18.41
Mean	10.9	12.23	17.2	13.69	47.63	37.41	7.81	14.16	17.32	22.50
Gulf of Aqaba										
10	15.13	5.89	18.5	9.13	9.83	52.77	3.01	8.12	53.69	24.10
11	8.35	5.95	18.21	6.00	28.81	58.11	1.56	10.19	43.19	19.75
12	11.32	7.49	12.91	9.15	6.21	31.71	N.D	23.87	69.57	27.77
13	7.67	11.42	22.38	8.54	34.91	20.08	N.D	27.16	35.04	32.79
14	14.22	20.88	23.16	5.14	6.42	16.66	N.D	36.74	56.19	20.58
15	18.95	35.04	1.48	0.66	9.54	18.98	N.D	16.76	70.02	28.56
Mean	12.61	14.45	16.11	6.44	15.95	33.05	2.29	20.47	54.62	25.59
Red Sea proper										
16	10.57	3.87	24.84	14.45	17.58	28.06	10.11	8.00	36.9	45.63
17	8.42	13.14	14.45	0.71	20.17	11.22	7.2	47.34	49.76	27.60
18	1.89	4.17	4.85	7.86	2.47	47.60	0.95	10.57	89.84	29.80
19	4.51	0.95	1.94	37.43	3.12	1.02	N.D	15.28	90.42	45.32
20	16.88	5.97	11.47	0.02	66.55	28.80	N.D	16.27	5.11	48.94
21	5.17	4.77	10.04	6.36	50.27	38.43	N.D	30.42	34.52	20.02
22	7.42	7.61	17.42	3.83	13.56	13.27	N.D	32.13	61.6	43.16
23	10.96	0.45	1.21	0.72	7.01	4.63	N.D	11.50	80.82	82.70
24	8.76	17.43	17.73	8.72	60.27	28.95	N.D	33.29	13.25	11.60
Mean	8.29	6.48	11.55	8.90	26.78	22.44	6.09	22.76	51.36	39.42

Wt: weigh, St: Station, F1: Exchangeable, F2: Carbonates, F3: Fe and Mn oxides, F4: Organic matter and F5: Residual. Scheme I was performed based on Tessier et al. 1979 as modified by Ajay and Van Loon 1989: Yong and Phandungchewit 1993).

Table 11: Distribution of different fractions of Pb and Cd (µg/g: dry wt.) applying scheme II

St.	F1%		F2%		F3%		F4%		F5%		F6%		F7%	
	Pb	Cd	Pb	Cd	Pb	Cd	Pb	Cd	Pb	Cd	Pb	Cd	Pb	Cd
Gulf of Suez														
1	5.76	19.03	17.81	7.58	17.17	24.12	10.97	4.61	N.D	11.36	37.42	7.58	10.87	25.73
2	8.65	10.91	18.43	16.74	8.48	20.51	23.57	1.23	N.D	5.35	1.39	19.20	39.48	26.06
3	15.51	22.12	4.88	33.55	24.51	12.60	34.07	2.18	N.D	5.54	12.33	12.49	8.71	11.51
4	2.70	11.22	8.55	30.84	7.81	32.62	36.49	8.47	N.D	3.63	39.06	11.34	5.39	1.89
5	3.70	21.04	20.82	8.14	10.21	19.47	19.02	13.0	N.D	26.24	3.07	5.59	43.18	6.53
6	6.60	11.70	7.11	17.72	4.88	17.72	48.84	10.98	N.D	19.25	21.43	6.86	11.15	15.77
7	5.74	7.60	16.96	8.15	13.59	33.14	33.26	9.50	N.D	19.44	3.41	0.51	27.04	21.66
8	6.87	9.19	12.09	6.84	9.93	18.79	32.95	11.45	N.D	27.08	15.56	12.16	22.60	14.49
9	6.61	9.12	35.69	13.46	0.63	23.46	23.66	13.98	N.D	20.97	11.29	0.35	22.13	18.67
Mean	6.90	13.55	15.82	15.89	10.80	22.49	29.20	8.38		15.43	16.11	8.45	21.17	15.81
Gulf of Aqaba														
10	21.88	16.44	17.47	1.12	3.07	13.10	9.92	20.02	N.D	10.12	3.32	11.80	44.34	27.40
11	2.30	15.48	7.14	28.23	N.D	12.78	8.15	15.73	N.D	10.32	15.63	3.23	66.78	14.22
12	16.57	26.20	7.95	19.63	N.D	7.44	18.13	2.47	N.D	21.17	19.88	2.72	37.47	20.37
13	3.10	27.89	19.43	24.91	N.D	6.89	8.84	11.92	N.D	4.50	36.85	3.20	31.78	20.68
14	9.19	17.38	3.28	10.66	N.D	7.98	ND	27.88	N.D	0.92	14.73	2.02	72.80	33.17

15	4.59	8.85	4.03	26.30	N.D	5.49	9.40	15.24	N.D	16.47	20.22	13.11	61.76	14.54
Mean	9.60	18.71	9.89	18.48	3.07	8.95	10.89	15.54		10.58	18.44	6.01	52.49	21.73
Red Sea proper														
16	10.41	14.59	22.51	1.43	2.12	31.63	7.60	2.11	N.D	26.02	N.D	4.71	57.35	19.52
17	11.33	4.70	28.02	23.62	3.19	10.94	3.40	7.07	N.D	30.40	N.D	4.67	54.06	34.63
18	5.31	11.02	10.48	10.79	9.43	10.28	16.72	17.25	N.D	17.39	5.86	16.58	52.20	16.69
19	3.21	10.66	4.83	18.85	2.86	7.05	4.83	9.46	N.D	16.4	23.62	18.56	60.66	18.96
20	8.57	8.84	24.81	19.19	3.26	10.91	10.17	18.96	N.D	12.06	6.54	11.54	46.64	18.50
21	8.84	15.09	29.29	3.53	9.23	25.66	6.68	23.61	N.D	15.56	15.45	2.21	30.52	14.34
22	10.24	16.98	17.73	33.50	4.95	6.30	6.95	22.94	N.D	5.09	19.64	9.12	40.48	6.08
23	4.32	6.7	10.74	38.99	10.23	7.14	1.77	3.21	N.D	0.41	2.56	12.34	70.39	31.17
24	7.75	19.19	16.92	15.88	9.36	27.95	3.79	13.52	N.D	2.03	20.31	6.82	41.87	14.60
Mean	7.78	11.98	18.37	18.42	6.07	15.32	6.88	13.13		13.94	13.43	9.62	50.46	19.65

Wt: weigh, St: Station, F1: Soluble-exchangeable F2: Surface adsorbed, F3: Organic matter, F4: Mn oxides, F5: Poor crystalline Fe oxides, F6: Crystalline Fe oxides and F7: Residual. Scheme II was performed according to Silveira et al.2006

Table 12: Comparison of recoveries for speciation of Pb and Cd applying schemes I and II.

	Recovery of scheme I		Recovery of scheme II	
St.	Pb	Cd	Pb	Cd
Gulf of Suez				
1	110.69	109.65	117.86	124.09
2	78.62	99.49	113.70	127.20
3	114.93	108.09	101.87	110.71
4	92.44	96.90	131.86	85.64
5	90.24	73.68	106.30	85.30
6	88.93	106.50	95.25	100.06
7	78.28	105.17	121.00	116.46
8	74.48	107.97	98.46	124.01
9	75.29	87.74	130.69	108.65
Mean	89.32	99.47	113.00	124.60
Gulf of Aqaba				
10	88.55	103.50	121.81	90.56
11	90.24	111.08	114.04	119.78
12	100.41	89.19	121.62	129.57
13	92.69	99.31	96.20	99.67
14	74.93	83.35	128.25	104.32
15	78.24	104.02	112.04	111.41
Mean	87.51	98.41	115.66	107.42
Red Sea proper				
16	76.40	103.19	122.47	101.78
17	105.83	84.04	107.18	109.67
18	124.64	102.81	79.74	110.22
19	115.94	115.82	98.67	119.35
20	71.77	110.38	124.06	117.69
21	88.33	104.58	113.42	103.46
22	77.91	98.66	130.44	132.80
23	79.08	98.44	130.55	122.90
24	78.72	79.92	124.92	113.92
Mean	90.96	99.76	114.61	104.38

Table 13: Risk Assessment Code (RAC) (%Σ F1 +F2) for Pb and Cd applying scheme I.

Station	% Pb	%Cd
Gulf of Suez		
1	3.58	30.34
2	61.00	66.38
3	22.87	25.93
4	25.68	36.40
5	21.52	19.37
6	20.81	15.14
7	22.35	11.18
8	14.89	14.26
9	40.22	14.29
Mean	28.10	20.74
Gulf of Aqaba		
10	33.63	15.02
11	26.56	11.95
12	24.22	16.64
13	30.05	19.96

14	37.38	26.02
15	20.44	35.70
Mean	28.71	20.14
Red Sea proper		
16	35.41	18.32
17	22.87	13.85
18	6.74	12.03
19	6.46	38.38
20	28.34	5.99
21	15.21	11.13
22	24.84	15.99
23	12.17	1.17
24	26.48	26.15
Mean	19.84	16.67

Table 14 Comparison of Pb and Cd fractionation patterns between the areas of investigation with other worldwide records

Region	F1 (%)		F2 (%)		F3 (%)		F4 (%)		F5 (%)		References
	Pb	Cd	Pb	Cd	Pb	Cd	Pb	Cd	Pb	Cd	
Gulf of Suez	10.9	12.23	17.2	13.69	47.63	37.41	7.81	14.16	17.32	22.50	Present study
Ain Sukhna (SUMED)	5..33	6.04	16.18	13.33	68.4	57.4	5.24	16.52	4.82	6.71	
Ras Gharib	5.4	6.93	16.99	4.25	30.9	16.66	5.54	28.81	41.2	43.34	
Ras Shukeir	5.17	5.64	9.72	8.62	57.99	56.89	2.89	20.8	24.22	8.05	
El-Tur	14.39	4.96	25.83	9.33	36.97	49.76	<DL	17.55	22.81	18.41	
Gulf of Aqaba	12.61	14.45	16.11	6.44	15.95	33.05	2.33	20.47	55.33	15.59	
Ras Mohamed	15.13	5.89	18.5	9.13	9.83	52.77	3.01	8.12	56.54	24.1	
Red Sea proper	8.29	6.48	11.55	8..90	26.78	22.44	6.09	22.76	51.36	39.42	
Gulf of Suez Ain Sukhna	2.15	-	3.07	57.05	9.51	14.09	18.84	28.86	66.43	-	Hamed (2004)
Ras Gharib	1.59	-	3.85	17.59	3.09	58.33	8.32	13.89	83.15	10.18	
Ras Shukeir	0.55	-	1.21	22.93	8.35	66.92	17.71	10.15	68.26	-	
Adabiya port	28.8	3.6	67.8	5.0	3.39	3.7	<DL	4.2	<DL	83.3	Said and Hamed (2001)
Ras Shukeir	<DL	<DL	91.5	<DL	8.5	<DL	<DL	<DL	<DL	<DL	
El-Tur	22.3	<DL	77.7	<DL	<DL	<DL	<DL	<DL	<DL	<DL	
Ras Mohamed	1.48	-	7.9	45.78	2.45	54.22	13.86	-	74.31	-	Hamed (2004)
Suez Canal	1.45	1.95	10.7	11	49.2	31.9	7.33	11.9	31.2	43.1	Abd-El-Azim and El- Moselhy(2005)
Red Sea (mangrove sediment)	7	14.07	30	34.5	17.5	27.26	21.5	12.3	23	11.85	Okbah et al. (2005)
Aden Gulf	14.11	NR	7.19	NR	13.24	NR	9.56	NR	56.89	NR	Saleh (2006)
Lake Mariut	0.87	0.9	11.88	54.0	46.79	28.5	14.72	28.5	22.74	7.7	Saad and Ahdy (2006)
Abu Qir Bay	0.86	-	7.07	100	26.7	-	19.38	-	45.99	-	Ahdy (1999)
Western Harbour	0.9	NR	4.43	NR	27.98	NR	14.49	NR	51.2	NR	Mahmoud (1994)
The Nervion estuary (Bilbao, North Spain) upper layer	Sum (Pb) =2.89				2	NR	85	NR	15	NR	Arias et al 2008
Singapore Kranji	Sum (Pb) =5 Sum (Cd) =31.3				33.8	-	1.2	16.7	60	18.8	Cuong and Obbard (2006)
Soil reference material from Slovakia S-SP	Sum (Pb) =0.52 Sum (Cd)=30				68.99	60	4.09	6	26.47	4	Zemberyova et al. (2006)
Coastal area of Semarang, Indonesia	Sum (Pb) =3 to 22				40	NR	20	NR	35 to70	NR	Takarina et al. (2004)
Chesapeake Bay France	Sum (Pb) =5.5 Sum (Cd)= 68.8				31.8	6.1	4.5	4.7	56.6	9.5	Marin et al.(1997)
Canada Saint –Marcel	<DL	<DL	15.4	<DL	22.49	<DL	15.98	<DL	46.15	<DL	Tessier et al. (1979)

F1: Exchangeable, F2: Carbonates, F3: Fe and Mn oxides, F4: Organic matter and F5: Residual. NR; Not Recorded and DL: Detection limit

Application of principal component for speciation of Pb and Cd:

The output data revealed that four factors (PC1-PC4) affected Pb speciation with cumulative covariance of 85.6% could be evaluated individually Table (15) gave an overview on the nature of loading among different parameters. PC1, PC2, PC3 and PC4 have covariance % of 31.6, 20.56, 16.84 and 16.58, respectively. PC1 represented loading for the oxide fraction 0.940, probably due to the anthropogenic impact of Mn is in the oxide form, total carbonate in the sediment 0.965 and high negative factor loading with silicon content -0.957. PC2 represented loading for WC = 0.98 and P = 0.871. PC3 represented loading for residual fraction = 0.904 and total = 0.924, this leads to as concentration of zinc increases it will be concentrated in the residual fraction. PC4 represented loading for total organic matter in the sediment = 0.886 and moderately loading for Pb as carbonate fraction = 0.661. The higher the value of the loading the higher the effect on Pb speciation.

Four factors (PC1-PC4) also affected Cd speciation with cumulative covariance of 85.6%. PC1, PC2, PC3 and PC4 have covariance % of 31.6, 20.56, 16.84 and 16.59, respectively. PC1 represented loading for WC = 0.86, P = 0.854 and total carbonate in the sediment TC = 0.782, high negative loading for silicon content = -0.772. PC2 represented loading for Cd as organic fraction = 0.811, residual fraction = 0.852 and total = 0.932. PC3 represented loading for total organic matter in the sediment = 0.857. PC4 has loading for Cd as exchangeable fraction. This factor may be attributed to anthropogenic impact. The higher the value of loading the higher the effect on Cd speciation

Table 15: Varimax rotated component matrix for speciation of Pb and Cd

Variable	PC1		PC2		PC3		PC4	
	Pb	Cd	Pb	Cd	Pb	Cd	Pb	Cd
Exchangeable fraction	0.499	0.073	-0.091	-0.009	-0.391	0.032	-0.045	0.802
Carbonate fraction	0.336	-0.060	0.571	0.570	0.122	0.481	0.616	-0.410
Mn and Fe Oxide fraction	0.940	0.651	0.111	0.158	0.009	-0.146	0.179	0.293
Organic fraction	0.409	0.018	0.169	0.811	-0.003	-0.199	0.647	-0.187
Residual	-0.393	-0.077	-0.155	0.852	0.871	0.231	-0.145	0.175
Total	0.306	0.154	-0.015	0.932	0.924	0.225	0.097	0.116
WC	-0.058	0.860	0.980	-0.162	-0.046	0.268	0.103	-0.299
P	-0.009	0.854	0.975	-0.153	-0.058	0.256	0.111	-0.238
TC	0.965	0.782	-0.045	0.022	-0.035	-0.053	0.178	0.455
TOM	0.037	0.172	0.084	0.223	-0.030	0.857	0.886	-0.002
Si	*-0.957*	*-0.772*	-0.008	-0.179	-0.102	0.088	-0.153	-0.285
Mean size	0.532	0.639	0.382	0.045	0.471	*-0.616*	-0.514	-0.114
Variance	31.633	31.633	20.562	20.562	16.836	16.836	16.586	16.586
CV(%)	31.633	31.633	52.195	52.195	69.031	69.031	85.616	85.616

PC: principal component; [WC: water content; P: porosity;TC: total carbonate; TOM: total organic matter;
Si: silicon content (Cited from Shereadah et al.)] CV: cumulative variance; whereas bold number indicate positive correlation and –ve italic values indicate negative correlation.

Conclusion:

The results of the present study cleared out that the sediment of the Egyptian Red Sea coasts were highly enriched with Cd and significantly enriched with lead. Enrichment factors for Mn, Cu, Cr and Ni in most stations revealed anthropogenic impact of these metals. Application of PCA analysis revealed that Kabanon Beach; Ain Sukhna (SUMED); Ain Sukhna Porto Hotel; Ras Shukeir; El Hamarawein; Movenpick; Qusier Middle and Marsa Alam could be considered as hot spots.

Scheme I is fairly recommended for Pb and Cd speciation The geographical distribution of the factor scores at individual stations define where sediment is affected by heavy metals, total carbonate, organic matter and silicon content. According to principal component analysis data for metal speciation for Pb and Cd total organic matter played an important role in fractionation pattern.

REFERENCES

Abd El-Azim, H. and Kh.M. El-Moselhy, 2005. Determination and Partitioning of Metals in Sediments along the Suez Canal by Sequential Extraction. Journal of Marine Systems, 56: 363-374.

Ahdy, H.H., 1999. Dynamics of cadmium and lead in Abu-Qir Bay and their effects on marine organisms, Ph.D. Thesis, Faculty of Science, Alexandria University, Egypt, pp: 555.

Ajay, S.O. and G.W. Van loon, 1989. Studies on redistribution during the analytical fractionation of metals in sediments. The Science of the Total Environment., 87/88: 171-187.

Arias, R., A. Barona, G. Ibarra-Berastegi, I. Aranguiz and A. Elıas, 2008. Assessment of metal contamination in dredged sediments using fractionation and Self-Organizing Maps, Journal of Hazardous Materials, 151: 78-85.

Bakac, M., 2000. Factor analysis applied to a geochemical study of suspended sediments from the Gediz River, western Turkey. Environmental Geochemistry Health, 22: 93-111.

Bakon, G. and H.B. Ozkoc, 2007. An ecological risk assessment of the impact of heavy metals in surface sediments on biota from mild-Black Sea coasts of Turkey. International Journal of Environmental studies, 64(1): 45-57.

Baptista, N.J.A., B.J. Smith and J.J. McAllister, 2000. Heavy metals concentrations in surface sediments in a near shore environment, Jurujuba Sound, Southeast Brazil. Environmental Pollution., 109: 1-9.

Bruland, K.W., 1980. Oceanic distributions of cadmium, zinc, nickel and cupper in the North Pacific. Earth Planet Lett, 47: 176.

Cuong, D.T. and J.P. Obbard, 2006. Metal speciation in coastal marine sediments from Singapore using a modified BCR-sequential extraction procedure, Applied Geochemistry, 21: 1335-1346.

Davis, J.C., 1986. Statistics and Data Analysis in Geology. John Wiley & Sons. Inc., New York.

El-Iskandarani, M., S. Naser, M. Okaba and A. Jensen, 2004. Principal component analysis for quality assessment of the Mediterranean costal water of Egypt. Association for the advancement of modeling and stimulation Techniques in Enterprises (AMSE), Modeling C-2004 65(2): 69-83.

El-Sikaily, A., A. Khaled and A. El-Nemr, 2005. Leachable and total nine heavy metals in muddy and sandy sediment collected from Gulf of Suez. Egyptian Journal of Aquatic Research, 31: 99-119.

Ergin, M., C. Saydam, O. Basturk, E. Erdem and R. Yoruk, 1991. Heavy metal concentrations in surface sediments from the two coastal inlets (Golden Horn Estuary and Izmit Bay) of the Northeastern Sea of Marmara. Chemical Geology, 91: 269-285.

Fifield, F.W. and P.J. Haines, 2000. Environmental analytical chemistry, 2nd edition Blackwell Science Ltd., Cambridge, pp: 363.

Ford, R.G., A.C. Scheinost and D.L. Sparks, 2001. Frontiers in metal sorption/ precipitation mechanisms on soil mineral surfaces. Advanced Agronomy, 74: 41-62.

Giordano, R., L. Musmeci, L. Claralli, I. Vernillo, M.C hirico, A. Piccioni and S. Costantini, 1992. Total Contents and Sequential Extractions of Mercury, Cadmium, and Lead in Coastal Sediments. Marine Pollution Bulletin, 24: 350-357.

Hamed, M.A., 2004. Chemical Forms of Copper, Zinc and Cadmium in Sediments of the Northern Part of the Red Sea Egypt. Egyptian Journal of Aquatic Research, 30(A): 1-10.

Han, F.X., A. Banin and G.B. Triplett, 2001. Redistribution of heavy metals in arid-zone soils under a wetting drying cycle soil moisture regime. Soil Science, 166: 18-28.

Jin, C.W., S.J. Zheng, Y.F. He, G.D.Z hou and Z.X. Zhou, 2005. Lead contamination in tea garden soils and factors affecting its bioavailability. Chemosphere, 59: 1151-1159.

Liaghati, T., M. Preda and M. Cox, 2003. Heavy metal distribution and controlling factors within coastal plain sediments, Bells Creek catchments, southeast Queensland, Australia. Environment International., 29: 935-948.

Liu, C.W., K.H. Lin and Y.M. Kuo, 2003. Application of factor analysis in the assessment of groundwater quality in a Blackfoot disease area in Taiwan. The Science of the Total Environment., 313: 77-89.

Long, E.R., D.D. MacDonald, S.L. Smith and F.D. Calder, 1995. Incidences of adverse biological effects within ranges of chemical concentrations in marine and estuarine sediments. Environmental Management., 19: 81-97.

Long, Y.Y., L.F. Hu, C.R. Fang, Y.Y. Wu and D.S. Shen, 2009. An evaluation of the modified BCR sequential extraction procedure to assess the potential mobility of copper and zinc in MSW Microchemical Journal., 91: 1-5.

Loska, K. and D. Wiechula, 2003. Application of principal component analysis for the estimation of source of heavy metal contamination in surface sediments from the Rybnike Reservoir. Chemosphere., 51: 723-733.

Mahmoud, W.M.A., 1994. Chemical Investigations on Lead in the Western Harbour of Alexandria. M Sc. thesis, Faculty of Science Alexandria University, Egypt, pp: 223.

Marin, B., M. Valladon, M. Polve and A. Monaco, 1997. Reproducibility testing of sequential extraction scheme for the determination of trace metal speciation in a marine reference sediment by inductively coupled plasma- mass spectrometry. Analytica Chimica Acta, 342: 91-112.

Masoud, M.S., M. EL-Samra and M.M. EL-Sadawy, 2007. Heavy-metal distribution and risk assessment of sediment and fish from El-Mex Bay, Alexandria, Egypt Chemistry and Ecology, 23(3): 201-216.

Meherm, M., 2002. Assessment of the state of pollution by Antifouling paints in marine Environment of Alexandria coastal Region. Ph.D. in Maritime transport technology (Environmental protection), Arab Academy for Science and Technology and Maritime transport, pp: 125.

Mil-Homens, M., V. Branco, C. Lopes, C. Vale, F. Abrantes, W. Boer and M. Vicente, 2009. Using Factor Analysis to Characterize Historical Trends of Trace Metal Contamination in a Sediment Core from the Tagus Prodelta, Water Air Soil Pollution., 197: 277-287.

Mucha, A.P., M.T.S.D. Vasconcelos and A.A. Bordalo, 2003. Macrobenthic community in the Doura estuary: relations with trace metals and natural sediment characteristics. Environmental Pollution., 121: 169-180.

Nriagu, J.O., 1990. Global metal pollution. Poisoning the biosphere Environment Nature., 32(7): 7-33.

Okbah, M.A., M.A. Shata and M.A. Shreadah, 2005. Geochemical forms of trace metals in mangrove sediments- Red Sea (Egypt). Chemistry and Ecology, 21(1): 23-36.

Pardo, R., B.A. Helenab, C. Cazurroa, C. Guerrab, L. Debana, C.M. Guerrab and M. Vegaa, 2004. Application of two- and three-way principal component analysis to the Interpretation of chemical fractionation results obtained by the use of the B.C.R. procedure. Analytica Chimica Acta, 523: 125-132.

Powell, K.J., P.L. Brown, R.H. Byrne, T. Gajda, G. Hefter, S. Sjoberg and H. Wanner, 2005. Chemical speciation of environmentally significant heavy metals with inorganic ligands. Part I: The Hg^{2+}, $C1^{-}$ ، OH^{-} , CO_3^{2-} , SO_4^{2-}, and PO_4^{3-} aqueous systems Pure Applied Chemistry, 77: 739-800.

Rodrıguez, L., E. Ruiz, J. Alonso-Azcarate and J. Rincon, 2009. Heavy metal distribution and chemical speciation in tailings and soils around a Pb–Zn mine in Spain. Journal of Environmental Management., 90: 1106-1116.

Ruiz, F., M.L. Gonzalez-Regalado, J. Borrego, J.A. Morales, J.G. Pendon and J.M. Munoz, 1998. Stratigraphic sequence, elemental concentrations and heavy metal pollution in Holocence sediments from the Tinto-Odiel estuary, Southwestern Spain. Environmental Geology, 34: 270-278.

Rutten, A. and G.J. De Lange, 2003. Sequential extraction of iron, manganese and related elements in S1 sapropel sediments, eastern Mediterranean. Paleogeography, Palaeoclimatology, Paleoecology, 190: 79-101.

Saad, M.A.H. and H.H. Ahdy, 2006. Speciation of Heavy Metals in Lake Mariut Core sediments 7th Intern. Conference on Geochemistry, Faculty of Science, Alexandria University Egypt, 6-7 September 2006, VIII: 73-86.

Saleh, Sh.M.K., 2006. Environmental assessment of heavy metals pollution in bottom sediments from the Gulf of Aden, Yamen. Ph.D. Thesis, Institute of Graduate Studies and Research, Alexandria University, Alexandria, Egypt.

Schiff, K.C. and S.B. Weisberg, 1999. Iron as a reference element for determining trace metal enrichment in Southern California coast shelf sediments. Marine Environmental Research, 48: 161-176.

Shreadah, M.A., T.O. Said, El-Zokm G. and Masoud M. S. (2008). Physico-chemical Characteristics of the Surficial Sediments along the Egyptian Red Sea Coasts. Egyptian Journal of Aquatic Research, 34(4): 16-34.

Silveira, M.L., L.R. Alleoni, G.A. Connor and A.C. Chang, 2006. Heavy metal sequential extraction methods- A modification for tropical soils. Chemosphere., 64: 1929-1938.

Singh, K.P., D. Mohan, V. Singh and A. Malik, 2005. Studies on distribution and fractionation of heavy metals in Gomti river sediments a tributary of the Ganges, India. Journal of Hydrology, 312: 14-27.

Takarina, N.D., D.R. Browne and M.J. Risk, 2004. Speciation of heavy metals in coastal sediments of Semarang, Indonesia Baseline. Marine Pollution Bulletin, 49: 854-874.

Tessier, A., P.G.C. Campbeil and M. Bisson, 1979. Sequential Extraction Procedure for the Speciation of Particulate Trace Metals. Analytical Chemistry, 51(7): 844-850.

Tevah, A., E. Adely, M. Al Koshman and P. Warburg, 1993. Protecting the Gulf of Aqaba. A regional Environmental challenge. Washington, DC, pp: 512.

UNEP/IAEA, 1986. References Methods for Marine Pollution Studies. PERSGA- UNECO. 39.

Usero, J., E.G. Regalado and I. Gracia, 1996. Trace metals in bivalve molluscs Chameleo gallina from the Atlantic Coast of Southern Spain. Marine Pollution Bulletin., 32: 305-310.

Yong, R.N. and T. Phandungchewit, 1993. pH Influence on Selectivity and Retention of Heavy metals in Some Clay Soil. Analytical Geotechnology, 30: 821-833.

Zemberyova, M., J. Bartekova and I. Hagarova, 2006. The utilization of modified BCR three- steps sequential extraction procedure for the fractionation of Cd, Cr, Cu, Ni, Pb and Zn in soil reference materials of different origins. Talanta, 70: 973-978.