

SPATIAL VARIATION AND ECOLOGICAL RISK ASSESSMENT OF HEAVY METAL IN THE SURFICIAL SEDIMENTS ALONG THE EGYPTIAN RED SEA COAST.

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Abstract: The concentrations of certain heavy metals (Fe, Mn, Zn, Cr, Ni, Pb, Cu, and Cd) of sandy sediment samples collected from eight sites along the Egyptian Red Sea coast were investigated in order to evaluate the pollution status and ecological risk assessment of the study area. The results of the partitioning study showed that the average concentrations of the heavy metals analyzed in investigated sediment exhibited the following decreasing order Fe > Mn > Zn > Cr > Ni > Pb > Cu > Cd. The degree of surface sediment contamination was computed using Metal Pollution Index (MPI) and Geoaccumulation index (I_{geo}). Metal Pollution Index showed that station 5 (Qusier Middle) suffered with metal pollutions. Association with adverse effects to marine organisms was determined using the classification of the sediments according to SQGs. Sediment quality guidelines based on the consensus approach revealed that Pb and Cu had no adverse ecological effects.

1. Introduction

Rapid industrialization and economic development in coastal regions have undoubtedly introduced heavy metals into these regions all over the world and it is more so in Red Sea, wherein the industrial growth has been phenomenal during the last decade. Coastal sediments act as ultimate sinks for metals that are discharged into this environment. Recent studies have shown that sediment from coastal milieu near industrial and urban areas have been contaminated to some extent by heavy metals, which are toxic to biota (Feng et al. 2004; Romano et al. 2004; Santos et al. 2005). Thus, studies of metals in the sediment are important to decipher the source, to evaluate their enrichment pattern and to assess any probable localized influence. This leads to better understanding of their behavior in an aquatic environment and also helps in detecting the source of the pollution (Jayaprakash et al. 2008; Pekey 2006; Buccolieri et al. 2006). Sediments are also important carriers of metals in the hydrological cycle, because metals are partitioned with the surrounding waters, and thus they reflect the quality of an aquatic system. Metals accumulated in this process may be subsequently released to the overlying water column as a result of either physical disturbance or diagenesis and the sediments may persist as a source of pollutants long after the cessation of direct discharges. Moreover, diagenetic reactions are also important near the sediment–water interface responding to redox changes and affecting metal concentrations in vertical sediment profiles. Thus, this study provides some information on the surface sediment geochemistry of the investigated area to improve the sediment data inventory, characterize the geochemistry of heavy metals in surface sediments as well as understand the influence of anthropogenic activities and distribution of metals in sediments along Red Sea Coast.

2. Material and Methods

2.1. Area of Study

The Red Sea is one of the most important repositories of marine biodiversity on a global scale and features a range of important coastal habitats. Although the Red Sea is still one of the least ecologically disturbed seas relative to other enclosed water bodies. There is a growing risk of marine pollution, and environmental degradation from urban expansion, tourism and industrial development; this causes excessive sedimentation, which in turn leads to suffocation of benthic communities and ecosystem damage (gesamp 2001). Coastal habitat is being converted for urban and industrial development. Tourism and recreation usage are growing quickly. The Red Sea remains one of the busiest marine transport regions of the world, making this multi-national sea prone to major metals and oil pollution. It is extended from 22° 15' to 27° 15' N and from 33° 0' to 37° 0' E. (Abo-El-Khair et al. 2008).

Table 1. List of names, sites codes and different sampling locations of the Red Sea Coast:

Name	Site Code	Latitude	Longitude
Red Sea			
1- Hurghada (Sheraton Hotel)	RE-1	27° 1' 37.5"	33° 50' 48.4"
2- Safaga North (Suma Bay)	RE-2	26° 47' 34.9"	33° 56' 12.5"
3- Safaga Middle	RE-3	26° 30' 20"	34° 0' 20"
4- El Hamarawein	RE-4	26° 15' 9"	34° 12' 5"
5- Qusier Middle	RE-5	26° 8' 30"	34° 14' 30"
6- Qusier South	RE-6	25° 55' 48"	34° 36' 36"
7- Marsa Alam	RE-7	25° 4' 6.1"	34° 45' 0.4"
8- Bir Shalatin	RE-8	23° 9' 9.9"	35° 36' 48.3"

2. Sample collection and analyses

Surface sediment samples were collected from eight stations in the depth 3-5 m after tidal zone using Hydro-Bios stainless steel grab sampler along Egyptian Red Sea Coast (Fig 1). Each sample was placed in polyethylene plastic bags and they were then kept in an ice box. As soon as the field work was finished, samples were brought to laboratory and stored at -20 freezers for future analysis. The samples for assessment were dried using room tempresur and kept in an acid washed container for future use.

The total metals were extracted from the sediment samples according to standard operating procedures for trace metals (UNEP/IAEA, 1986). An exact weight (1g) 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 10 ml with double deionized distilled water. All digested solutions were analyzed in duplicate using an atomic absorption spectrophotometer (AAS Perkin Elmer analyst, Model 100) and the results were expressed in $\mu\text{g/g}$; dry weight. Reagents of analytical grade were utilized for the blanks and calibration curves. Precision was checked against standard reference material and lied within the range of certified values with 90-97% recovery for all metals studied.

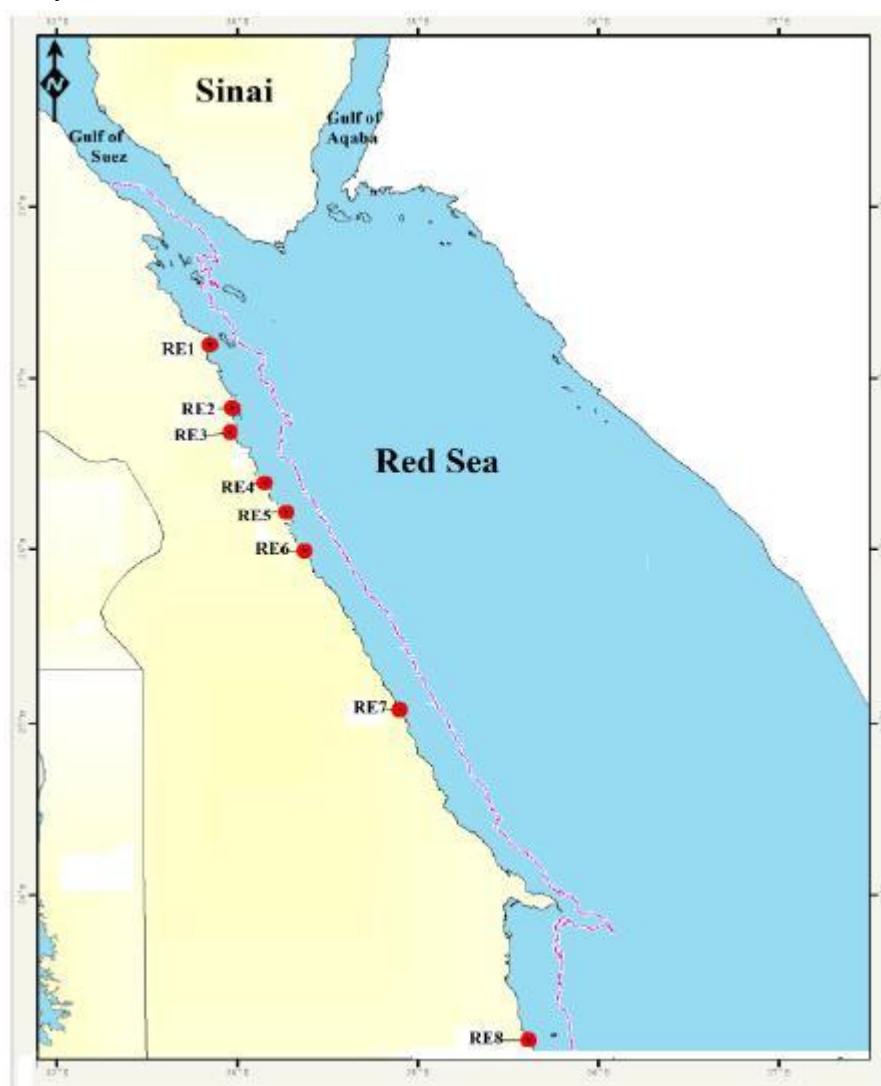


Figure 1: Sampling Sites of the Study Area.

Water content (WC %) Measurement is carried out gravimetrically after drying at a maximum temperature of 105°C over night to constant weight. Controlled period of time, is sufficiently high to eliminate “free” forms of water and sufficiently low not to cause a significant loss of organic matter and unstable salts by volatilization (Pansu and Gautheyrou 2006). The carbonates were determined by destroyed using hydrochloric acid and the volume of released carbon dioxide is measured at controlled temperature and pressure. This method is part of the international standard (NF ISO 10693) an improvement of this method using the pressure calcimeter. The pressure change caused by the reaction between HCl and the soil or sediment (0.5g dry and sieved) sample is measured with a digital plunge-in Manometer through a silicone–rubber septum placed on a screw-capped tube (Balazs et al. 2005).

The result is generally expressed as a percentage of limestone:

$$\text{CaCO}_3 \% = \frac{V \times M \times 2.28 \times 100}{1.000 \times P}$$

V: volume of evolved CO₂ per sample (ml), M: mass in g of 1 L of CO₂ in titration pressure and temperature conditions (M= 1.773) P: weight of sample (g) and 2.28 is the ratio between the molecular weight of CaCO₃ to that of CO₂.

A grain-size analysis was carried out using the conventional method (Folk 1974). About 30g of washed and quartered dried sample was subjected to the combined technique of dry sieving and pipette analysis. Granulometric analysis was carried out manually to describe the sediment. Organic carbon was determined using acid/dichromate titration method as described by (Gaudette et al. 1974). The results of the analysis were calculated by the following equation:

$$\% \text{ Organic Carbon} = 10 (1-T/S) [1.0N (0.003) (100/W)]$$

Where T= sample titration, ml ferrous solution, S= standardization blank titration, ml ferrous solution. N= normality of K₂Cr₂O₇, and W= weight of sediment sample in grams.

Metal Pollution Index (MPI), Geoaccumulation Index (I_{geo}), Sediment quality guidelines (SQGs) were calculated to determine the degree of metal pollution as well as to predict adverse biological effects in contaminated sediments of the investigated area.

Person's correlation was applied to determine correlation matrix between metal concentrations, TOC%, CaCo₃% and grain size in surface sediments of Red Sea coast using Statistical Package for Social Science (SPSS) version 15.

3. Results and discussion

3.1 Sediments characterization

The water content is an important factor in controlling the early diagenetic processes of sediments. It affects the rate of reactions particularly, the redox processes and the pH. The result of water content of the collected samples showed that, the Red Sea sediments have water in its pore ranged from 19.8 % at Marsa Alam site to 9.06 % at Bir Shalatin site (Table 1). Water content reflects the ability of sediment to hold water molecules between its particles, which are mainly a function of particle size and mineral composition (Mehrem 2002).

Maxwell (1968), classified sediments based on carbonate content to high carbonate (>80%), impure carbonate (80 – 60%), transitional (60 – 40%), terrigenous (40 – 20%) and high terrigenous (<20%). The results of the present study showed that, sediments from Safaga

North (Suma Bay) and Safaga Middle are characterized by high percentage of CaCO_3 with value 91.50 % and 90 % respectively. The major sources of carbonate in these stations are weathering of limestone rock on the sea floor in addition to the detrital fragmental molluscal shells and skeletons (Madkour, 2004). Transitional carbonate was found in Hurghada (Sheraton Hotel) and Marsa Alam with value 50 % and 59.10 % respectively. While El Hamarawein , Qusier Middle , Qusier South and Bir Shalatin sites belonging to terrigenous carbonate with value 40 % , 40 % , 30 % and 30 % respectively .

Total Organic Carbon (TOC) contents in the investigated sediments ranged from 1.77 % Qusier South to 0.66 % Marsa Alam area. It was noticed that the sediments in the study area are relatively low in TOC content. This reflect to the high productivity of the water column that contributes organic detritus to bottom sediment. It also reflects, terrestrial input from land-based sources. The organic matter is mainly derived from the autolysis of dead cells or actively excreted by diverse organisms as benthic algae, copepods, sea urchins planktonic species (Kenneth, 1988). TOC is composed of light-weight materials, and there is a close connection between the presence of fine sediments and the contents of organic matter (El-Askary et al., 1988). Fine sediments contained higher organic matter than coarser ones. Coarse sediments usually have larger pores, thus faster circulation and movement of interstitial water and oxygen-rich seawater.

Table 2: Sediments characterization along the area of study.

stations	sand	silt	clay	TOC	WC	CaCO_3	sediment type
Re1	99.76	0.24	0	1.453	14.53	50	sand
Re2	99.62	0.38	0	1.483	14.93	91.5	sand
Re3	100	0	0	1.356	13.56	90	sand
Re4	100	0	0	1.571	15.71	40	sand
Re5	99.95	0.05	0	0.79	15.83	40	sand
Re6	99.39	0.61	0	1.77	17.68	30	sand
Re7	100	0	0	0.66	19.8	59.1	sand
Re8	83.23	14.58	2.19	0.91	9.06	30	sand

Grain size analysis of the Egyptian Red Sea coastal sediments revealed the dominance of the sand fraction in all of the investigated samples (Table 2). The mean size of sediments ranged from -0.64Φ at Safaga Middle to 2.14Φ at Bir Shalatin (i.e. from very coarse sand to fine sand). Sorting changed from 0.48 at El Hamarawein to 1.91 at Bir Shalatin (i.e. from well sorting to poorly sorting). Skewness varying from -0.62 at Qusier South to 0.49 at Safaga Middle (i.e. from strongly coarse skewed to strongly fine skewed). Kurtosis varying from 0.35 at Safaga Middle to 1.26 at El Hamarawein (i.e. from very platykurtic to leptokurtic). Samples characterized by the presence of quartz, feldspar, aragonite, epsomite, Mg-calcite and calcite. Types of flux of clastic sediments, diversity of skeletal grains and the effectiveness of currents and wave actions produce this variation in

the sediment characteristics. The relative abundance of the fine sediments in some samples of the different areas is not only due to the abundance of terrigenous fine sediments but also due to the landfilling and dredging in these areas. Our results are in agreement with Madkour et al. (2008) and Mansour et al. (2000).

3.2 Spatial distribution of total heavy metals

The total concentrations of Fe, Mn, Pb, Zn, Ni, Cr, Cd and Cu. in surface sediments of the Egyptian Red sea coast are given in Table 3. Iron (Fe) concentrations were ranged between 12755 to 45869 mg kg- stations 1 and 7 with average concentration 261.5163 mg kg-1. Fe concentrations of the shallow marine sediments in different transects along the Red Sea coast are relatively high indicating the terrigenous contamination (Mansour et al. 2000).

The manganese content in the investigated sediments ranged between 32.94 mg kg-1 to 153.6 mg kg-1 at stations 1 and 7 with average concentration 102.175 mg kg-1. Iron was the most abundant metal measured followed by Mn and there are wide variations in the levels of the two metals among the sites of the study area. A significant correlation with $r = 0.81$ ($p = 0.05$) was found between the concentration of Fe and Mn reflecting the occurrence of these two metals is mainly controlled by natural processes such as coastal erosion deposition (Nasr et al., 1990). The concentrations of lead (Pb) in this study fluctuated from 11.16 to 29.66 mg kg-1 with average value 20.8688 mg kg-1 this may be attributed to anthropogenic activities in Bir Shalatin such as fishing boats, resulting in the release of large amount of Pb to the surrounding environment.

Zinc (Zn) concentration values recorded in this study ranged between 0.0193 to 207.6 $\mu\text{g/g}$ with an average value 62.4350 $\mu\text{g/g}$. Zinc showed a common trend of increase towards El Hamarawein due to the disposal of municipal wastewaters at El Hamarawein harbor. The range concentrations (mg kg-1) of Ni, Cr and Cu were 6.033 to 45.53, 5.674 to 52.65 and 1.895 to 17.81 with average concentrations (mg kg-1) were 22.5029, 30.438 and 8.9381(mg kg-1).

Ni, Cr and Cu showed a common trend of increase towards Marsa Alam may be attributed to the terrigenous origin and the increase of human activities in the region such as tourism, landfilling and marinas (Mansour et al., 2007). While the concentrations range of Cd were 0.752 mg kg-1 to 2.453 mg kg-1 with average 1.6048 mg kg-1. The high Cd concentrations in the sediments of Bir Shalatin may be attributed to the high intensity of fishing boats activities in this area. The total heavy metal concentration in the bed sediments of the Red sea coast decreases in the order of $\text{Fe} > \text{Mn} > \text{Zn} > \text{Cr} > \text{Ni} > \text{Pb} > \text{Cu} > \text{Cd}$.

Table 3. Metal concentrations ($\mu\text{g/g}$) in sediments of The Red Sea Coast:

Stations	Fe	Mn	Pb	Zn	Ni	Cr	Cd	Cu	MPI
1	207.96	32.94	11.16	6.32	6.033	5.674	0.752	1.895	8.3472
2	261.03	61.84	21.25	13.49	11.51	15.86	1.649	3.462	16.2333
3	268.18	117.1	21.48	0.0211	16.47	27	1.11	7.991	9.3038
4	270.91	130.9	15.7	187.1	30.52	36.49	1.233	9.67	32.9314
5	270.87	124.7	24.99	207.6	24.06	42.16	2.274	11.88	38.4749
6	270.21	123.7	17.97	84.91	25.44	40.35	1.374	7.607	29.3270
7	276.9	153.6	24.74	0.0193	45.53	52.65	1.993	17.81	14.2788
8	266.07	72.62	29.66	0.0197	20.46	23.32	2.453	11.19	10.5010
Mean	261.5163	102.175	20.8688	62.4350	22.5029	30.438	1.6048	8.9381	19.9247
Aver. Shale ^a	4.7	805	20	95	68	90	0.30	45	-
*TEL ^d	n.a.	n.a.	30	124	18	52	0.7	19	-
*TET ^d	n.a.	n.a.	112	271	61	160	4.2	108	-

a Turekian and Wedepohl (1961).

d. MacDonald et al. (2000).

4. Heavy Metals Contamination and Risk Assessment:

4.1 Metal Pollution Index (MPI):

The overall metal contents at the sites investigated in this study were compared, using the metal pollution index (MPI) calculated according to Usero et al. (1996 and 1997) to estimate the degree of pollution with the formula:

$$\text{MPI} = (\text{MFe} \times \text{MMn} \times \text{MZn} \times \text{MPb} \times \text{MCd} \times \text{MCu} \times \text{MCr} \times \text{MNi})^{1/8}$$

The MPI values of Fe, Mn, Pb, Zn, Ni, Cr, Cd and Cu in the collected samples are summarized in Table (3). MPI indicated metal pollution load at the each site. The highest MPI values were measured at the site 5 (Qusier Middle) suffered from metal pollutions with values of 38.4749. this may be due to impact from human related activities such as tourism, Fishing, Boats .

4.2. Geoaccumulation Index (Igeo)

The Geoaccumulation Index (Igeo) was calculated to determine metals contamination in sediments of Egyptian Red Sea Coast. This expression was proposed by Müller (1979) in order to calculate metals concentration in sediments by comparing current concentrations with undisturbed or crustal sediment (control) levels. Müller (1981) has classified Igeo in relation to contamination levels into seven classes, Unpolluted (Class 0, $\text{Igeo} < 0$), unpolluted to moderately polluted (Class 1, $0 < \text{Igeo} < 1$), moderately polluted (Class 2, $1 < \text{Igeo} < 2$), moderately to strongly polluted (Class 3, $2 < \text{Igeo} < 3$), strongly polluted (Class 4, $3 < \text{Igeo} < 4$), strongly to very strongly polluted (Class 5, $4 < \text{Igeo} < 5$) and very strongly polluted (Class 6, $\text{Igeo} > 5$), the highest grade reflecting a 100-fold enrichment above baseline values. The geoaccumulation (Igeo) is expressed by the following pattern:

$$\text{Igeo} = \log_2 (\text{Bn} / 1.5 * \text{Cn})$$

Where Cn is the measured concentration of the sediment for metal (n), Bn is the geochemical background value of metal (n) and factor 1.5 is the possible variations of background data due to lithogenic impacts. The values of geoaccumulation index (Igeo) of investigated metals were shown in table (4). This suggests that the Fe concentrations were very strongly polluted ($\text{Igeo} > 5$) except station 1 was strongly to very strongly polluted ($4 < \text{Igeo} < 5$). While the investigated sediments were Unpolluted ($\text{Igeo} < 0$) at all stations by Mn, Pb, Ni, Cr and Zn except stations 8 and 9 which were unpolluted to moderately polluted ($0 < \text{Igeo} < 1$) by Zn , Whereas the concentration of Cd had variation so recorded at many classes , unpolluted to moderately polluted ($0 < \text{Igeo} < 1$) at station 1, moderately polluted ($1 < \text{Igeo} < 2$) at stations 2, 3, 4 and 6 but at stations 5, 7 and 8 was moderately to strongly polluted ($2 < \text{Igeo} < 3$). .

Table 4. Geoaccumulation Index (Igeo) values in surface sediments of Red Sea coast:

Stations	Fe	Mn	Pb	Zn	Ni	Cr	Cd	Cu
1	4.90	-5.29	-1.43	-4.51	-4.09	-4.59	0.74	-5.17
2	5.23	-4.38	-0.50	-3.41	-3.16	-3.10	1.88	-4.30
3	5.27	-3.46	-0.48	-12.77	-2.64	-2.33	1.31	-3.09
4	5.28	-3.30	-0.94	0.39	-1.75	-1.89	1.46	-2.81
5	5.28	-3.37	-0.26	0.54	-2.09	-1.68	2.35	-2.51
6	5.28	-3.38	-0.74	-0.75	-2.01	-1.75	1.62	-3.16
7	5.31	-3.06	-0.28	-12.89	-1.17	-1.36	2.15	-1.93
8	5.26	-4.15	-0.02	-12.86	-2.33	-2.54	2.45	-2.60

4.3 Sediment Quality Guideline (SQGs)

In order to predict adverse biological effects in contaminated sediments, numerous sediment quality guidelines (SQGs) have been developed over the past decade (MacDonald et al., 2000). In the present study, we compared the concentration of investigated metals with SQG of threshold effect level (TEL), which includes threshold effect concentrations, and toxic effect threshold (TET), which includes probable effect concentrations (PEC) as described by MacDonald et al. (2000) to assess the possible biological consequences of the metal concentrations in the surface sediments (Table 3). Threshold effect concentrations should be used to identify sediments that are unlikely to be adversely affected by sediment-associated contaminants, while the PECs should be used to identify sediments that are likely to be toxic to sediment-dwelling organisms (MacDonald et al., 2000).

The results of the present showed that the concentrations of Pb and Cu at all sediment samples are lower than TEL indicated that there are no harmful effects from this metal. Concentration of Zn in sediment samples at all stations lower than TEL except stations 4 (El Hamarawein) and 5 (Qusier Middle) with values 187.1 µg/g and 207.6 µg/g respectively, which higher than TEL and lower TET. But concentration of Ni recorded values between TEL and TET except stations 1(Hurghada), 2 (Safaga North) and 3 (Safaga Middle) with values (6.033, 11.51 and 16.47 respectively) lower than TEL. This indicated that these stations were in potential risk. Cr was lower than TEL at all sediment stations except station 7(Marsa Alam) with value 52.65 µg/g higher than TEL and lower TET. On the other hand, the concentration of the Cd at all sediment stations has values between TEL (0.7) and TET (4.2).

4.4 Correlation Matrix

Pearson's correlation matrix was used to determine the relationships between Fe, Mn, Pb, Zn, Ni, Cr, Cd, Cu, CaCO₃%, TOC% and grain-size of surface sediments (Table 5). The result indicated that most metals Fe, Mn, Ni, Cr, Cd and Cu have positive significant association with in metals but there are negative correlation between Pb and Zn ($r = -0.11$). On the other hand, CaCO₃ recorded negative correlation with Fe, Mn, Pb, Zn, Ni, Cr, Cd, Cu and grain size ($r = -0.02, -0.13, -0.03, -0.46, -0.29, -0.29, -0.29, 0.28$ and -0.05 respectively). There are negative correlations between TOC and metals except Zn was significant positive correlation ($r = 0.05$). There were negative correlation between grain size and TOC, CaCO₃, Fe, Mn, Ni, Cr and Cu except Pb, Zn and Cd were significant positive correlation with grain size ($r = 0.41, 0.03$ and 0.61 respectively). The sediments in our study area of investigation were mainly sand, thus the total metal concentrations were not grain size controlled with between total metal concentration and mean size of each sediment sample. Significant correlations between most of these metals were probably due to influxes of some non-lithogenic and natural sources into the surface sediments.

Table 5. Pearson's correlation coefficient between metals, CaCo₃%, TOC% and grain-size

	Fe	Mn	Pb	Zn	Ni	Cr	Cd	Cu	CaCo ₃ %	TOC%	Grain Size
Fe	1										
Mn	0.81	1									
Pb	0.65	0.29	1								
Zn	0.30	0.43	-0.11	1							
Ni	0.69	0.87	0.36	0.24	1						
Cr	0.79	0.96	0.39	0.43	0.93	1					
Cd	0.57	0.26	0.92	0.12	0.42	0.44	1				
Cu	0.70	0.79	0.65	0.17	0.91	0.86	0.65	1			
CaCo ₃ %	-0.02	-0.13	-0.03	-0.46	-0.29	-0.29	-0.29	-0.28	1		
TOC%	-0.28	-0.27	-0.73	0.05	-0.46	-0.40	-0.76	-0.74	0.09	1	
Grain Size	-0.10	-0.35	0.41	0.03	-0.19	-0.1	0.61	-0.01	-0.50	-0.31	1

4 Conclusions

This study showed that heavy metal concentrations in the sediments along the Egyptian Red Sea coast were in the following decreasing order Fe > Mn > Zn > Cr > Ni > Pb > Cu > Cd. The degree of surface sediment contamination was computed using Metal Pollution Index (MPI) and Geoaccumulation index (I_{geo}). Metal Pollution Index showed that station 5 (Qusier Middle) suffered with metal pollutions.

The Geoaccumulation Index (I_{geo}) exhibited the concentrations of Fe were very strongly polluted (I_{geo}>5) except station 1 was strongly to very strongly polluted (4< I_{geo}<5). While the investigated sediments were Unpolluted (I_{geo}<0) at all stations by Mn,Pb,Ni,Cr and Zn except stations 8 and 9.

sediment quality guidelines (SQGs) showed that the concentration of Pb and Cu at all sediment samples are lower than TEL. On the other hand, the concentration of the Cd and Ni at all sediment stations have values between TEL and TET.

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