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Health Risk Assessment of Some Heavy Metals in Water and Sediment at Marsa-Matrouh, Mediterranean Sea, Egypt

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Abstract

In an attempt to evaluate the environmental quality of Marsa-Matrouh city which covered the most famous beaches in Egypt, an environmental risk assessment was performed, including a screening level ecological risk assessment. The aim of this work was to determine which metals could possibly pose toxic adverse ecological effects to marine organisms and to determine whether hot spots exist or not. To fulfill the goals of study, surfacial sediment and water samples were collected from ten different locations covering Marsa-Matrouh city during four seasons (2010-2011). The average concentrations of Cd, Cu, Fe, Ni, Pb and Zn were 2.381 ± 3.389, 9.307 ± 14.159, 68.969 ± 9.397, 2.642 ± 1.004, 16.712 ± 8.469, 31.168 ± 15.322 µg/l in water and 0.755 ± 0.240, 5.363 ± 1.581, 962.131 ± 975.084, 3.972 ± 2.180, 15.210 ± 4.434 and 24.608 ± 7.706 µg/g dry weight in sediment respectively. The concentrations of the investigated six metals in water were within the acceptable limits except for two stations (Cleopatra and El-Obayed) which exhibited higher values than the permissible level of Cd during autumn 2010. Metal pollution assessment for both water and sediment was studied. Heavy metal pollution index indicates that water is not critically polluted with respect to the investigated metals. For sediment samples, threshold effect concentrations (TEC HQ) were lower than 1 except for Cd which showed higher value than 1, indicating the possibility of occurrence of toxic adverse ecological effects to benthic organisms for Cd, while rare adverse ecological effects are expected to occur with respect to Cu, Ni, Pb and Zn.

Keywords

Trace Metal, HQ, Human Health Risk, Marsa-Matrouh, Mediterranean Sea, Egypt

1. Introduction

Metals are naturally occurring elements that ultimately originate from weathering of rock substrates. These metals are mainly chemically bound to alumino-silicates and are therefore not readily bio-available [1]. In contrast to the natural occurring of metals, the anthropogenic origin of these metals is more readily available to organisms due to the fact that they are more loosely bound in sediments [2]. One of the most crucial properties of heavy metals is that they are not biodegradable in the environment. In marine ecosystems, sediments show a great capacity to accumulate and integrate heavy metals and organic pollutants even from low concentrations in the overlying water column [3] [4] [5] [6] and so it acts as the main sink for metals [7] [8] and other pollutants [9]. Although most pollutants adsorbed on the sediments are not bioavailable, certain mechanisms may induce the release of pollutants back to the water column including sediment resuspension, desorption, redox reactions or (bio-)degradation of the sorptive substance [10] [11] [12] [14] [15] that can have toxic adverse effects on living organisms [16] [17] [18]. As a combined result of these factors, metal concentrations in the sediment change in space and time. In fact, during the last few decades, industrial and urban activities have contributed to the increase of metals contamination into marine environment and have directly influenced the coastal ecosystems [19]. Interactions between solid sedimentary matter and dissolved metals play an important role in the regulation of dissolved metal concentrations (which are the most bioavailable) in the water [20].

The Marsa-Matrouh City has an area of 212,112 km^2 and 193,000 inhabitants, or 0.9 in habitants/km^2 [21]. The town of Marsa-Matrouh is the only important town on the 500 kilometers long stretch of the Mediterranean coast between Alexandria and the Libyan border. In summer, the number of visitors to Marsa-Matrouh increases (more than one million visitors enjoy the beautiful white sand beaches and clear seawater), and hence the human activity in this site increases which reflects the changing in the environmental conditions.

The main aim of this work was to determine the spatial variations of Cd, Cu, Ni, Zn and Fe contents in water and sediment samples collected from Marsa-Matrouh City. The samples were collected from ten beaches along the Marsa-Matrouh coast which were selected to cover the most famous beaches to estimate the degree of contamination by using heavy metal pollution index for water and the geo-accumulation index, enrichment factor and the modified degree of contamination for sediment.

2. Materials and Methods

Seasonal water and sediment samples were collected from ten beaches (El-Remelah, Alam El-Roum, Mena Hashesh, El-Fayrouz, Romel, El-Boseet, Cleopatra, El-Gharam, El-Obayed and Ageba) during (2010-2011), which covered approximately 500 Km from the Egyptian Mediterranean coastline. Location of the sampling points was showed in **Figure 1** and **Table 1**.

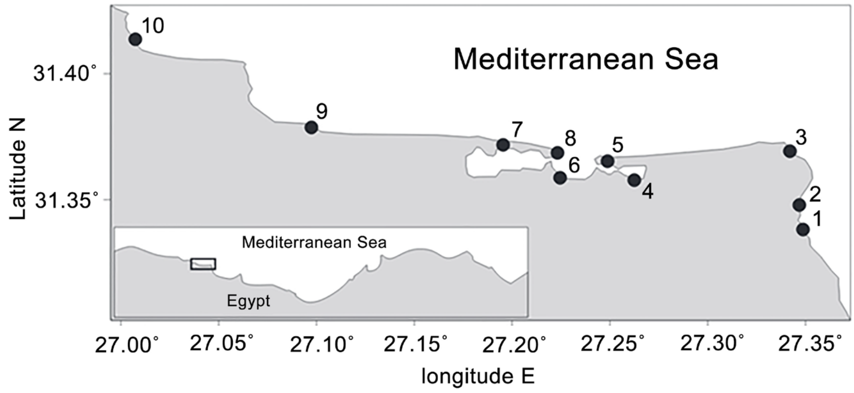

Figure 1. Sampling locations of Marsa-Matrouh, Egyptian mediterranean sea coast.

Table 1. Sampling locations of Marsa-Matrouh Beaches.

Station	Location	Latitude (N)	Longitude (E)
1	El-Remelah	31˚20'16.7"	27˚20'53.2"
2	Alam El-Roum	31˚20'16.7"	27˚20'50.1"
3	Mena-Hashish	31˚22'6.7"	27˚20'30.1"
4	El-Fayroz	31˚21'28.8"	27˚15'46.6"
5	Romel	31˚21'55.4"	27˚14'55.5"
6	El-Boseet	31˚21'32.5"	27˚13'29.1"
7	Cleopatra	31˚22'17.3"	27˚11'44.8"
8	El-Gharam	31˚22'6.5"	27˚13'24.7"
9	El-Obayed	31˚22'45.7"	27˚5'45.6"
10	Ageba	31˚24'46.3"	27˚0'24.2"

Coastal water samples were collected from the ten stations using Nansen bottles at 2 m depth, and then, stored in acid-washed polyethylene bottles until analysis. All the precautions recommended by [22] to minimise risks of sample contamination were followed during collection and treatment of samples. Dissolved heavy metals were determined according to [23], as modified by [24]. Water samples were filtered immediately after collection using pre-acid cleaned Millipore membrane filters (0.45 mm pore size; 47 mm diameter). The filtrates were acidified to pH 2, with HNO_3 of supra pure grade; they were stored, in acid-cleaned high-density polyethylene bottles, in plastic bags. The samples were passed through columns filled with an ion exchange resin (Chelex-100, mesh 200 - 400), via a peristaltic pump in a clean air laboratory. After removal of the alkalis, the metals were eluted from the resin with a mixture of 2 N HNO_3:1 N HCl (1:3). A 100-fold pre-concentration factor was achieved. Trace metal concentrations were determined in elutes.

The surface samples (about 1 Kg) were collected from the ten beaches with the water samples from the same places at (3 - 5 cm) depth during the four seasons. Sediment samples were collected using a Van-Veen grab coated with polyethylene [25]. Sediment sampling location position was detected using GPS localisation. Subsamples were taken from the central part of the grab to avoid contamination. The samples were kept in self-sealed acid pre-cleaned plastic bags, rinsed with metal-free water. The samples were deep-frozen until analysis. The samples were dried in the oven at 50˚C under vacuum (Medline-OV-12) and sieved, using plastic sieve to separate the shells and stones, crushed and homogenized prior to the analysis. The heavy metals in bottom sediments were digested according to the method described by [26]. An exact weight of dry sample (about 0.2 g) was placed in Teflon beaker, 3 ml of concentrated nitric acid was added to the sample and evaporated to dryness at 80˚C, 5 ml of $HNO_3/HClO_4/HF$ mixture (3:2:1) was added to each sample. After complete digestion, the sample was evaporated to dryness; the temperature was increased gradually to 120˚C to remove the $HClO_4$ residue. The sample was cooled at room temperature and 5 ml of 0.1 N HCl was used to rinse and transfer the residue to 25 ml volumetric flask. The metals concentrations were determined by AAS (Shimadzu, AA-6800) and the results were expressed in μg/l (ppb) for water samples and μg/g (ppm) dry weights for sediment samples, Cd and Pb were analysed by graphite furnace and Ni, Cu, Zn and Fe by flame.

2.1. Assessment of Metal Pollution

2.1.1. Heavy Metal Pollution Index

Heavy metal pollution index (HPI) is a technique of rating that provides the composite influence of individual heavy metal on the overall quality of water. The rating is a value between zero and one, reflecting the relative importance of individual quality considerations and inversely proportional to the recommended standard (Si) for each parameter [27] [28] [29]. The heavy metal pollution index (HPI) were calculated by the Equation:

$$\text{HPI} = \frac{\sum_{i=1}^{n}(\text{QiWi})}{\sum_{i=1}^{n}(\text{Wi})}$$

where Qi is the sub-index of *i*th parameter, Wi is the unit weightage for *i*th parameter (calculated according to [30], *n* is the number of parameters considered. The critical pollution index value is 100.

2.1.2. Sediment Quality Guidelines (SQGs)

The effect characterization was based on several sets of sediment quality guidelines (SQGs) reported in literature. Some authors have developed the consensus based approach trying to harmonize the existing values [31] [32] [33], which was used in the present study for the risk calculations and for pointing out the presence of any hot spots in Marsa-Matrouh City. In the consensus approach (CA), consensus-based SQGs are derived from the existing SQGs that have been established for the protection of sediment-dwelling organisms. First, the SQGs for the protection of sediment-dwelling organisms are grouped into two categories according to their original narrative intent, including threshold effect concentrations (TECs) and probable effect concentrations (PECs). TECs group are intended to identify concentrations below which harmful effects on sediment-dwelling organisms are unlikely to be observed, included effect range low (ERL) [34], threshold effect level (TEL) [35] [36] and logistic regression models including T20, which represents the probability of occurrence of adverse ecological effects in 20% of the investigated samples (T20) [37]. The PECs are intended to identify concentrations above which harmful effects on sediment-dwelling organisms are likely to be frequently or always observed [31] [33], included probable effect level (PEL) [35] [36] [38], effect range medium (ERM) [34] [35] [36], logistic regression models including T50, which represents the probability of occurrence of adverse ecological effects in 50% of the investigated samples [37] and the apparent effect threshold low (AET-L) [39]. For some sediment quality guidelines, values representing higher level of adverse ecological effects are available (T80 and AET-H), where extreme adverse ecological effects could be expected as showed in **Table 2**.

2.1.3. Hazard Quotient

In the present study, the risk was characterized by comparing the maximum concentration of each pollutant with its corresponding sediment quality guideline. The selected approach was the hazard quotient (HQ). Two HQs were calculated for each pollutant; TEC HQ which was calculated by dividing the maximum concentration of each pollutant by the calculated consensus-based TEC (CBSQGTEC) and the PEC HQ, which was calculated by dividing the maximum concentration of each pollutant by the calculated consensus-based PEC (CBSQGPEC). When TEC HQ < 1 for a given pollutant, rare adverse ecological effects are expected to occur with respect to this pollutant, when PEC HQ > 1, frequent adverse ecological effects are expected to occur and when TEC HQ > 1 > PEC HQ, adverse ecological effects are possible but less frequent than the previous level.

$$\text{TEC HQ} = \frac{\text{Concentration of the pollutant}}{\text{CBSQG}_{\text{TEC}}}$$

$$\text{PEC HQ} = \frac{\text{Concentration of the pollutant}}{\text{CBSQG}_{\text{PEC}}}$$

2.1.4. Geoaccumulation Index

[40] defined Geoaccumulation index (Igeo) in order to determine metals contamination in sediments. To compare the current concentration with pre-industrial levels, Igeo was calculated by the following Equation:

$$\text{Igeo} = \text{Log2}\left[\text{Cn}/(1.5)\text{Bn}\right]$$

where Cn is the measured concentration of the studied metal "n" in the sediment and Bn is the geochemical background concentration of the metal "n". Factor 1.5 is used because of possible variations in background values for a given metal in the environment, as well as very small anthropogenic influences. Müller had distinguished seven classes of geoaccumulation index [41] as described in **Table 3**.

Table 2. Summary of the effect concentration levels from different SQGs.

Effect		Metal (μg/g dw)				
		Cd	Cu	Ni	Pb	Zn
Threshold Effect	ERL	1.20	34.0	20.9	46.7	150.0
	TEL	0.68	18.7	15.9	30.2	124.0
	T20	0.38	32.0	15.0	30.0	94.0
	TEC	**0.70**	**27.3**	**17.1**	**34.8**	**121.0**
Probable Effect	ERM	9.60	270.0	51.0	218.0	410.0
	PEL	4.21	108.0	42.0	112.0	271.0
	AET-L	2.70	390.0	110.0	430.0	460.0
	T50	1.40	94.0	47.0	94.0	240.0
	PEC	**3.50**	**181.0**	**58.1**	**177.0**	**333.0**
Extreme Effect	AET-H	14.00	1300	371	1200	3800
	T80	4.90	280	150	300	640
	EEC	**8.30**	**603**	**236**	**600**	**1560**

Table 3. Igeo classification according to Müller, 1981.

Igeo	Igeo class	Designation of sediment quality
> 5	6	Extremely contaminated
4 - 5	5	Strongly to extremely contaminated
3 - 4	4	Strongly contaminated
2 - 3	3	Moderately to strongly contaminated
1 - 2	2	Moderately contaminated
0 - 1	1	Uncontaminated to moderately contaminated
<0	0	Uncontaminated

2.2. Statistical Analysis

Spearman (non-parametric) rank order correlations, Principal component analysis (PCA) and cluster analysis (CA) are the most common multivariate statistical methods used in environmental studies [42]-[48]. In the present study, SPSS for Windows, Version 15, was utilized for the multivariate analysis and for correlation analysis.

2.2.1. Principal Component Analysis

Multivariate analysis (Principal component analysis, PCA) has been applied on the data set for ten sediment samples and six variables (Cd, Cu, Pb, Ni, Zn, and Fe). R-mode factor analysis with VARIMAX rotation with Kaiser Normalization, as well as the Eigen values was applied to the previous metals in the sediment samples.

2.2.2. Cluster Analysis

Hierarchical cluster analysis (HCA) was carried out using the average linkage clustering which was applied on the Pearson correlation for the four groups of pollutants under investigation. This dendrogram was confirmed by applying two other clustering methods: This dendrogram was confirmed by applying two other clustering methods: 1) Complete linkage, using the cluster method further neighbor with interval Pearson correlation, 2) Centroid linkage, with the interval Pearson correlation.

3. Results and Discussion

3.1. Water

The distribution of heavy metal concentrations for the ten beaches of the investigated area were reported in **Table 4** and **Table 5**.

The dissolved cadmium concentration in water of Marsa-Matrouh beaches ranged between 0.168 μg/l determined at El-Obayed during summer 2011 and 48.977 at Cleopatra during autumn 2010. The average concentration of Cd in the five trips under investigation was increased in the order of winter 2011 > spring 2011 > summer 2011 ≈ summer 2010 > autumn 2010, with the total annual average of 2.381±3.389 μg/l which exceed the natural concentration of seawater (0.1 μg/l) according to [49]. All the concentrations of Cd in the present study recorded lower concentrations than the [50] (5 μg/l) except the two stations Cleopatra and Obayed in autumn 2010 which exhibited higher values (48.977 and 48.977 μg/l respectively).

The concentrations of dissolved copper in the investigated beaches were fluctuated between 1.701 at Agiba station in winter 2011 and 148.050 μg/l at El-Obayed during autumn 2010. Based on the annual average concentration of copper in Marsa-Matrouh beaches, it was 9.307 ± 14.159 μg/l which is higher than that of natural sea water concentration (2 μg/l) according to [49] but it was within the acceptable limits (5 - 112 μg/l) for all stations in the investigated area except station El-Obayed during autumn 2010 which recorded a relatively higher value (148.050 μg/l) according to the [51] of heavy metals. Copper recorded the highest level during autumn 2010 followed with that recorded in spring 2011 while the lowest value was recorded during winter 2010. The lower value of Cu in winter may be due to the low organic matter degradation. Similar to that observed for Cd, copper recorded nearly similar values during the two overlapping summer seasons (5.514 and 5.946 μg/l for 2010 and 2011 respectively).

Iron is present in very low iron concentrations in the oceans, despite its enhanced abundance in the earth's crust, and is a vital constituent of plant life [52]. It found in the natural sea water at level of 2 μg/l. in the present study, the dissolved iron concentration was fluctuated between 15.167 and 158.445 μg/l recorded at El-Remelah and El-Gharam stations during autumn and spring, respectively with an annual average of 68.969 ± 9.397 μg/l. It was noted that the dissolved iron concentrations recorded in the Matrouh Beaches were lower than the permissible Limits (300 μg/l) according to the Canadian acceptable limits [53]. The highest average concentration of Fe was recorded during spring 2011 followed by summer 2010 and 2011 while the lower value was observed during autumn 2010.

Table 4. Distribution of Cd, Cu and Pb (μg/L) concentrations in different water samples collected from Marsa-Matrouh beaches during 2010-2011.

Station	2010			2011		Annual Average
	Summer	Autumn	Winter	Spring	Summer	
Cadmium (μg/L)						
El-Remelah	1.587	0.747	0.192	0.588	0.441	0.711
Alam El-Roum	0.747	0.747	0.401	0.603	0.341	0.568
Mena-Hashish	2.007	2.147	0.320	0.603	0.192	1.054
El-Fayroz	0.397	0.583	0.657	1.176	2.793	1.121
Romel	0.397	0.817	0.371	0.834	1.610	0.806
El-Boseet	4.200	2.753	0.320	0.699	1.797	1.954
Cleopatra	0.280	48.977	0.488	0.792	2.933	10.694
El-Gharam	0.373	0.607	0.572	0.185	0.365	0.420
El-Obayed	0.280	29.563	0.422	0.285	0.168	6.144
Ageba	0.397	0.513	0.204	0.350	0.252	0.343
Min	0.280	0.513	0.192	0.185	0.168	0.343
Max	4.200	48.977	0.657	1.176	2.933	10.694
Average	**1.067**	**8.745**	**0.395**	**0.612**	**1.089**	**2.381**
Copper (μg/L)						
El-Remelah	11.130	4.830	2.313	3.002	2.799	4.815
Alam El-Roum	11.527	2.380	2.367	4.226	5.495	5.199
Mena-Hashish	2.870	3.337	2.102	3.695	3.213	3.043
El-Fayroz	4.783	11.597	3.213	6.683	15.260	8.307
Romel	2.660	4.433	3.006	3.965	8.658	4.544
El-Boseet	3.547	3.150	2.205	4.662	3.569	3.427
Cleopatra	7.653	3.733	3.609	5.504	6.836	5.467
El-Gharam	2.380	10.383	2.318	5.081	4.064	4.845
El-Obayed	4.923	148.050	2.552	85.581	5.882	49.398
Ageba	3.663	4.830	1.701	6.260	3.681	4.027
Min	2.380	2.380	1.701	3.002	2.799	3.043
Max	11.527	148.050	3.609	85.581	15.260	49.398
Average	**5.514**	**19.672**	**2.539**	**12.866**	**5.946**	**9.307**
Lead (μg/L)						
El-Remelah	16.590	8.633	8.588	10.907	15.675	12.079
Alam El-Roum	21.070	7.303	8.675	12.024	11.159	12.046
Mena-Hashish	6.463	13.440	8.244	9.717	13.019	10.177
El-Fayroz	43.610	11.620	19.953	46.806	65.579	37.514
Romel	6.977	17.920	12.842	20.870	42.032	20.128
El-Boseet	6.977	7.793	15.372	12.362	31.931	14.887
Cleopatra	6.790	16.753	10.392	13.398	38.945	17.256
El-Gharam	7.303	7.957	12.281	7.901	28.158	12.720
El-Obayed	7.957	9.287	37.616	31.527	23.087	21.895
Ageba	7.793	8.120	9.189	9.387	7.616	8.421
Min	6.463	7.303	8.244	7.901	7.616	8.421
Max	43.610	17.920	37.616	46.806	65.579	37.514
Average	**13.153**	**10.883**	**14.315**	**17.490**	**27.720**	**16.712**

Table 5. Distribution of Ni, Zn and Fe (μg/L) concentrations in different water samples collected from Marsa-Matrouh beaches during 2010-2011.

Station	2010		2011			Annual Average
	Summer	Autumn	Winter	Spring	Summer	
Nickel (μg/L)						
El-Remelah	1.423	3.057	2.117	2.134	2.607	2.273
Alam El-Roum	1.913	1.307	2.126	2.182	3.194	2.144
Mena-Hashish	19.903	1.773	1.389	2.369	1.422	5.371
El-Fayroz	2.263	1.237	3.006	3.811	3.925	2.848
Romel	1.703	1.213	2.382	3.212	3.978	2.498
El-Boseet	1.26	1.727	1.623	2.222	3.339	2.034
Cleopatra	2.123	1.633	2.05	3.033	2.351	2.238
El-Gharam	0.84	1.12	3.025	4.229	2.391	2.321
El-Obayed	1.307	1.353	2.905	6.069	2.213	2.769
Ageba	1.423	1.143	2.899	2.279	1.881	1.925
Min	0.840	1.120	1.389	2.134	1.422	1.925
Max	19.903	3.057	3.025	6.069	3.978	5.371
Average	**3.416**	**1.556**	**2.352**	**3.154**	**2.730**	**2.642**
Zinc (μg/L)						
El-Remelah	12.273	30.473	22.935	36.405	32.408	26.899
Alam El-Roum	38.103	31.313	11.64	38.865	57.18	35.420
Mena-Hashish	4.48	25.993	16.643	28.305	23.558	19.796
El-Fayroz	12.25	22.003	50.708	42.135	35.79	32.577
Romel	14.14	22.05	37.815	48.803	43.103	33.182
El-Boseet	11.993	28.07	17.94	28.208	24.69	22.180
Cleopatra	13.3	252.957	33.548	36.285	23.243	71.867
El-Gharam	20.603	20.557	34.89	18.698	20.423	23.034
El-Obayed	6.393	31.36	32.843	35.22	25.118	26.187
Ageba	15.493	10.337	38.098	25.118	13.658	20.541
Min	4.480	10.337	11.640	18.698	13.658	19.796
Max	38.103	252.957	50.708	48.803	57.180	71.867
Average	**14.903**	**47.511**	**29.706**	**33.804**	**29.917**	**31.168**
Iron (μg/L)						
El-Remelah	132.533	15.167	71.805	45.108	79.008	68.724
Alam El-Roum	62.3	22.4	83.226	42.453	85.506	59.177
Mena-Hashish	50.867	97.067	42.126	64.278	31.098	57.087
El-Fayroz	132.3	32.9	75.765	74.709	76.842	78.503
Romel	77	112.7	65.076	70.053	103.503	85.666
El-Boseet	90.3	22.867	45.327	54.048	104.979	63.504
Cleopatra	49	136.5	54.456	80.515	45.582	73.211
El-Gharam	36.867	22.4	101.196	158.445	66.531	77.088
El-Obayed	27.3	52.733	71.805	120.474	56.421	65.747
Ageba	51.567	27.3	95.775	61.44	68.834	60.983
Min	27.300	15.167	42.126	42.453	31.098	57.087
Max	132.533	136.500	101.196	158.445	104.979	85.666
Average	**71.003**	**54.203**	**70.656**	**77.152**	**71.830**	**68.969**

The dissolved nickel concentrations along Marsa-Matrouh beaches ranged between 0.840 and 19.903 µg/l determined at El-Gharam and Mena-Hashish stations during summer 2010, respectively. The annual average concentration of Ni in the investigated beaches was 2.642 ± 1.004 µg/l which is higher than that of natural sea water (0.5 µg/l) according to [49], but it was still lower than the permissible limits (25 - 150 µg/l) recorded for Canadian acceptable limits [53]. The highest level was recorded during summer 2010 followed by spring and summer 2011, may be attributed to the phytoplankton pollution occurring in spring and summer seasons.

The annual average concentration of dissolved lead in the investigated area was 16.712 ± 8.469 µg/l which ranged from 6.463 and 65.579 µg/l recorded at Mena-Hashish and El-Fayroz stations during summer 2010 and 2011, respectively. Based on the annual average concentration of lead, it is higher than that of natural sea water concentration (0.03 µg/l) according to Fifield and Haines (2000) but it still lower than acceptable limits (100 µg/l) according to the Russian limits [50] of heavy metals. The higher average level of Pb was recorded during summer 2011 while the lowest value was observed during autumn 2010.

Zinc may occur in natural sea water at level reaches to 10 µg/l [49]. The concentration of zinc in the investigated area ranged between 4.480 and 252.957 µg/l determined at Mena-Hashish and Cleopatra during summer and autumn2010, respectively. The annual average concentration was 31.168 ± 15.322 µg/l which is lower than the [50] (30 - 2000 µg/l). The odd record of Zn concentration in Cleopatra station during autumn 2010 (252.957 µg/l) reflect an unmoral case and there is an external source of pollution in this station. The highest average concentration was recorded during autumn 2010 followed by spring 2010 while the lowest value was investigated during summer 2010. The low levels recorded during summer 2010 and 2011 may be attributed to high precipitation process of zinc salt from water column to sediment due the high temperature in summer season. The relatively high concentrations of Zn in cold seasons (winter and autumn) were reported by the low adsorption of Zn with temperature decreasing [54].

Generally, it was observed that, all studied beaches are not polluted with heavy metal and the reported concentrations of the investigated heavy metals are still far away below the acceptable international limits except for some stations which are polluted with Cu and Cd such as Cleopatra and El-Obayed stations.

3.1.1. Heavy Metal Pollution Index

In computing the HPI for the present study, the mean concentration values of the selected metals (Pb, Cd, Zn, Cu, Ni and Fe) have been taken into account. The value of Heavy Metal Pollution Index (HPI) was to be found in the range from 7.11 to 79.55. The highest value of HPI was found for water samples collected from Cleopatra Beach followed by El-Obeyad Beach (53.83) while the lower value was detected for Ageba Beach. The higher values of HPI may be attributed to sewage dumping into these areas. The HPI values of the samples within study area are found below the critical pollution index (100), above which the overall pollution level should be considered unacceptable [27] [28] [29]. This indicates the water is not critically polluted with respect to the investigated heavy metals (**Figure 2**). However, Cleopatra station is not very far from the critically pollution index value (79.55) (100).

3.1.2. Statistical Analysis

By applying the Spearman (non-parametric) rank order correlations, the results revealed that the dissolved form of Cu is correlated with both dissolved forms of lead and Zn (0.624 and 0.588 respectively). Furthermore, there is a good correlation between the dissolved form of Zn with the dissolved forms of Cd, Pb and Fe (0.822, 0.745 and 0.576 respectively) as showed by **Table 6**. This result revealed that these metals have the same source of contamination.

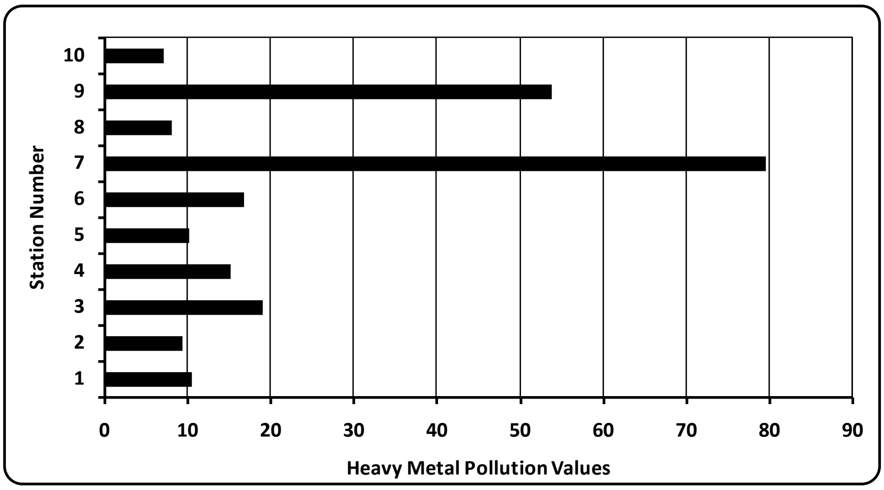

Figure 2. Percentage of heavy metal pollution index in water samples.

Table 6. Correlation in water and in sediment.

	Metal	Cd	Cu	Pb	Ni	Zn	Fe
Water	Cd	1					
	Cu	0.176	1				
	Pb	0.345	0.624*	1			
	Ni	0.285	0.248	0.200	1		
	Zn	0.152	0.588*	0.745*	0.454	1	
	Fe	0.042	0.321	0.321	0.430	0.576*	1
Sediment	Cd	1					
	Cu	−0.104	1				
	Pb	−0.205	0.878**	1			
	Ni	−0.229	0.515	0.310	1		
	Zn	−0.521	0.634*	−0.768**	0.406	1	
	Fe	−0.388	0.806**	0.644*	0.635*	0.5210	1

Note: *Correlation is significant at the 0.05 level; **Correlation is significant at the 0.01 level.

1) Principal component analysis

Multivariate analysis (Principal component analysis, PCA) has been applied on the data set for ten water samples and six variables (Cd, Cu, Pb, Ni, Zn and Fe). R-mode factor analysis with VARIMAX rotation with Kaiser Normalization, as well as the Eigen values was applied to the previous inorganic pollutants in the sediment samples. The PCA results of water data set are presented in **Table 7**. PC1, PC2 and PC3 account for 37.202, 23.082 and 16.975 % of the total variance, respectively. PC1 has high loadings of Cd, Zn and moderate loading of Fe. PC2 is loaded on Cu and Pb. PC3 is loaded on Ni only.

2) Cluster analysis

By applying, the cluster analysis for both the complete and centroid linkages. Similar relations between pollutants were obtained by the two studied clustering methods. The resultant dendrograms confirm the results obtained with PCA. Indeed, there were five clusters, which can be identified as follows: the first cluster (A) contains (Cd and Zn) at distance 1 (which was well correlated in Factor 1 in PCA); at a higher distance (about 14) Fe is fused with cluster (A) formed cluster (C) (which is also correlated in Factor 1 but with moderate value). The second cluster (B) contains (Cu and Pb) at distance 10 (which was well correlated in Factor 2 in PCA). At distance 22, Ni is fused with cluster (B) forming cluster (D) (which appear at Factor 3 alone) as illustrated by **Figure 3**. At distance 25 the two clusters (C and D) are fused forming the cluster (E).

3.2. Sediment

The distribution of investigated metals (Cd, Cu, Ni, Pb, and Zn) along Marsa-Matrouh Beaches (summer 2010 spring 2011) were reported in **Table 8** and **Table 9**.

The highest average concentration of Cd was noticed in autumn 2010 (1.235 ± 0.720 μg/g) followed by spring 2011 (0.754 ± 0.208 μg/g), while winter 2011 recorded the lowest average value for Cd (0.473 ± 0.501 μg/g). On the other hand, Agiba station recorded the highest values of Cd during summer and autumn 2010 (1.015 and 2.628 μg/g respectively) while Romel station recorded the highest Cd values during both winter and spring 2010 (1.841 and 1.115 μg/g respectively). The lowest value of Cd was detected at El-Gharam station during winter 2011 (0.164 μg/g).

The average concentrations of copper during the four seasons were decreased in the order: summer 2010 (5.976 ± 3.261 μg/g) > spring 2011 (5.256 ± 1.546 μg/g) > autumn 2010 (4.482 ± 0.727 μg/g) > winter 2011 (3.852 ± 0.574 μg/g). The lowest value of copper was observed at Cleopatra station during summer 2010 (1.525 μg/g), station Alam El-Roum during autumn 2010 (3.702 μg/g), El-Obayed station during winter 2010 (3.196 μg/g) and both stations El-Obayed and Mena-Hashish during spring 2011 (3.812 and 3.817 μg/g respectively). On the other hand the highest values of Cu were recorded at El-Fayroz station during both summer 2010 and winter 2011 (11.937 and 4.928 μg/g respectively) and at Romel station during both autumn 2010 and spring 2011 (6.234 and 4.928 μg/g respectively).

Table 7. VARIMAX normalization rotated factor loading for three factors obtained according to pollutants in the water samples along Matrouh Beaches.

Variable	Factor 1	Factor 2	Factor 3
Cd	**0.877**	−0.124	0.437
Cu	0.400	**0.746**	0.317
Pb	0.424	**0.682**	−0.466
Ni	−0.164	0.300	**0.556**
Zn	**0.834**	−0.507	0.071
Fe	**0.634**	−0.011	−0.443
Variance %	37.202	23.082	16.975
Cumulative %	37.202	60.284	77.259

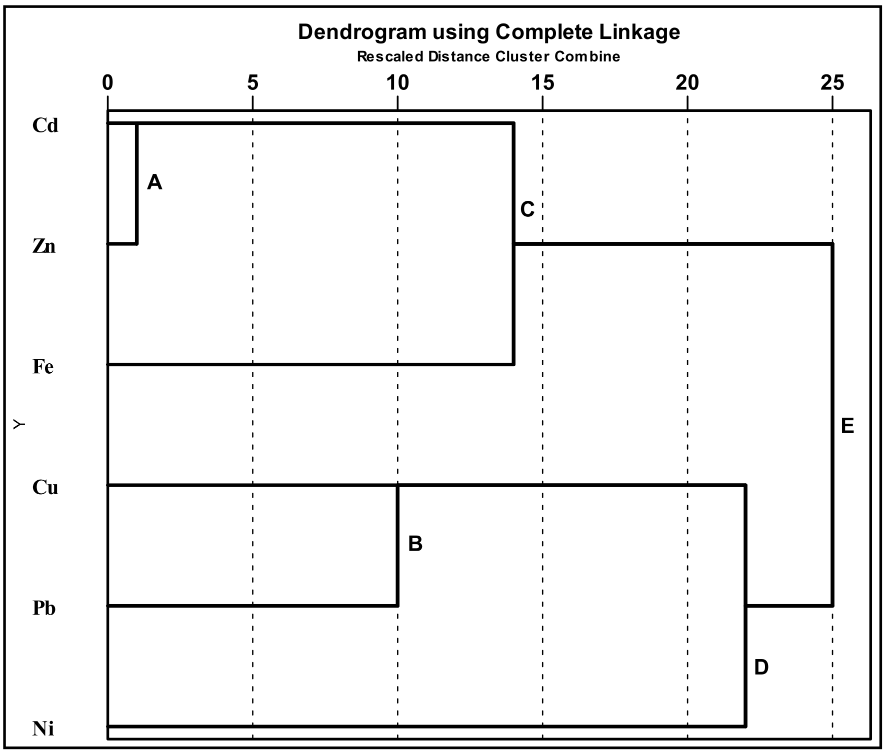

Figure 3. Dendogram obtained by hierarchical clustering analysis for metals in water samples.

The highest average concentration of iron was detected at summer 2010 (3886.404 ± 6946.007 µg/g) followed by autumn 2010 (474.277 ± 152.904 µg/g) while the lowest concentration was noted in spring 2011 (361.189 ± 204.498 µg/g). The highest value of iron was observed at Cleopatra station during summer 2010 (21260.351 µg/g), Alam El-Roum station during autumn 2010 (770.874 µg/g), El-Remelah station during both winter and spring 2011 (696.694 and 789.596 µg/g respectively). The lowest concentration of iron was detected at Agiba station during summer 2010 (99.859 µg/g), El-Gharam station during autumn 2010 (306.179 µg/g), El-Obayed station during winter 2011 (243.041 µg/g), and at Alam El-Roum station during spring 2011 (145.134 µg/g).

Table 8. Distribution of Cd, Cu and Pb (μg/L) concentrations in different sediment samples collected from Marsa-Matrouh beaches during 2010-2011.

Location	2010		2011		Annual Average
	Summer	Autumn	Winter	Spring	
Cadmium (μg/g dw)					
El-Remelah	0.311	1.238	0.500	0.549	0.649
Alam El-Roum	0.484	0.805	0.335	0.905	0.632
Mena-Hashish	0.517	0.868	0.601	0.716	0.676
El-Fayroz	0.417	0.629	0.277	0.514	0.459
Romel	0.433	0.777	1.841	1.115	1.042
El-Boseet	0.485	0.654	0.176	0.641	0.489
Cleopatra	0.604	0.833	0.347	0.854	0.659
El-Gharam	0.799	1.592	0.164	0.505	0.765
El-Obayed	0.521	2.329	0.192	0.982	1.006
Ageba	1.015	2.628	0.293	0.754	1.173
Min	0.311	0.629	0.164	0.505	0.459
Max	1.015	2.628	1.841	1.115	1.173
Average	**0.559**	**1.235**	**0.473**	**0.754**	**0.755**
Copper (μg/g dw)					
El-Remelah	4.472	4.326	3.823	5.998	4.655
Alam El-Roum	6.355	3.702	3.627	4.095	4.445
Mena-Hashish	3.546	4.811	3.907	3.817	4.020
El-Fayroz	11.937	4.463	11.000	5.521	8.230
Romel	9.862	6.234	4.603	8.977	7.419
El-Boseet	6.492	3.800	3.806	5.404	4.876
Cleopatra	1.525	8.800	8.000	9.000	6.831
El-Gharam	3.480	4.800	3.276	4.139	3.924
El-Obayed	3.759	4.450	3.196	3.812	3.804
Ageba	8.335	4.360	3.253	5.738	5.422
Min	1.525	3.702	3.196	3.812	3.804
Max	11.937	8.800	11.000	9.000	8.230
Average	**5.976**	**4.975**	**4.849**	**5.650**	**5.363**
Lead (μg/g dw)					
El-Remelah	13.713	17.029	3.517	12.858	11.779
Alam El-Roum	21.216	13.017	5.853	7.651	11.934
Mena-Hashish	13.685	13.321	5.170	8.318	10.124
El-Fayroz	14.152	33.363	19.909	22.593	22.504
Romel	29.754	15.799	18.820	19.554	20.982
El-Boseet	21.935	23.930	9.642	13.051	17.140
Cleopatra	22.369	24.233	15.371	9.710	17.921
El-Gharam	27.868	4.000	3.875	27.904	15.912
El-Obayed	18.203	4.189	6.213	10.714	9.830
Ageba	16.903	10.158	11.943	16.897	13.975
Min	13.685	4.000	3.517	7.651	9.830
Max	29.754	33.363	19.909	27.904	22.504
Average	**19.980**	**15.904**	**10.031**	**14.925**	**15.210**

Table 9. Distribution of Ni, Zn and Fe (μg/L) concentrations in different sediment samples collected from Marsa-Matrouh beaches during 2010-2011.

Location	2010		2011		Annual Average
	Summer	Autumn	Winter	Spring	
		Nickel (μg/g dw)			
El-Remelah	1.231	3.67	2.348	2.416	2.416
Alam El-Roum	2.452	2.347	2.300	2.366	2.366
Mena-Hashish	16.66	2.846	2.804	7.437	7.437
El-Fayroz	7.815	4.926	4.668	5.803	5.803
Romel	6.023	3.009	4.328	4.453	4.453
El-Boseet	2.251	3.049	2.540	2.613	2.613
Cleopatra	16.905	2.412	2.777	7.365	7.365
El-Gharam	2.448	1.775	2.024	2.082	2.082
El-Obayed	2.625	0.91	1.694	1.743	1.743
Ageba	3.35	3.623	3.341	3.438	3.438
Min	1.231	0.910	1.694	1.743	1.743
Max	16.905	4.926	4.668	7.437	7.437
Average	**6.176**	**2.857**	**2.882**	**3.972**	**3.972**
		Zinc (μg/g dw)			
El-Remelah	13.110	16.031	19.469	32.888	20.375
Alam El-Roum	15.951	14.119	13.252	28.237	17.890
Mena-Hashish	12.288	21.808	22.120	35.088	22.826
El-Fayroz	44.301	44.073	12.598	31.200	33.043
Romel	42.330	19.423	21.707	40.501	30.990
El-Boseet	22.914	24.668	12.354	91.598	37.884
Cleopatra	61.339	31.811	10.611	16.025	29.947
El-Gharam	11.993	18.423	10.974	38.939	20.082
El-Obayed	13.804	23.365	12.048	15.241	16.115
Ageba	16.228	18.696	15.939	16.845	16.927
Min	11.993	14.119	10.611	15.241	16.115
Max	61.339	44.073	22.120	91.598	37.884
Average	**25.426**	**23.242**	**15.107**	**34.656**	**24.608**
		Iron (μg/g dw)			
El-Remelah	1731.956	650.486	696.694	789.596	967.183
Alam El-Roum	591.729	770.874	453.669	145.134	490.352
Mena-Hashish	380.22	451.78	315.330	244.21	347.885
El-Fayroz	9018.639	426.673	397.551	365.981	2552.211
Romel	2819.793	460.001	426.372	419.115	1031.320
El-Boseet	551.939	392.369	371.593	402.411	429.578
Cleopatra	10260.351	603.325	546.361	235.757	2911.448
El-Gharam	266.114	306.179	274.466	217.22	265.995
El-Obayed	143.444	363.229	243.041	185.895	233.902
Ageba	99.859	317.851	541.473	606.568	391.438
Min	99.859	306.179	243.041	145.134	198.553
Max	10260.351	770.874	696.694	789.596	2911.448
Average	**2586.404**	**474.277**	**426.655**	**361.189**	**962.131**

Stations Mena-Hashish and Cleopatra recorded the highest values of Ni in summer 2010 (16.660 and 16.905 µg/g respectively) and spring 2011 (7.437 and 7.365 µg/l respectively). El-Fayroz station recorded the highest values during autumn 2010 and winter 2011 (4.926, 4.668 µg/g respectively). On the other hand, El-Obayed station recorded the lowest values of Ni during autumn 2010, winter and spring 2011 (0.910, 1.694, 1.743 µg/g respectively) while El-Remelah station recorded the lowest value during summer 2010 (1.231 µg/g). The highest mean value of nickel was detected during summer 2010 (6.176 ± 5.925 µg/g) while the lowest ones were recorded during winter 2011 (2.882 ± 0.966 µg/g) and autumn 2010 (2.857 ± 1.106 µg/g).

The average concentration of lead decreased in the order autumn 2010 (23.814 ± 10.654 µg/g) > summer 2010 (19.980 ± 5.718 µg/g) > spring 2011 (13.925 ± 6.133 µg/g) > winter 2011 (9.031 ± 5.116 µg/g). The lowest value of Pb was observed at El-Remelah station during winter 2011 (3.517 µg/g) while its highest value was detected at El-Obayed station during autumn 2010 (44.189 µg/g). Romel station recorded the highest values of Pb during summer 2010 and winter 2011 (29.754 and 18.820 µg/g respectively) while El-Gharam station 8 recorded the higher value during spring 2011 (27.904 µg/g). The lower values of Pb were recorded at Mmena-Hashish during summer 2010 (13.685 µg/g), at Alam-El-Roum and Mena-Hashish during autumn (13.017 and 13.321 µg/g respectively) and at Alam El-Roum during spring 2011 (7.651 µg/g).

The highest average concentration of zinc during the period of study was observed during spring 2011 (34.656 ± 22.092 µg/g) followed by summer 2010 (25.426 ± 8.852 µg/g) while the lowest was detected in winter 2011 (15.107 ± 4.428 µg/g). During summer the highest value was detected at Cleopatra station (61.339 µg/g), during autumn the highest value was observed at El-Fayroz station (44.073 µg/g), during winter the highest value was recorded at Mena-Hashish station (22.120 µg/g) but during spring the highest value was noted at El-Boseet station (91.598 µg/g). The lowest values of Zn were recorded at El-Gharam station during summer 2010 (11.993 µg/g), at Alam El-Roum station during autumn 2010 (14.119), Cleopatra and El-Gharam stations during winter 2011 (10.611 and 10.974 µg/g respectively), and El-Obayed station during spring 2011 (15.241 µg/g).

3.2.1. Assessment of Metal Contaminatio

1) Sediment quality guidelines (SQGs)

By comparison the present data by the different available SQGs, the concentrations of Cu, Ni, Pb and Zn in the four investigated seasons (summer 2010-spring 2011) are lower than the threshold effect concentrations revealing that there is no toxic adverse effect on the sediment-dwelling organisms along Marsa-Matrouh beaches. On the other hand, the concentration of Cd exceeding the threshold effect concentrations in 20%, 60%, 10% and 50% of investigated stations in summer 2010, autumn 2010, winter 2011 and spring 2011 respectively but still lower than the probable effect concentrations. This result revealed that the toxic adverse effect on the sediment-dwelling organisms from Cd may be fluctuated from 20% to 50%.

2) Hazard quotient

Calculated hazard quotient (HQs) for the Cd, Cu, Ni, Pb and Zn in the investigated sediments are shown in Figures 4-8. Based on the calculated values of PEC HQ, it can be recognized that all investigated metals had values lower than one. Thus it can be concluded that no frequent toxic adverse ecological effects are expected to occur with respect to these metals. TEC HQ calculated for all the investigated trace metals were lower than 1 except for Cd which showing higher value than 1, indicating the possibility of occurrence of toxic adverse ecological effects to benthic organisms from Cd. On the other hand, rare toxic adverse ecological effects are expected to occur with respect to Cu, Ni, Pb and Zn. These results were in agreement with the Sediment quality guidelines calculations.

3) Geoaccumulation index

By apply Muller equation on the annual average concentration for all stations uder investigation, the sample percentages according to Müller's classes [41],

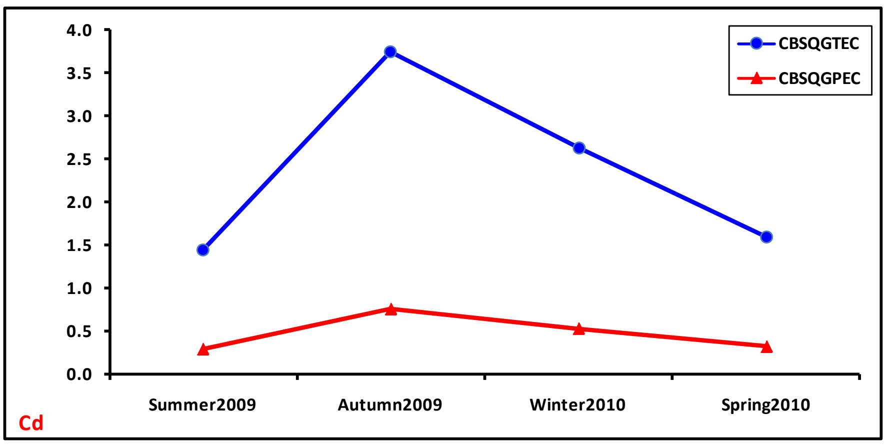

Figure 4. CBSQTEC and CBSQPEC for Cd in sediment samples collected from Marsa-Matrouh beaches.

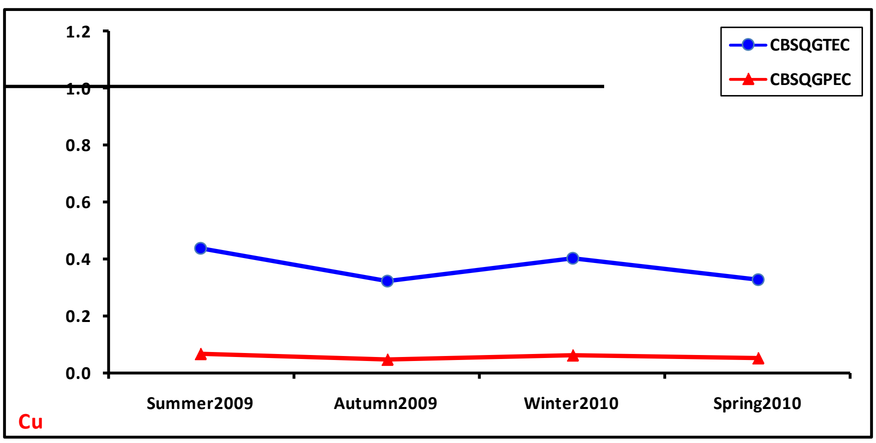

Figure 5. CBSQTEC and CBSQPEC for Cu in sediment samples collected from Marsa-Matrouh beaches.

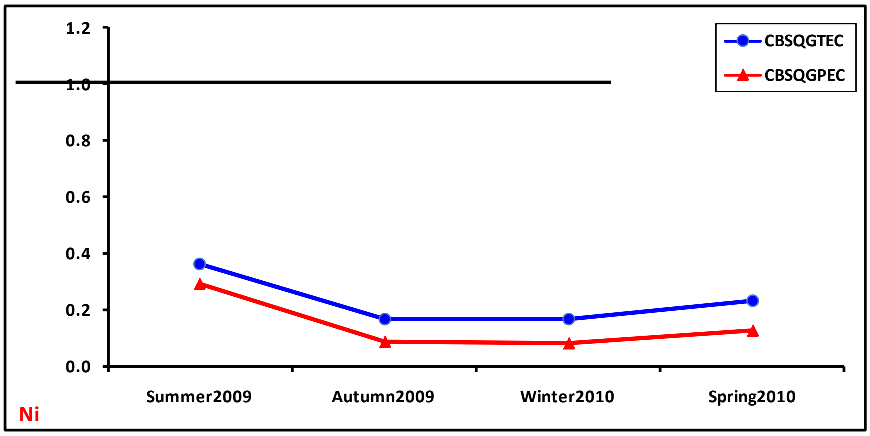

Figure 6. CBSQTEC and CBSQPEC for Ni in sediment samples collected from Marsa-Matrouh beaches.

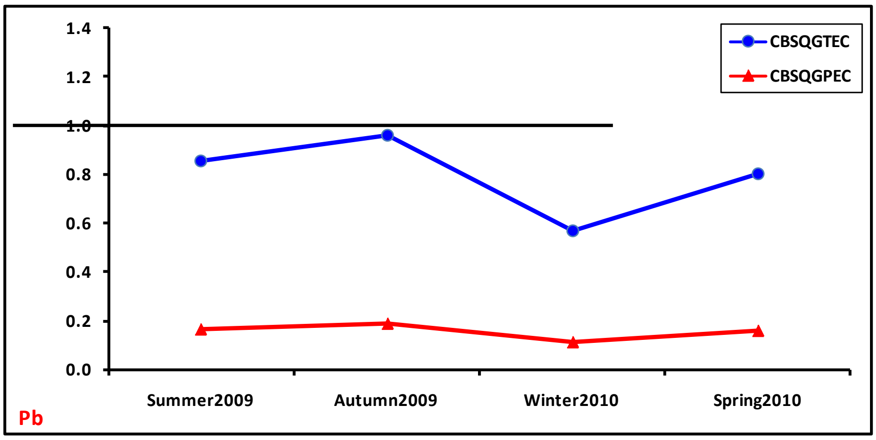

Figure 7. CBSQTEC and CBSQPEC for Pb in sediment samples collected from Marsa-Matrouh beaches.

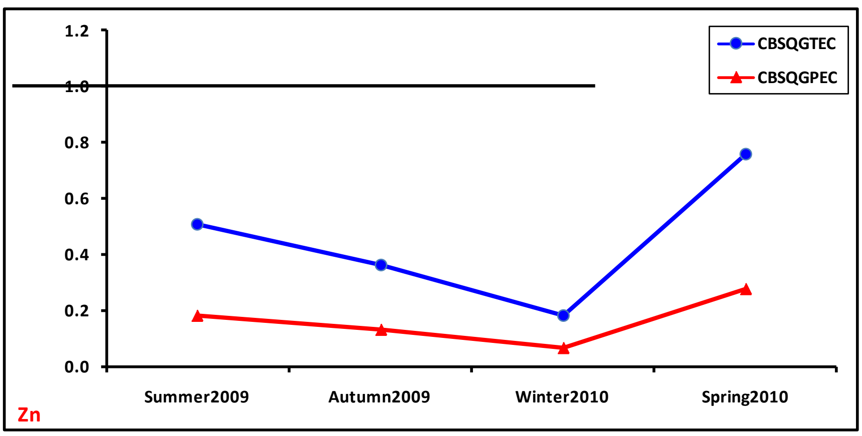

Figure 8. CBSQTEC and CBSQPEC for Zn in sediment samples collected from Marsa-Matrouh beaches.

showed that all sediment samples fall in class 0 for Cu, Fe, Ni, Pb, and Zn indicating that Marsa-Matrouh City is not contaminated area for these metals during the period of study (Table 10). On the other hand, 80% of stations recorded fall in class 2 indicating that these stations are moderately contaminated with Cd and the other two stations (Stations 4 and 6) fall in class zero and classified as uncontaminated with Cd.

3.2.2. Statistical Analysis

By applying the Pearson rank order correlations, the results revealed that the Cu in sediment is well correlated with Pb and Zn (0.878 and 0.634 respectively). Furthermore, there is a correlation between the Zn and Pb (0.768), between Fe and Cu, Pb, Ni (0.806, 0.644, 0.635 respectively) as showed by Table 6. On the other hand, there are significant correlations between each of dissolved form of Fe and Ni and their corresponding concentration in the sediment (0.574 and 0.551 respectively).

1) Principal component analysis

Multivariate analysis (Principal component analysis, PCA) has been applied on the data set for ten sediment samples and six variables (Cd, Cu, Pb, Ni, Zn and Fe). R-mode factor analysis with VARIMAX rotation with Kaiser Normalization, as well as the Eigen values was applied to the previous inorganic pollutants in the sediment samples (Table 11). PC1 and PC2 account for 54.608 and 23.013 % of the total variance, respectively. PC1 has high loadings of Cu, Pb and Fe; moderate loading of Ni and Zn. PC2 is loaded on Cd only.

2) Cluster analysis

By applying, the cluster analysis for both the complete and centroid linkages. Similar relations between pollutants were obtained by the two studied clustering methods. The resultant dendrograms confirm the results obtained with PCA. Indeed, there were five clusters, which can be identified as follows: the first cluster (A) contains (Cu and Pb) at distance 1, at a higher distance (about 5) Fe is fused with cluster (A) formed cluster (B). At distances 7 and 11, Zn and Ni are also fused with cluster (A) forming cluster (D). All these clusters appear at Factor 1. At very high distance 25, Cd is fused with cluster (D) forming cluster (E) (Figure 9).

Table 10. Geo-accumulation Index of Cd, Cu, Fe, Ni, Pb and Zn.

Station	Igeo					
	Cd	Cu	Fe	Ni	Pb	Zn
1	1.114	−2.067	−4.334	−3.013	−0.934	−2.044
2	1.075	−2.133	−5.314	−3.043	−0.915	−2.231
3	1.171	−2.278	−5.809	−1.391	−1.152	−1.880
4	0.615	−1.539	−2.676	−2.022	−0.609	−1.346
5	1.796	−1.394	−4.241	−2.131	−0.101	−1.439
6	0.704	−2.000	−5.504	−2.900	−0.393	−1.149
7	1.136	−2.421	−1.784	−1.405	−0.328	−1.488
8	1.351	−2.313	−6.196	−3.227	−0.104	−2.064
9	1.746	−2.358	−6.381	−3.484	−0.182	−2.382
10	1.967	−1.847	−5.639	−2.504	−0.067	−2.311

Table 11. VARIMAX normalization rotated factor loading for three factors obtained according to pollutants in the sediment samples along Matrouh Beaches.

Variable	Factor 1	Factor 2
Cd	−0.095	**−0.977**
Cu	**0.976**	−0.017
Pb	**0.890**	0.105
Ni	**0.612**	0.230
Zn	**0.681**	0.531
Fe	**0.828**	0.280
Variance %	54.608	23.013
Cumulative %	54.608	77.621

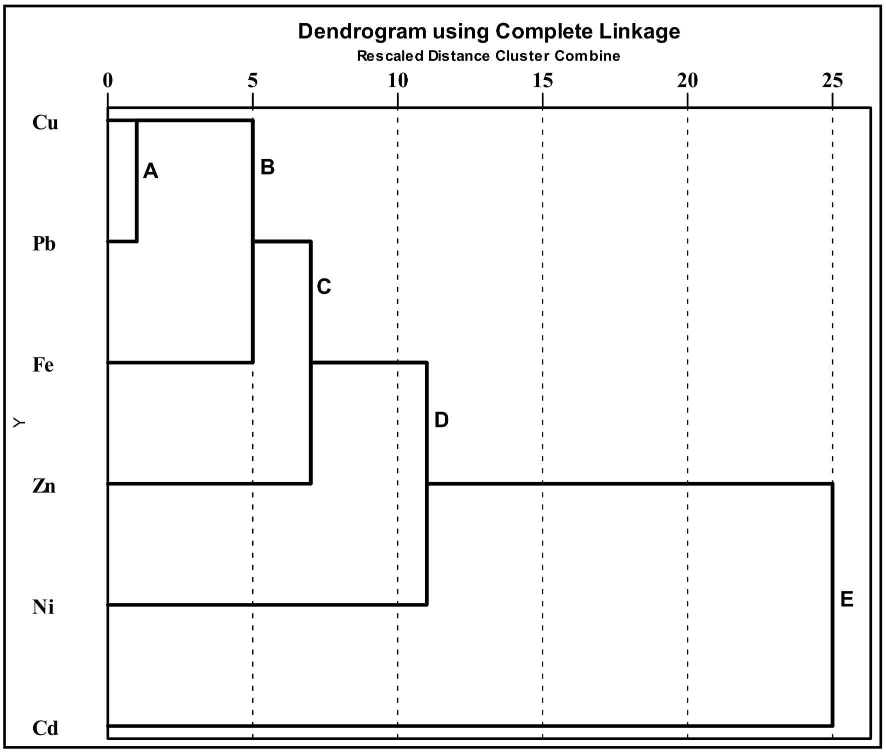

Figure 9. Dendogram obtained by hierarchical clustering analysis for metals in sediment samples.

4. Conclusion

Sediments are important hosts for trace metals and as such should be included in environmental monitoring programs. The investigation of sediments in Marsa-Matrouh city revealed that the investigated area is not enriched with Cu, Ni, Pb, Zn and Fe. On the other hand some locations along the city beach are relatively contaminated by Cd in their sediment samples but still lower than the frequent adverse ecological effects for benthic marine organisms. The spatial distribution of the different investigated metals showed that the area is influenced by the wastewaters discharged specially in summer season where the number of visitors increases to more than one million. Based on the above the results, establishment of few routine monitoring sites, especially near the major sources of pollution must be done. Prevention, reduction and control of pollution caused by discharges from land-based activities and shipping activities could be greatly helpful in the improvement and the future management of the Marsa-Matrouh beaches.

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