Pollution, 4(4): 759-774, Autumn 2018
DOI: 10.22059/poll.2018.253426.444
Print ISSN: 2383-451X Online ISSN: 2383-4501
Web Page: https://jpoll.ut.ac.ir, Email: jpoll@ut.ac.ir

Ecological Risk Assessment of Heavy Metals in Hurghada Coastal Sediment, Red Sea, Egypt

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Receive: 8.3.2018 Accepted: 6.6.2018

ABSTRACT: Twenty samples of Ø3, Ø4 and Ø5 (fine fractions) were collected from four coastal areas (Sheraton, Magawish, Marina and Al mina) in Hurghada, Egypt. Total organic matter (TOM), total organic carbon (TOC) and heavy metals were estimated in the recommended fractions. Results showed that Fe and Pb recorded the highest concentrations with 71.7 and 39 mg/kg respectively. Marina area fractions has the highest carbonate content varied between 50.7 and 65.7 while Magawish area fractions have the lowest organic matter content and carbonate between 10% and 9.40%. On the other hand, Sheraton area has the highest organic matter content. The Principal Component Analysis (PCA) indicate the anthropogenic sources of Zn and Pb at the Red Sea coast based on Sediment Quality Guidelines (SQGs). According to the Enrichment factor (EF) and the geo-accumulation factor (Igeo), Cu and Pb were the highest enriched elements due to anthropogenic contamination; consequently, the studied areas were classified as moderately to highly contaminate by Cu and Pb at Hurghada.

Keywords: Enrichment factor, Contamination Factor, Pollution Loading; Geo-accumulation.

INTRODUCTION

The Red Sea belongs to category of land-locked seas that have very restricted water exchange (Idris et al., 2007). This partial isolation condition makes this body of water vulnerable to impact of land-based pollution. For a long time, the Red Sea environment was regarded relatively unpolluted (Hanna & Muir, 1990). Heavy metals Pollution is one of the global environmental problems because of their toxicity, environmental persistence, non-biodegradable nature and incorporation into food

chains (Förstner & Wittman, 1983 and Gargouri et al., 2011). For these reasons, a lot of effort is expanded to assess their availability, toxicity and ecological risk to marine organisms (Salem et al., 2014). Sediments are the principal sink of heavy metals in the aquatic coastal system, but under certain chemical and physical conditions, metals can readily release into the water column again and become a source of metal to marine organisms (Dickinson et al., 1996; Dar, 2014;

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Esmaeilzadeh et al., 2016; Farsad et al., 2011 and Vaezi et al., 2014).

Therefore, the distribution of heavy metals in the sediments can serve as environmental indicator of current and past conditions of the pollutant discharged in the surface marine sediments (Förstner & Salomons, 1980; Abu-Hilal & Badran, 1990; Esmaeilzadeh et al., 2016; Vaezi et al., 2015 and Vaezi et al., 2016). Metals are not equally distributed in the different sediment fractions, for that reason, heavy metals were widely determined in the finer grains in order to minimize the variation effect (Salomons & Förstner, 1984). Finer particles usually contain high concentrations of heavy metals due to possessing large surface area and high association with clay and organic matter (Irvine & Birch, 1998; Yu et al., 2012). It is important to evaluate the ecological risk of heavy metals in the fine sediments not only due to their high content of heavy metals but also because they can easily move by the wave wind moving and currents to adjacent places which may host biologically sensitive communities (Karbassi et al., 2017; Karbassi, 2017; Karbassi & Nasrabadi, 2017; Dar et al., 2016 and Vaezi et al., 2016).

The assessment of heavy metal concentrations alone cannot describe the ecological risk to the marine environment or evaluate the contribution ratios from terrestrial and anthropogenic sources (Zhu et al., 2012). Therefore, other methods were adopted to evaluate the biological and ecological risk of heavy metals in marine sediments such as sediment quality guidelines (SQGs), pollution loading index (PLI), enrichment factor (IF) and geo-accumulation Index (Igeo), (Zrelli et al., 2015 and Hassaan et al., 2017).

The main objective of the present work is to study the heavy metals concentrations from the land-based activities and their environmental risk in Hurghada coastal sediments.

MATERIAL AND METHODS

The area of study is covering the northern east of Hurghada coast at the Red Sea. It is located between 27º150º30´N and 33º56´0ººE (Fig. 1). The distance from the coast to the Giftun Islands is about (11-20 km wide) and is surrounded by Desert Mountains with negligible inputs of fresh water or run off. This area has a hot and dry climate with average temperature ranged between 21ºC and 27ºC in winter and summer, respectively. The net evaporation in the area along the coast is 0.5-1cm/day. Samples were taken seasonally (summer and autumn) from the northern east coast of Hurghada. The area of study is located between Hurghada coast and Giftun Island about 15 km away from the coast. The samples were collected from 20 stations distributed in four transects, Al Mina (A-1:A2), Marina (M-1: M-6), Sheraton(S-1: S-6) and Magawish (G-1: G-6). 100 g of air-dried sediment samples were sieved each one phi (Ø) interval to obtain textural properties according to (Folk, 1974). Seven fractions were distinguished: gravel (Ø−1 > 2.00 mm), very coarse sand (Ø0 = 2.00 to 1.00 mm), coarse sand (Ø1 = 1.00 to 0.50 mm), medium sand (Ø2 = 0.50 to 0.25 mm), fine sand (Ø3 = 0.250 to 0.125 mm), very fine sand (Ø4 = 0.125 to 0.063 mm) and mud (silt & clay) (Ø5 < 0.063 mm). For the analysis of carbonate content and total organic matter, 10 g of the dried bulk sediments were completely grinded. The carbonate content and TOM were determined according to (Gross, 1971 and Dean, 1974).

Eight heavy metal (Co, Cu, Zn, Ni, Cd, Mn, Fe and Pb) were measured in the finest fractions of samples (Ø3, Ø4 and Ø5). 0.5 g of each fraction was digested with a mixture of HNO_3 and $HClO_3$ to near dryness then diluted with de-ionized distilled water (DDW) to 25 ml and filtered to remove residuals (Chester et al. 1994). The proposed metals were

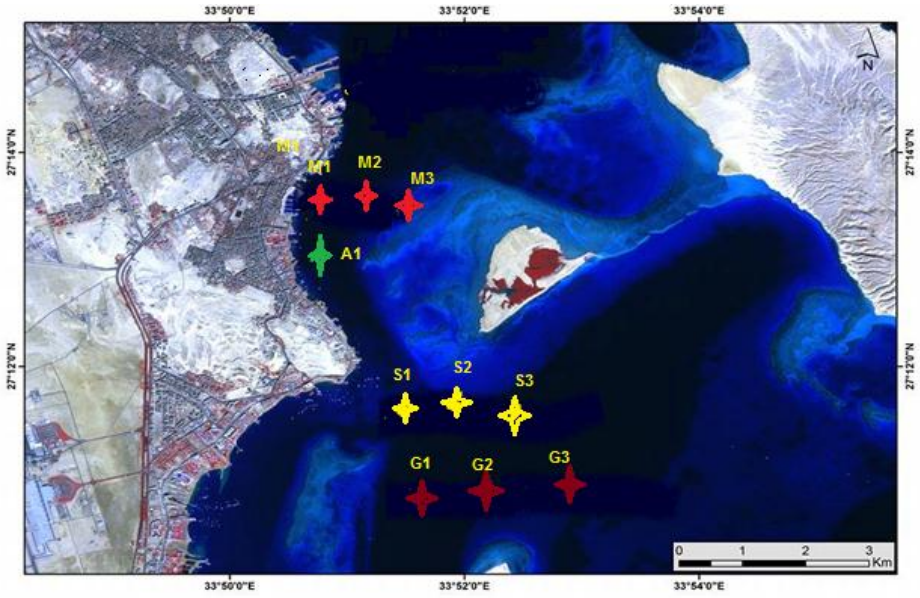


Fig.1. The four studied sites along Red Sea coast (Al Mina, Marina, Sheraton and Magawish).

determined in these extracts using flame atomic absorption spectrophotometer (AAS, GBC-932). For maximum accuracy, samples were done in triplicates and the differences were always less than 3 %. The results were expressed in (mg/kg). All statistics were performed using graph pad Prism. Pearson's correlation matrix and principal component analysis (PCA) were also used.

RESULTS AND DISCUSSIONS

Many characteristics of the marine sediments such as texture, organic matter and carbonate content may manipulate the distribution of metals in sediments (Chen et al., 2007). At Marina sites, the fine fractions percentages (Ø3, Ø4 and Ø5) varied between 1.1% and 28% in M-4, while in Magawish the fine fractions percentages fluctuated between 1 in G-2 and 28% in G-3. On the other hand, at Sheraton sites the fine fractions percentages varied between 1% in S-2 and 57% in S-5, meanwhile at Al Mina sites these percentages varied between 1.68% and 12.1% at both A-2 and A-1, (Table 1) and (Fig. 2). The high percentages of the fine fractions at the four studied sites indicating the different sources of depositions mostly from the maritime activities, terrestrial runoff, phosphate shipments and the nearby land based activities.

The percentages of carbonate and TOM at the studied areas were listed in (Table 2). The studied stations at Marina sector recorded the highest percentages of carbonates, which varied between 50.7 and 65.7% indicating that the biogenic source materials which constituted significant portion of the sea sediments; Magawish station recorded significant variations in the carbonate percentages between 10% and 9.40% while the carbonate percentage was less than 50% at Al Mina station.

The above-mentioned data illustrated the biological productions in Marine offshore area along the Red Sea coast have a strong contribution in the high carbonate percentage; while the effects of maritime activities and terrestrial runoff of terrigenous materials were the main reasons in carbonate percentage declining at Marina ports. Considerable variations were observed in TOM contents at Magawish and Sheraton sites due to the local effects of the anthropogenic effluents. At Magawish site, it was varied between 3.83% in G-1 and 9.7% in the G-4, while at Sheraton varied between 2.63% in S-1 and

3.83% at S-3. On the other hand, Marina station recorded insignificant variation in TOM percentages, which ranged from 2.79 at M-4 to 11.5% M-6. The recorded variation in the TOM of the studied stations at Red Sea coast is usually related to the local hydrodynamics, algal and sea grass flourishing, the terrigenous and domestic wastewater. (Mansour et al., 2013) attributed the recorded high percentage of TOM at Hurghada to the sea grass patches and the algal bottom faces.

Table 1. The grain size distribution in the four studied areas

Site	Season	C.sediment % Ø0	M.sediment % Ø1	F.sediment % Ø2	f.sediment % Ø3	very.f sediment % Ø4	mudfraction% Ø5
M-1		23.5	65.3	21.3	25.1	9.5	1.8
M-2	Summer	28.8	40.3	31.7	18.0	13.6	6.9
M-3		20.9	34.2	12.5	14.9	10.7	3.5
M-4		12.1	50.4	37.5	28.4	8.0	1.1
M-5	Autumn	27.6	24.3	48.1	22.5	17.8	8.0
M-6		15.6	23.6	40.1	21.5	13.6	5.6
G-1		14.9	9	20.2	17.0	7.0	1.0
G-2	Summer	20.2	19.2	35.8	15.0	14.9	9
G-3		14.9	9	20.2	28	8	1
G-4		23.2	52.2	24.6	14.9	8.5	1.14
G-5	Autumn	20.5	25.2	19.5	11.2	6.2	5.5
G-6		7.4	18.4	12.3	20	11.2	4.6
S-1		12.8	36.0	52.4	26.0	24.2	2.1
S-2	Summer	11.2	16.2	16.6	16.1	9.3	1.0
S-3		15.5	30.8	33.3	20.5	43.3	8.2
S-4		12.8	36.0	52.4	20.5	43.3	8.2
S-5	Autumn	13.3	7.8	88.9	24.9	57.5	6.5
S-6		10.5	15.5	40.5	18.1	35.5	4.5
A-1	Summer	8.04	1.07	12.1	12.1	6.2	3.5
A-2	Autumn	6.8	2.5	10.1	10.5	5.9	1.68

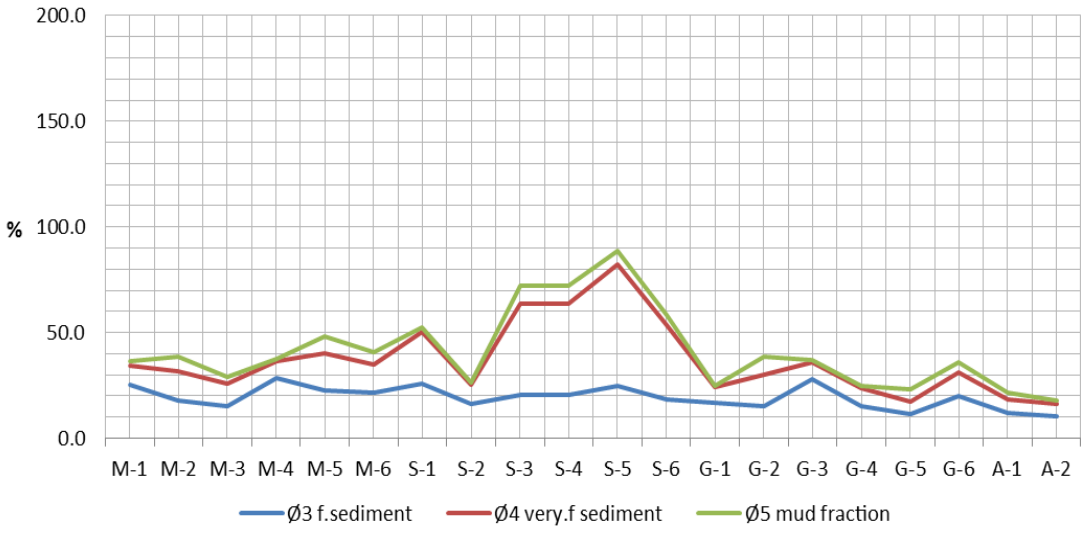


Fig. 2. The Distribution patterns of the different size fractions and the percentages of the finest fractions (F%) Ø3, Ø4 and Ø5 at the studied stations.

Table 2. The averages of carbonates%, TOM% and Heavy metals (mg/kg) in fine sediment fractions at the area of study

Sites	Season	TOM %	CO3 %	Pb	Cd	Co	Ni	Zn	Mn	Fe	Cu
M-1		10.1	65.7	39	1.1	9.17	4.78	15.62	31.92	14.75	7.1
M-2	Summer	6.8	47.03	21	5	20.77	7.58	11.25	19.2	5	45
M-3		6.2	50.7	30	1.2	17.01	7.8	6.75	6.27	2.75	5.62
M-4		2.79	60.3	30	ND	14.25	6.54	6.52	8.55	2.64	4.72
M-5	Autumn	4.6	63.5	25	1.35	5.92	11.12	19.58	40.52	71.72	10.35
M-6		11.5	50.5	22	2.975	15.52	16.9	8.35	10.4	7.54	6.55
G-1		3.8	45.1	12	0	26.7	9.8	19.2	31	48	5
G-2	Summer	3.7	65.8	37	5.025	22.4	8.77	8.09	8.02	6.35	5.62
G-3		8.8	9.02	ND	1.1	14.3	12.7	41.7	11.3	14.74	47.55
G-4		9.7	14.5	28	ND	ND	20.77	38.17	9.6	5.57	4.62
G-5	Autumn	6.8	30.6	ND	0.6	19.45	6.97	9.08	6.67	ND	0.575
G-6		4.8	18.6	14	14	9.6	5	5.62	9.08	14	ND
S-1		2.6	18.8	40	2.475	15.55	15.55	12.25	14.01	170.8	7.58
S-2	Summer	2.8	62.5	19	0.075	ND	ND	89.25	180.25	33	9
S-3		8.8	53.0	45	4.125	24.35	15.52	8.22	6.6	4.02	3.67
S-4		2.5	32.3	5	16.05	21.05	11.25	35.5	9.02	28.42	14.72
S-5	Autumn	8.3	33.6	2.5	19	14	9	14	5.62	7.1	8.09
S-6		5.6	32.2	25	15.62	12.7	4.02	31.92	12.25	3.67	41.7
A-1	Summer	4.3	19.2	ND	0.53	7.175	ND	45.07	14	112.25	48.07
A-2	Autumn	3.3	17.5	24	22.4	0.53	41.7	25	5	2.975	2.75

ND = Not Detected

It was observed that, there is a great distinction in the distribution of granules in the studied areas along the Red Sea coast and this distribution could be a major reason for the high level of accumulated heavy metals in the sediment of Red Sea coast.

Generally, the fine fractions in all stations was the essential heavy metal carrier. At Marina sites, there was a clear variation in the distribution of granules that differs from medium fractions (Ø1+Ø2) with a variation between 23.6 at M-6 and 65.3% at M-1 to the fine fraction (Ø3+Ø4+Ø5) with a variation between 12% at M-3 to 48% at M-5.

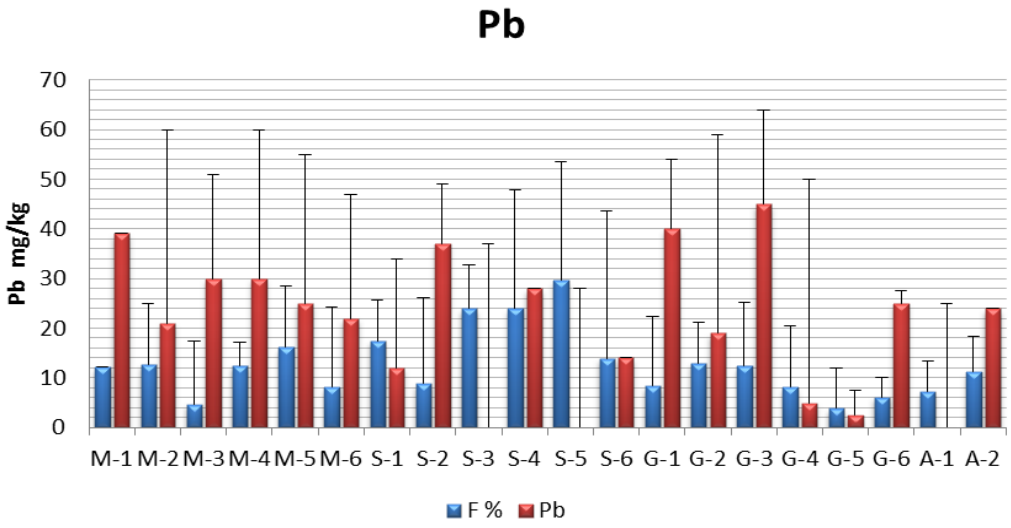
The main heavy metals that recorded the highest values in Marina station were Fe and Pb which record 71.7 and 39 mg/kg at M-5 and M-3 respectively. (Madkour & Dar 2007) and (Dar et al., 2016b) certified the high accumulation of heavy metals in the Marina sediments to the repairing, maintaining, antifouling paint remains and ship constructing.

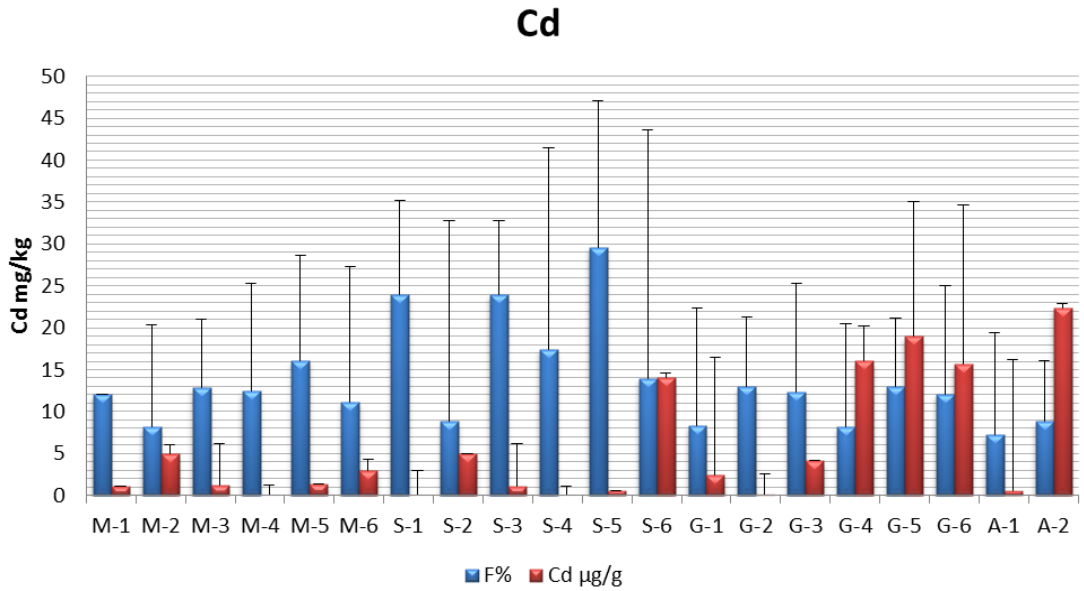
At Sheraton area fine sediment fraction (Ø3+Ø4+Ø5) recorded the highest percentages as it ranged between 16 at S-2 and 88% at S-5. Mn, Zn and Fe showed the highest concentrations in this fraction in S-2 and S-1 respectively in a sequence of 180.25, 89.53 and 170 mg/kg. Dar et al. (2016b) concluded that the high Zn and Mn at Sheraton marine area attributed to the high quantities of pollutants enriched with Zn from antifouling paint remains while, Mn derived from the terrestrial runoff from the phosphate shipments.

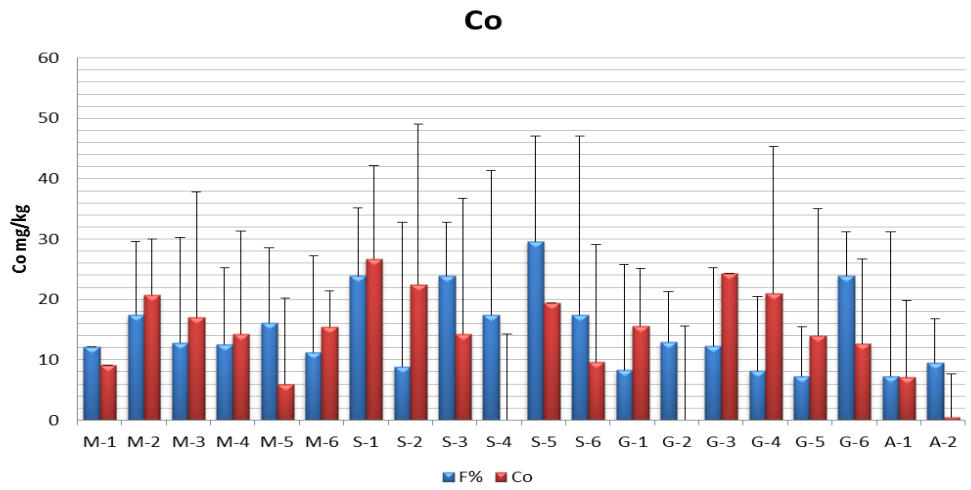
Zn and Cu showed the highest concentration in Magawish stations with 38.17 and 47.55 mg/kg respectively at G-4 and G-3 and they were found in the leachable fine fraction (Ø3+Ø4+Ø5). It has been found that Magawish area fine fraction distribution ranged between 12% at G-6 and 35% at G-2. The marine area of Al Mina recorded the highest values of Fe 112.25 mg/kg at the fine fractions (Ø3+ Ø4+ Ø5) this is may be attributed to the terrestrial runoff from the subsurface wastewater and shipping activities.

It was interesting to observe that the distribution of Fe and Mn were generally lower in Marina area (significant in most cases at $p \leq 0.05$) comparing to Sheraton and

Magawish stations (Fig. 3). In consistence with our results, previous work showed general elevation levels of Fe and Mn in these sites, which were used for shipping of ores, especially ports as, recorded in Sheraton and Magawish. Mn and Fe are essential elements and have relatively low toxicology to aquatic organisms. The values of Fe in the present study were significantly lower than that in Port Kembla harbor, Australia He and (Morrison, 2001). While, the recorded Mn values were comparable with those reported in Sydney Harbor (Irvine & Birch, 1998) and Victoria Harbor (Wong et al., 1995 and Tang et al., 2008) but were much lower than Hamilton Harbor (Poulton et al., 1996). The heavy metals availability in this study was below the recorded levels in other harbors around the worldwide (Table 3).






Co
Co mg/kg
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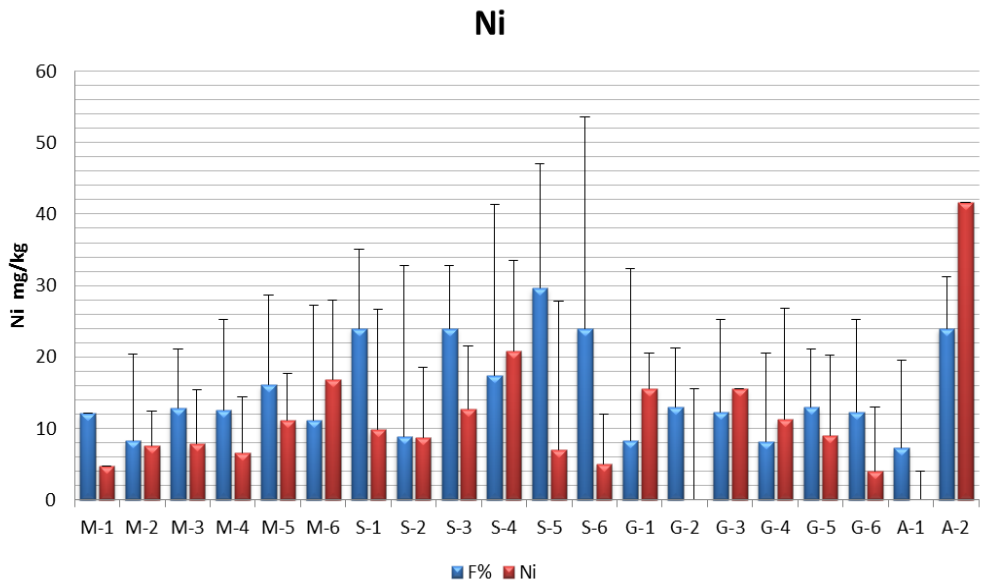
30
20
10
0
M-1 M-2 M-3 M-4 M-5 M-6 S-1 S-2 S-3 S-4 S-5 S-6 G-1 G-2 G-3 G-4 G-5 G-6 A-1 A-2
F% Co


Ni
Ni mg/kg
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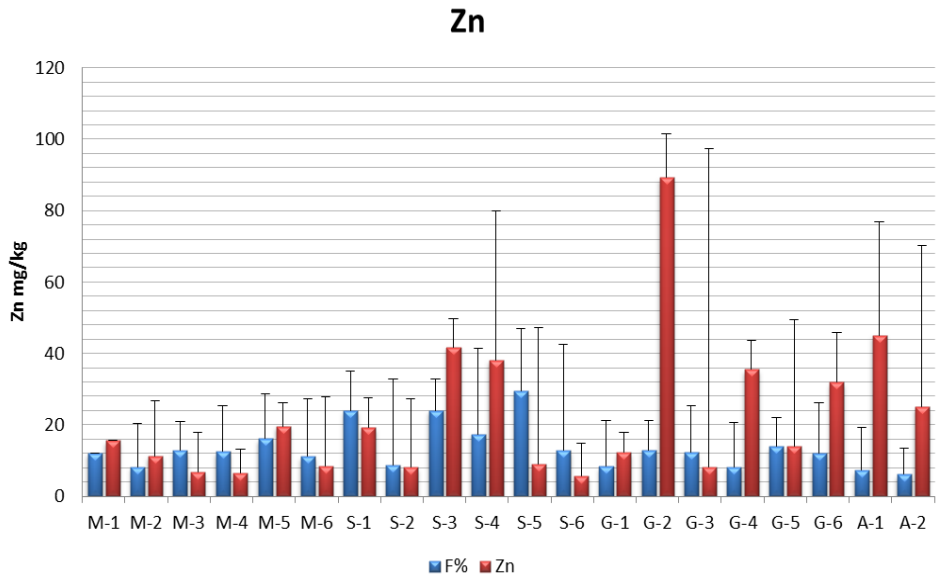
M-1 M-2 M-3 M-4 M-5 M-6 S-1 S-2 S-3 S-4 S-5 S-6 G-1 G-2 G-3 G-4 G-5 G-6 A-1 A-2
F% Ni


Zn
Zn mg/kg
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M-1 M-2 M-3 M-4 M-5 M-6 S-1 S-2 S-3 S-4 S-5 S-6 G-1 G-2 G-3 G-4 G-5 G-6 A-1 A-2
F% Zn

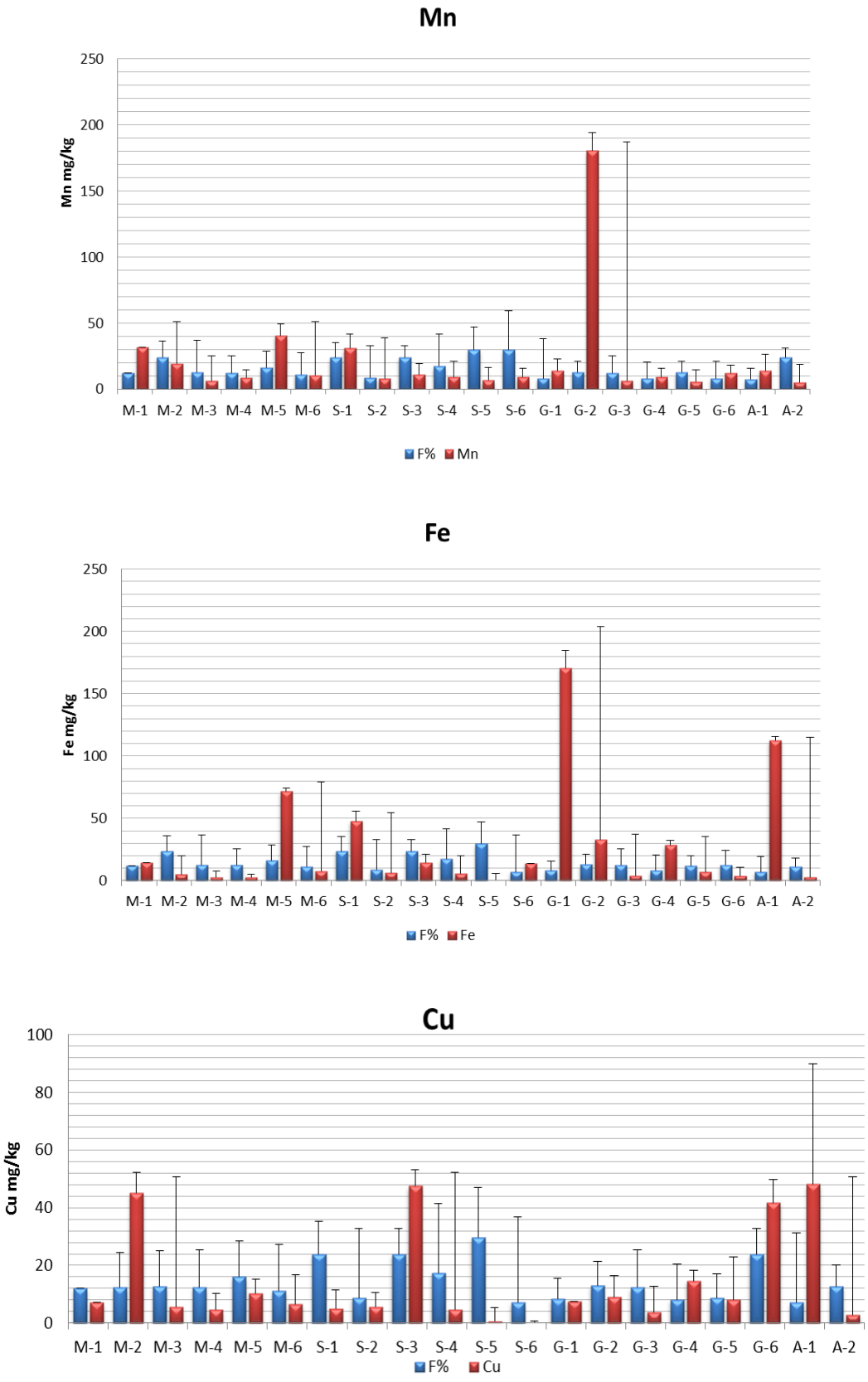

Fig. 3. The average concentrations of the eight studied Heavy metals and it's Percent in the fine fractions (F%), (Ø3+Ø4+Ø5).

Table 3. A Comparison between the heavy metal (mg/Kg) levels in the present study and the other worldwide previous studies.

Site	Stations	Pb	Cd	Co	Ni	Zn	Mn	Fe	Cu	Reference
Red Sea Coast	Sheraton	39.9	3.11	19.3	17.1	10.7	10.78	29.7	4.58	Present study
	Magawish	8.08	1.24	7.58	6.02	45.5	76.3	20.7	7.63	present study
	Marina	25.7	1.43	11.36	9.26	13.7	20.4	27.1	6.6	present study
	Al Mina	0	0.25	0	0.26	17.3	20.1	43.9	19.8	present study
Suez Gulf	Suez01	3.74	0.12	1.76	7.45	38.8	145.6	1.72	1.85	Fo¨rstner and Wittmann, 1983.
	Suez05	2.21	0.14	1.54	5.8	12.1	45.2	1256	2.01	Beltagy, 1984.
	El Tour	1.92	0.026	53.4	2.64	10.8	52.8	6163	1.31	Fo¨rstner and Wittmann, 1983
Aqaba Gulf	Newbia	3.45	0.063	4.65	4.502	16.68	126.4	3661	1.37	El Nemr et al., 2013.
	Dahab	3.24	0.027	39.7	4.23	30.1	453.9	10413	1.97	El Nemr et al., 2013.
	Ras Mohamed	2.59	0.032	4.4	3.39	12.7	64.01	16666	0.94	El Nemr et al., 2013.
Red Sea Proper	Noif-Hurghada	2.45	0.089	1.42	5.71	17.79	51.7	831.8	0.958	CCME, 2002.
	Sheraton	4.34	0.032	1.94	10.5	22.6	52.3	1721	1.87	FAO,1983.
	Safaga	5.12	0.104	4.54	10.05	38.9	20.6	5381	1.804	CCME, 2002.
	El Quiser	4.27	0.307	7.78	31.5	39.06	169.2	5048	3.652	CCME, 2002.
	Marsa-Alam	2.85	0.061	15.08	72.4	39	20.2	9946	9.066	El Nemr et al., 2013.
	Bir-Shelaten	2.86	0.086	2.65	2.68	16.07	36.6	1175	1.48	El Nemr et al., 2013.
Trade Harbours (south Korea)		9.9-41.2	.03-,22	ND	10.3-28.8	47-112	ND	ND	8.6-28.2	Choi et al., 2012
Red Sea Harbor		<0.01-101	<0.01-4.19	<0.01-5.85	13.9-91.4	9.1-330	9.3-306	551-7483	10.1-298	Metwally et al., 2017

ND = not detected

For studying the sediment quality guidelines and Ecological Risk indices were investigated. Biological adverse effects were evaluated by comparing levels of t heavy metals with the numerical sediment quality guidelines (SQG's) proposed by (Persuad et al., 1992). The contamination status was assessed by comparing the results of present study with available data given in previous literatures for leachable heavy metals in sediments from various worldwide ports.

Several indices have been applied to assess the ecological risk of heavy metals in various aquatic environments (Fujita et al., 2014) including; metal pollution load index (MPI) (Tomlinson et al., 1980), enrichment factor (EF) (Salomons & Förstner, 1984) and the geo-chemical index (Igeo) (Müller, 1979). The interpretation of these indices is depending on the comparison with a background levels. It is very difficult to establish Bn values for the sediments of some studied areas, as a reference. So, in some works Bn value (references point) has been taken as equal to the metals concentration in shale rocks (Hassaan et al., 2016).

Metal pollution load index (MPI) is a simple method to describe the total effect of metal contamination. The values (>1) showed the gradual deterioration in sediments quality (El-Said and Youssef, 2013). MPI was obtained from the following formula:

$$MPI = (CF_{Co} \times CF_{Cu} \times CF_{Zn} \times CF_{Ni} \times CF_{Cd} \times CF_{Mn} \times CF_{Pb} \times CF_{Fe})^{1/n}$$

Where, the contamination factor (CF) is the concentration of metal in obtained sample (C metal) divided by the background concentration (C background in Shale rocks) of the same metal and (n) is the number of measured metals.

The values of MPI at the area of study ranged between (0 and 1), (Table 4). The highest MPI values (1) found in Sheraton area followed by Marina area while the lowest MPI values (0) were recorded in Magawish and Al mina areas. The highest

contamination values of Pb, Cd and Co were recorded at both Sheraton and Marina locations with values of (18.29, 11.38 and 7.90) respectively, while Fe, Zn, Mn and Cu has the lowest contamination effects, (Table 4).

on the other hand, the enrichment factor (EF) represents the actual contamination level in sediments since it is differentiates between natural and anthropogenic sources of metals (Chen et al., 2007 and Amin et al., 2009). EF was calculated from the equation:

$EF = (Metal / Fe)_{sample} / (Metal / Fe)_{(Bn)\ Background}$

Table 4. Contamination factor (CF) and MPI in different sites of area of study

Sites	Season	Pb	Cd	Co	Ni	Zn	Mn	Fe	Cu	MPI
M-1		8.63	2.38	2.52	0.44	0.72	0.34	0.01	0.36	0.63
M-2	Summer	9.00	8.88	5.73	0.97	0.44	0.09	0.00	0.39	0.61
M-3		13.58	3.25	3.77	0.88	0.59	0.07	0.00	0.42	0.46
M-4		4.51	0.00	4.72	0.05	0.34	0.12	0.01	0.25	0.00
M-5	Autumn	7.17	3.38	2.22	0.55	0.78	0.27	0.02	0.46	0.68
M-6		4.16	1.03	1.11	0.45	0.44	0.14	0.01	0.23	0.00
G-1		4.13	0.00	1.64	0.21	0.21	0.05	0.00	0.10	0.00
G-2	Summer	0.00	2.50	0.02	0.00	3.73	1.55	0.01	0.51	0.00
G-3		9.33	8.75	5.71	0.97	0.34	0.06	0.00	0.21	0.47
G-4		0.00	1.81	5.25	0.70	1.48	0.08	0.01	0.84	0.00
G-5	Autumn	0.00	2.52	2.69	0.31	1.24	0.04	0.00	0.42	0.00
G-6		0.00	5.80	1.34	0.00	0.12	0.02	0.00	0.21	0.00
S-1		0.00	2.50	0.02	0.00	3.73	1.55	0.01	0.51	0.00
S-2	Summer	7.12	11.38	5.48	0.55	0.37	0.07	0.00	0.32	0.50
S-3		14.04	8.25	6.15	1.34	0.53	0.10	0.02	0.30	1.00
S-4		18.29	9.56	7.86	1.56	0.52	0.09	0.02	0.35	1.00
S-5	Autumn	4.32	2.27	7.90	5.33	0.34	0.50	0.00	0.05	0.00
S-6		15.14	1.16	6.87	3.56	0.46	0.63	0.00	0.35	2.01
A-1	Summer	3.19	0.85	0.80	0.16	1.12	0.23	0.02	1.66	0.49
A-2	Autumn	5.81	0.78	0.61	0.26	2.58	0.65	0.50	1.66	0.58

Table 5. The enrichment factor (EF) in the studied areas

Sites	Season	EF_{Pb}	EF_{Cd}	EF_{Co}	EF_{Ni}	EF_{Zn}	EF_{Mn}	EF_{Fe}	EF_{Cu}
M-1		10.81	2.97	3.15	0.55	0.90	0.42	6.12	0.45
M-2	Summer	53.05	52.32	33.75	5.72	2.59	0.54	1.21	2.28
M-3		251.09	60.08	69.63	16.29	10.82	1.28	0.36	7.75
M-4		5.23	0.00	5.47	0.06	0.39	0.14	9.42	0.29
M-5	Autumn	7.38	3.47	2.28	0.57	0.81	0.27	5.87	0.47
M-6		21.04	1.25	1.24	0.13	5.24	0.14	5.22	0.25
G-1		36.78	0.00	14.61	1.86	1.90	0.43	3.12	0.88
G-2	Summer	0.00	3.61	0.02	0.00	5.38	2.24	3.75	0.74
G-3		110.38	103.48	67.51	11.48	4.05	0.67	1.12	2.47
G-4		0.00	3.04	8.79	1.18	2.48	0.13	1.97	1.40
G-5	Autumn	0.00	1.05	33.20	5.22	0.50	1.12	0.53	0.44
G-6		0.00	1.03	4.34	0.24	1.24	0.01	1.43	0.20
S-1		0.00	3.61	0.02	0.00	5.38	2.24	3.75	0.74
S-2	Summer	53.35	85.27	41.04	4.11	2.78	0.52	1.15	2.40
S-3		13.19	7.75	5.78	1.26	0.50	0.09	9.86	0.28
S-4		14.03	7.34	6.03	1.20	0.40	0.07	10.35	0.27
S-5	Autumn	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
S-6		12.01	3.12	2.34	0.00	1.34	0.00	5.43	0.13
A-1	Summer	2.28	0.61	0.57	0.11	0.80	0.17	2.33	1.19
A-2	Autumn	1.14	0.31	0.43	0.00	0.40	0.03	1.10	0.04

The calculated EF values showed that heavy metals are in the following order Pb>Cd> Co> Ni> Fe> Zn> Mn> Cu. Zhang and Liu (2002) reported that the lowest values (EF <1.5) indicating to natural sources of heavy metals (crustal materials) and the highest values (EF >1.5) indicating to the significant anthropogenic sources.

In general, the EF values represent moderate enrichment for Co (41.04) and (Ni) (11.48), meanwhile Pb (251.09) was highly enriched at the whole area of study. Marina showed high EF by Co, Ni and Zn with values of (69.63, 16.29 and 10.82) respectively, which may indicate a relation to the anthropogenic sources from ships repairing, antifouling paints and fuels leakage as well as boats mooring. The studied areas of Sheraton, Magawish and Al Mina were enriched with Zn (10.82) and Fe (10.35) due to shipment different operations (Table 5).

Geo-accumulation index (Igeo) has been proposed by (Müller 1969) to evaluate the contamination level in sediments by comparing current status with the pre-industrial levels according to the formula:

$$I_{geo} = \log_2 (C_n / (1.5*B_n)$$

where Cn is the current concentration of metal, Bn is the geochemical background value of the same metal in Shale rocks, and the factor 1.5 is the matrix correction factor of the background. According to Müller (1981), Igeo is likely over seven categories; uncontaminated sediments (Igeo≤0), uncontaminated to moderately contaminated (0< Igeo≤1), moderately contaminated (1< Igeo≤2), moderately to strongly contaminated (2< Igeo≤3), strongly contaminated (3< Igeo≤4), strongly to extremely contaminated (4< Igeo≤5) and extremely contaminated (Igeo≥5).

The resulted values of Geo-accumulation factor of concentrations of different heavy metals showed a varied pollution levels as it classifies the Red Sea coast sediment from unpolluted, moderately polluted and highly polluted. Marina area showed the highest accumulation level of heavy metals as the following sequence Fe> Mn> Zn> Ni> Cu> Pb> Cd> Co. Sheraton area is moderately polluted by Pb> Cd> Co, while Magawish and Al mina areas has the lowest level of contamination as described in (Table 6).

Table 6. Geo-accumulation (Igeo) indices for sediment samples in the four different studied areas.

Sites	season	Pb	Cd	Co	Ni	Zn	Mn	Fe	Cu
M-1		1.15	0.32	0.34	0.06	0.10	0.04	0.00	0.05
M-2	Summer	24.30	0.43	15.46	74.52	75.78	368.01	7268	35.90
M-3		1.81	0.43	0.50	0.12	0.08	0.01	0.00	0.06
M-4		0.60	0.00	0.63	0.04	0.36	0.60	1.82	0.20
M-5	Autumn	0.96	0.06	0.30	0.39	0.83	1.37	2.06	0.36
M-6		0.43	0.03	0.20	32.21	64.34	134.01	1.03	0.13
G-1		0.55	0.00	0.22	0.03	0.03	0.01	0.00	0.01
G-2	Summer	0.00	0.33	0.00	0.00	0.50	0.21	0.00	0.07
G-3		1.24	1.17	0.76	0.13	0.05	0.01	0.00	0.03
G-4		0.00	0.24	0.70	0.09	0.20	0.01	0.00	0.11
G-5	Autumn	0.00	0.12	0.10	0.04	0.50	0.01	0.	0.00
G-6		0.12	0.01	7.23	0.00	0.10	0.10	0.00	0.06
S-1		0.00	0.33	0.00	0.00	0.50	0.21	0.00	0.07
S-2	Summer	0.95	1.52	0.73	0.07	0.05	0.01	0.00	0.04
S-3		1.87	1.10	0.82	0.18	0.07	0.01	0.00	0.04
S-4		2.44	1.28	1.05	0.21	0.07	0.01	0.00	0.05
S-5	Autumn	1.84	0.26	0.84	0.11	0.05	0.02	0.00	0.01
S-6		0.42	0.13	0.42	0.00	0.02	0.01	0.00	0.00
A-1	Summer	0.43	0.11	0.11	0.02	0.15	0.03	0.00	0.22
A-2	Autumn	0.21	0.00	0.00	0.01	0.04	0.01	0.00	0.11

Correlation matrix and Principal Component Analysis (PCA) estimated the statistical relationship among heavy metals as well as between sediment characteristics and the heavy metals. Additionally, PCA was used to infer the hypothetical associations and sources of leachable heavy metals contamination, (Dou et al., 2013; Qiao et al., 2013; Fujita et al., 2014 and Yang et al., 2015).

The correlation matrix for the different heavy metals in sediment fractions showed a strong association between heavy metals in the fine fraction Ø3, Ø4 and Ø5. Two significant associations were observed; the first one was the strong positive correlation between metal pairs of; Cd, Ni, Pb and Ni to lesser extents of total organic matter, while the second association was the negative correlation with Mn and Fe and strong negative relation with total carbonate as shown in (Table 7).

As shown in (Fig. 4) components in Ø3, Ø4 and Ø5 between metals, the obtained results of the PCA showed wide accordance with the correlation matrix. Two main components with accumulative account for 68.95% of the total variance were found. In the first component (43.39% of the total variance), Zn, Mn were grouped with positive loading and carbonate content with negative loading. The second component (12.78% of the total variance) grouped positive loading of Cu and Fe. On the other hand the PCA of the variance of 43.39% was associated with negative loading of Ni, Co, Pb and Cd beside negative carbonate and organic matter loading.

Table 7. Correlation coefficient between metals and geochemical characteristics of fine fraction

Variables	TOM %	CO3 %	Pb	Cd	Co	Ni	Zn	Mn	Fe	Cu
TOM %	1	-0.179	0.215	0.028	0.311	0.391	-0.271	-0.341	-0.237	-0.082
CO3 %	-0.179	1	0.101	0.011	-0.118	-0.159	-0.103	0.040	0.013	-0.351
Pb	0.215	0.101	1	0.523	0.718	0.848	-0.626	-0.551	-0.046	-0.411
Cd	0.028	0.011	0.523	1	0.620	0.685	-0.273	-0.249	-0.112	-0.260
Co	0.311	-0.118	0.718	0.620	1	0.836	-0.659	-0.689	-0.167	-0.400
Ni	0.391	-0.159	0.848	0.685	0.836	1	-0.520	-0.558	-0.023	-0.280
Zn	-0.271	-0.103	-0.626	-0.273	-0.659	-0.520	1	0.962	0.208	0.282
Mn	-0.341	0.040	-0.551	-0.249	-0.689	-0.558	0.962	1	0.168	0.124
Fe	-0.237	0.013	-0.046	-0.112	-0.167	-0.023	0.208	0.168	1	0.547
Cu	-0.082	-0.351	-0.411	-0.260	-0.400	-0.280	0.282	0.124	0.547	1

Values in bold are different from 0 with a significance level alpha=0.05

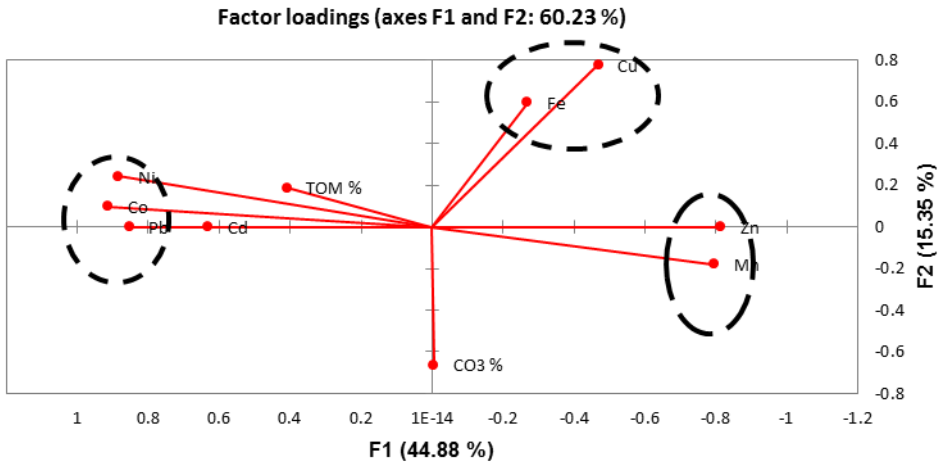

Fig. 4. PCA analysis of the eight studied heavy metals.

PCA revealed two main components with accumulative account approximately 60.23% of the total variance. Evidently, the first factor was more correlated with the variables than the other factor. Factor 1 explained 44.88 % of the total variance, it have a strong positive loading with cobalt Co and lead Pb this factor has a negative loading of carbonate and moderately correlation with total organic matter and cadmium metal which may explain its organic source. Factor 2 had a strong positive relation with copper Cu and iron Fe, this factor explain 15.35 % of the total variance, it also has a negative loading with carbonate which show that its source could be anthropogenic.

The overall multivariate analyses showed two major patterns. The first pattern suggested that the metals Ni, Co, Pb and partially Cd were originated from the terrigenous sources and were negatively correlated with carbonate, this mainly due to phosphate ores sedimentation and coastal activities.

Previous work in many locations of Red Sea area showed high levels of Pb and Cd associated with terrestrial inputs e.g., (Mansour et al., 2011; Madkour et al., 2012; Dar et al., 2016a; 2016b and El-Metwally et al., 2017). The second pattern showed that high portion of Cu, Zn and Fe that mostly have anthropogenic sources since the highest impacts were observed at Magawish and Marina stations.

CONCLUSION

Distribution and ecological risk of heavy metals were investigated in finest fractions of the surface sediments of Red Sea coast at Hurghada City. The total of the finest fractions (Ø3, Ø4 and Ø5) was varied between 1% and 57% with considerable varied percentages of the different sites indicating to different sources of precipitates mostly from the maritime activities, terrestrial runoff, shipments and the nearby coastal based activities.

Carbonate percentage showed large decline with increasing the terrigenous inputs at Al Mina followed by Magawish and Sheraton, however, Marina site showed high carbonate percentages due to the high marine productivity. TOM recorded variable percentages at the different sites may attribute to the local effects of the anthropogenic effluents. The distribution of Fe and Mn were generally lower in Sheraton sector ($p \leq 0.05$) comparing to Marina and Magawish sectors with distinctive high levels of Cu ($p<0.05$). A strong correlation observed between Fe, Mn and partially Cd, which attributed to the shipping process of raw materials from Marina and Sheraton sites.

The organic matter content showed no correlation with heavy metals in the surface sediments, and carbonate was negatively correlated with Cu, Zn and Pb. The levels of heavy metals in present study were similar or below the levels recorded in other ports worldwide. According to sediments quality guidelines (SQGs), the concentrations of heavy metals in sediments of the studied zones at the Red Sea coast were not expected to have biological adverse effects, except for Fe, Zn, Pb and Ni may poses some ecological risks to marine organisms near the coastal area of Hurghada.

ACKNOWLEDGEMENTS

Authors thank the outstanding contribution of STDF research teams (Science and Technology Development Fund, Egypt).

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