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Geochemistry and Environmental Assessment of Heavy Metals in the Surface Marine Sediments of Safaga Harbour at the Egyptian Red Sea Coast

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***Abstract**:*
The heavy metals distribution (Fe, Mn, Zn, Cu, Pb, Ni, Cd, and Hg) was determined in the surface sediments of Safaga Harbour. The surface seiments recorded an average value of 0.52%, 126.91 ppm, 22.5 ppm, 10.44 ppm, 20.33 ppm, 14.09 ppm, 0.18 ppm, and 0.01 ppm for Fe, Mn, Zn, Cu, Pb, Ni, Cd, and Hg, respectively. The beach and intertidal areas show the highest values of Pb at Safaga Harbour; this is attributed to coal disburdening, oil spills from ships in the harbour area, cement packing, and phosphate shipment, in addition to human activities at Fishermen's Port (marine paints as Pb chloride and oily waste from the boats). In comparison, the data on heavy metals gained from this study with guidelines showed that the average values of the studied heavy metals were lower than the threshold effect level. To determine possible relations between various variables, a correlation matrix has been implied. An arcGIS technique was also used to create spatial distribution maps of various variables. Principal component analysis (PCA) was applied to elucidate potential sources of metals in the area under study. The heavy metal results in the study area were ecologically assessed using different pollution indices: contamination factor (CF), contamination degree (C_d), modified degree of contamination (mC_d), pollution load index (PLI), enrichment factor (EF), and ecological risk indices (ER and IR).
***Keywords:** Marine sediments, Heavy metals, Pollution, Safaga, Red Sea, Egypt.*

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I. Introduction

Heavy metals are found in the Earth's crust as natural constituents. Because of the toxicity, persistence, and biological accumulation issues, heavy metals are one of the most significant pollutants in the marine environment [1]. As a result of urbanization, industrial, and agricultural activity, major ions and trace metals may be introduced into the aquatic environment [2]. Minerals and rocks contain metals that are normally innocuous until they dissolve in water, at which point they become potentially toxic. They are released into the environment as a result of the weathering of rocks, leaching of soils, vegetation, and volcanic activity [3]. The transfer of metals from point and non-point sources into coastal water is therefore of major interest in environmental geochemistry [4]. Both anthropogenic and natural processes can contribute to heavy metal contamination in coastal sediments.

II. Materials and Methods

Study area

Safaga Harbour is one of the important ports in the Red Sea region, as the harbour is currently used as a passenger port as well as a port for exporting and receiving grain. It also contains a special berth for receiving raw alumina (Bauxite) and green petroleum coke. The harbour is located at latitudes 26º 44' 56"N to 26º 44' 35"N and longitudes 33º 57' 5.6"E to 33º 56' 36.7"E. In Safaga Harbour, cement packing and phosphate ore shipments were conducted, which stopped more than twenty years ago. A port for fishermen is located in the southern portion of Safaga Harbour (Fig. 1).

Field work

Safaga Harbour is divided into three transects, SH1, SH2, and SH3, from north to south. Transect SH1 was taken under the harbour berth, transect SH2 was taken at the phosphate ore loading berth, and transect SH3 was taken at Fishermen's Port (Fig. 1). All transects of the study area were perpendicular to the coast. Twentyeight sediment samples were taken from these transects, which ranged in depth from 0 to 34 meters below sea level and were distributed 3096 meters from the shoreline (Fig. 2). Using an outboard-engine fiberglass boat, the samples were gathered in October 2018. Four diverse environments; beach, intertidal, subtidal, and supratidal are represented by the samples taken from the area. The sediment collected by a grab sampler or collected by scuba diving was placed in labeled plastic bags and stored in the laboratory at -20 ºC until analysis.

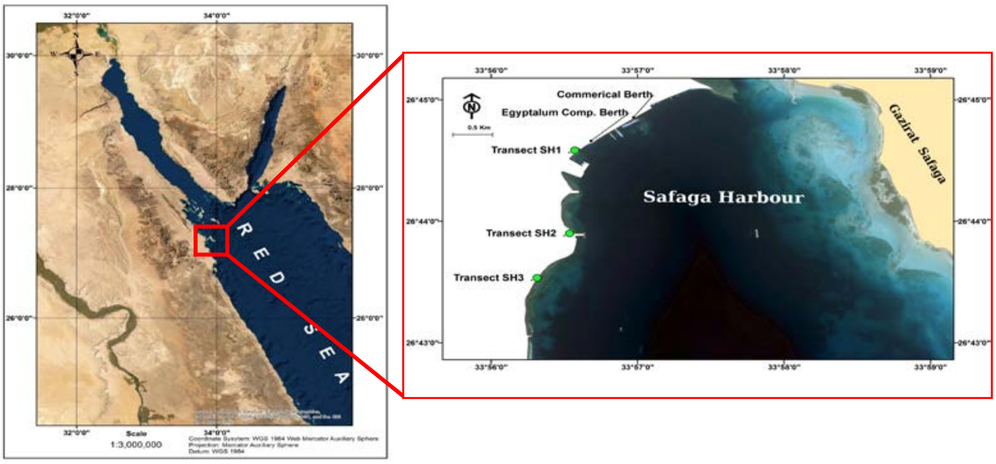


Fig. 1: The location map of the study area on the Red Sea coast, Egypt.

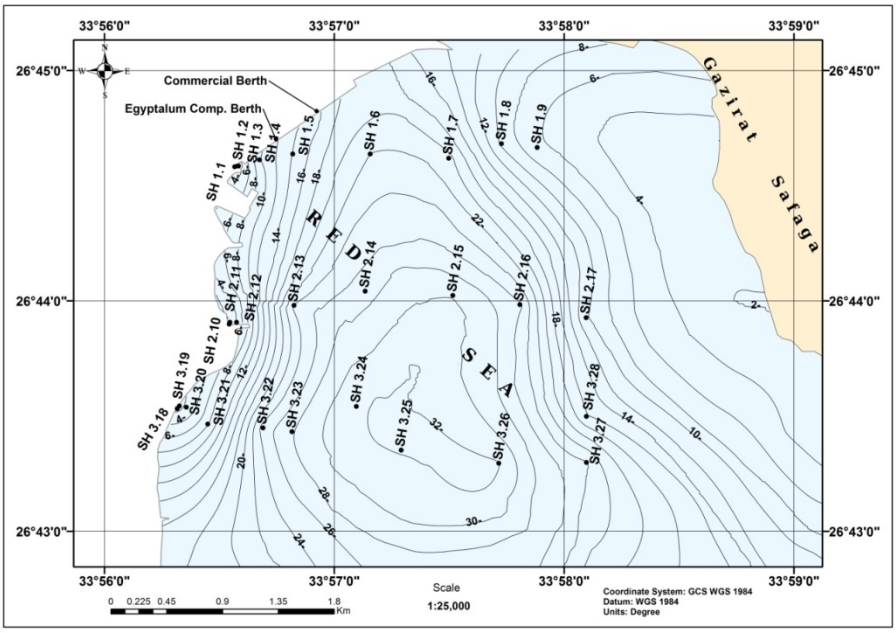


Fig. 2: Bathymetric and sample locations map of Safaga Harbour area.

Laboratory methods and treatment of data

The sediment samples had been gently washed with distilled water and spread out evenly on glass sheets to air-dry. The metals in the sediments were measured according to Chester *et al.* [5]. To obtain the concentration of Fe, Mn, Zn, Cu, Pb, Ni, and Cd, about 0.5 g of the prepared ground sample were completely digested in a teflon cup by using a mixture of conc. nitric, perchloric, and hydrofluoric acids, in the ratio 3: 2: 1, respectively. Acids were slowly added to the dried sample and left overnight before heating. Samples were heated for two hours on a hot plate at a temperature of approximately 200 ˚C, then left to cool and filtered to get rid of the nondigested parts. The solution was justified to a volume of 25 ml, and then the concentration of the elements was determined by AAS (flame atomic absorption spectrophotometer) fitted with a BGC-SR lamp for background correction (GBC-932 Ver. 1.1). Mercury was determined in Aqua regia sediment extract [6] with hydride vapour generator atomic spectrometry, using $SnCl_2$ and $NaBH_4$ as reductands.

Pearson's correlation analysis and principal component analysis (PCA) calculations were performed for the analyzed samples using IBM SPSS Statistics 15 software. The inverse distance weighted (IDW) method of the GIS software was also used to spatially distribute the different studied geochemical features. The status of the investigated pollutants in Safaga Harbour area was assessed using six indices.

III. Results and Discussion

Characteristics of heavy metal concentrations in marine sediments

Iron (Fe)

Iron is known for its redox chemistry, photochemistry, organic complexation, adsorption and desorption on particles, and uptake and cycling by organisms. These factors are further complicated by the low solubility and association of Fe with colloids in seawater [7]. In the present study, Fe content varied from 0.06% to 1.57%, averaging 0.52% (Table 1). The spatial distribution map of Fe in Safaga Harbour (Fig. 3a) illustrates that Fe shows high values in the area close to the harbour and continues as well in the deep area between the shoreline and Gazirat Safaga. This can be attributed to the landfilling and dredging operations in the harbour area.The results of the correlation matrix (Table 2) showed that Fe didn't show any significant relationship with other elements. In comparison (Table 3), Fe content in the sediments of the present study recorded a lower average value than that of Egyptian Red Sea coast sediments, except for Hurghada area, which recorded a lower average value (0.26%).

Manganese (Mn)

The tendency of soluble manganese compounds to adsorb to soils and sediments can be highly variable, depending mainly on the cation exchange capacity and the organic composition of the soil [8; 9]. Manganese is transported to the marine environment in the same way as iron. The Mn contents of the sediments in the studied area ranged between 13.5 ppm and 521.23 ppm, averaging 126.91 ppm (Table 1). As shown from the Mn distribution map (Fig. 3b), the high Mn concentrations are localized in the southern region of Safaga Harbour area, close to the shoreline. This is due to the impact of human activities that have been operating in Safaga Harbour region for more than two decades, such as phosphate shipment, in addition to human activities in the Fishermen's Port area (SH3 transect). From the correlation matrix (Table 2), Mn showed a significant positive correlation with TP (0.79), Cu (0.54), and Ni (0.53). In comparison, Mn content in the sediments of the present study recorded a lower average value than that of Egyptian Red Sea coast sediments, except for Hurghada area, which recorded a lower average value (49.0 ppm). Also, Naples Harbour showed a higher average value of Mn concentration than that in the present study (Table 3).

Zinc (Zn)

Zinc is a trace element that can be toxic in some cases but also has some useful physiological functions. Madkour [10] stated that the highest value of Zn content in marine sediments was recorded in Hamrawein Harbour, and the increase in Zn content in coral reef species in natural inputs is due to the influence of terrigenous fragments rich in this element and principally derived from volcanic and metamorphic rocks. In Safaga Harbour, Zn concentrations ranged between 2.27 ppm and 110.90 ppm, with an average of 22.50 ppm (Table 1). From the Zn distribution map (Fig. 3c), the high Zn concentrations are localized in the southern region of Safaga Harbour area, close to the shoreline, similar to Mn distribution in the area. The highest Zn value was recorded in the supratidal area (Sample SH 3.18) of the southern region of Safaga Harbour (Transect SH3). This is due to the impact of human activities that have been operating in Safaga Harbour area, such as phosphate shipment, in addition to human activities in the Fishermen's Port area (Transect SH3). Zinc has a strong positive correlation with Cu (0.96); it's also positively correlated with Hg (0.66), Ni (0.60), and TP (0.51), while it decreases with increasing distance from the shoreline (-0.55) and carbonate (-0.52) (Table 2). Zinc recorded a lower average value compared to previous studies on the Egyptian Red Sea coast, except for Safaga area [10], which recorded a comparable value, and Hurghada area, which recorded a lower average value. In the same context, Naples Harbour recorded a higher average value for zinc than that recorded in the current study (Table 3).

Copper (Cu)

Copper present in the hydrosphere comes from several types of sources; one of them is anthropogenic inputs, either directly into the water or leached after deposition on land. These include industrial and municipal effluents as well as antifouling coatings, pesticide residues, manure, and sludge [11]. Cu content of the sediments of Safaga Harbour varied between 1.76 ppm and 46.07 ppm, with an average of 10.44 ppm (Table 1). In Safaga Harbour, the highest recorded values of Cu were measured in the supratidal, beach, and intertidal samples at transect SH3 (Fishermen's Port) and transect SH2 (Phosphate loading berth) (Fig. 3d). These high values are due to human activities at Fishermen's Port (antifouling paints and disposal of waste), in addition to the phosphate shipping that was operated in the past.

The correlation matrix results (Table 2) show that Cu significantly positively correlated with Zn (0.96) and Hg (0.71) and positively correlated with Ni (0.59), Mn (0.54), and TP (0.54), while decreasing with increasing depth (-0.50), distance from shoreline (-0.58), and carbonate (-0.53). Cu recorded a lower average value compared to previous studies on the Egyptian Red Sea coast, except for Safaga area [10], which recorded a comparable value, and Hurghada area, which recorded a lower average value; additionally, Bilbao and Naples harbours recorded higher values for Cu than those recorded in the current study (Table 3).

Lead (Pb)

Lead bioaccumulates in most organisms, in particular in biota feeding primarily on particles, e.g., mussels and worms. Epidemiological studies suggest that low level exposure of the foetus and developing child may lead to reprotoxic effects, i.e., damage to the learning capacity and neuropsychological development [12]. In Safaga Harbour area, the Pb concentration of sediments ranged from 2.15 ppm to 55.87 ppm, with an average of 20.33 ppm (Table 1). The beach and intertidal area show the highest values of Pb at Safaga Harbour (Fig. 3e). This is attributed to coal disburdening, oil spills from ships at the harbour area, cement packing, and phosphate shipment, in addition to human activities at Fishermen's Port (marine paints as Pb chloride and oily waste from the boats).

The correlation coefficient of the marine sediments (Table 2) indicates that lead is negatively correlated with depth and distance from the shoreline (-0.56). The current study recorded lower lead values compared to other study areas in the Egyptian Red Sea, except for the Safaga area studied by Madkour [10], where similar values were recorded, while the current study recorded higher values for lead than those recorded in Hurghada area. Nables Harbour recorded a comparable average value to that in the current study, while Bilbao Harbour recorded very high values of lead (Table 3).

Nickel (Ni)

Nickel compounds are used as catalysts, pigments, and in batteries. Petroleum refining, cement manufacture, incineration, and glass production are three processes considered by Entec [13] as anthropogenic sources of nickel. In Safaga Harbour, Ni content ranged from 7.66 ppm to 23.56 ppm, with an average of 14.09 ppm (Table 1). The southern transects of the harbour (SH2 and SH3) display the highest Ni values (Fig. 3f). This is due to phosphate shipment and cement packing in the past, in addition to the impacts of anthropogenic activities at Fishermen's Port. Ni shows positive corelation with Hg, Zn, Cu, Mn, and TP (0.62, 0.60, 0.59, 0.53, and 0.52, respectively) (Table 2). Hurghada area and El Zaitiya Harbour recorded comparable values of nickel to those found in the current study, while other areas recorded higher concentrations of nickel, except for Safaga Harbour [14], which recorded values lower than those found in the current work (Table 3).

Cadmium (Cd)

Cadmium is toxic at very low exposure levels and has harmful acute and long-term consequences on the environment and human health. Due to the fact that cadmium is not naturally degradable, once it is introduced into the environment, it will remain in the ecosystem [15]. Cd content in the present study varied between 0.02 ppm and 0.92 ppm, averaging 0.18 ppm (Table 1). The occurrence of Cd in the study area is natural, probably due to the formation of cadmium carbonates, where its concentrations are within the background value suggested by SEPA (0.3 ppm) [16].

From the correlation matrix (Table 2), it is shown that Cd has no significant relationship with other elements. The Red Sea coast [17] and Safaga area [10] showed higher values for Cd than those shown in the current work, while Hurghada area and Safaga Harbour [14] recorded similar values compared to the current study. On a larger scale, Nables Harbour recorded a similar average value, while Bilbao Harbour recorded very high values compared to those in the current study (Table 3).

Mercury (Hg)

Mercury is a heavy, silvery-white liquid that vaporizes quickly at ambient temperatures. The main anthropogenic sources are from general waste/disposal and industrial activities [18]. It is still used in various products, e.g., batteries and electronics. The sediments of Safaga Harbour have Hg content ranged from ND (not detected) to 0.06 ppm, averaging 0.01 ppm (Table 1). The beach and intertidal samples of SH2 and SH3 transects of Safaga Harbour recorded the highest values (Fig. 3h). This may be attributed to past phosphate shipments and cement packing in the area. The correlation matrix (Table 2) shows that Hg has a significant positive correlation with Cu (0.71) and also correlates positively with TP, Zn, and Ni (0.68, 0.66, and 0.62, respectively). It's noted that Hg decreases with increasing water depth.

A comparison of the data gained from this study with guidelines (Table 3) shows that the average values of the studied heavy metals are lower than the threshold effect level.

Geochemical characteristics of major and minor constituents and mud of marine sediments
Carbonate

Sediment samples from Safaga Harbour have carbonate content vared from 8.14% to 88.87%, averaging 41.14% (Table 1). Furthermore, the supratidal, beach and intertidal samples are very terrigenous, terrigenous and transitional carbonates. Carbonate increases with increasing distance from the shoreline (Table 2).

Total organic matter

Carbon and nitrogen are two of the principal components of organic matter. High C:N ratios in marine sediments indicate a terrigenous organic matter contribution [19]. The total organic matter distribution along the studied area of Safaga Harbour ranged between 0.44% and 6.27%, with an average of 2.08% (Table 1).

Total phosphorus

Kpomb and Tabatabai [20] stated that Cd, Zn, Co, Ni, Pb, and Cu are abundant in phosphate rocks and hence should be considered in metal transport studies, ecosystem investigations, and environmental impact studies. The addition of phosphate dust accelerates nutrient content, causes algae development, and eutrophication [21]. Total phosphorous concentrations in the present work varied between ND and 5379.52 ppm, averaging 757.60 ppm (Table 1), where the supratidal, beach, and intertidal areas south of Safaga Harbour (Transects SH2 and SH3) recorded the highest values of total phosphorous concentrations in the studied area.

Mud

Mud fraction at Safaga Harbour area ranged between 0.11 and 35.23%, averaging 13.78% (Table 1). The highest contents of mud were detected at the deepest parts of the area, where the mud content increases with increasing water depth (Table 2).

Table 1: Heavy metals, major, minor, and mud constituents of marine sediments of Safaga Harbour.

Sa. No.	Fe%	Mn*	Zn*	Cu*	Pb*	Ni*	Cd*	Hg*	Carb.%®	TOM%®	TP*®	Mud®	Depth (m)	D. sh (m)
SH 1.1	0.25	115.02	26.71	13.06	38.23	10.06	0.06	ND	8.43	0.61	20.59	1.793	0	0
SH 1.2	0.5	84.61	15.54	7.99	55.32	9.03	0.17	ND	19.03	0.59	ND	0.109	0	0
SH 1.3	1.57	138.44	31.59	12.72	55.87	11.16	0.05	ND	9.65	1.13	25.63	3.202	0.5	20
SH 1.4	0.32	117.27	21.12	13.95	11.07	14.24	0.12	ND	17.76	2.15	35.89	20	14	39
SH 1.5	0.66	44.2	17.51	9.38	3.57	12.77	0.02	ND	8.14	0.98	ND	2.439	14	244
SH 1.6	0.79	86.6	21.87	8.43	7.73	13.35	0.1	ND	27.62	0.87	62.93	32.777	23	803
SH 1.7	0.78	13.5	16.98	5.24	4.34	12.28	0.09	ND	24.45	1.75	6.76	30.044	23	1415
SH 1.8	0.77	122.12	13.08	5.96	2.15	9.05	0.07	ND	38.13	1.18	10.66	13.092	7	1652
SH 1.9	0.13	78	11.46	5.89	4.64	9.5	0.26	ND	61.5	2.08	ND	14.069	5	1943
SH 2.10	0.21	153.33	30.76	8.03	19.4	16.18	0.28	0.03	22.11	1.74	4433.3	1.786	0	0
SH 2.11	0.46	223.82	28.49	15.79	16.9	23.56	0.26	0.05	16.99	1.53	2314.24	0.174	0	0
SH 2.12	0.91	196.07	57.45	26.86	54.73	18.46	0.18	ND	18.9	1.64	1858.28	7.263	0.7	47
SH 2.13	0.52	162.57	17.15	7.52	9.48	16.66	0.15	ND	48.87	2.03	634.23	31.186	30	550
SH 2.14	0.72	171.65	22.97	7.88	7.73	16.63	0.12	ND	51.37	5.43	231.76	30.603	26	1081
SH 2.15	0.47	146.65	16.18	6.87	30.28	17.48	0.92	ND	43.43	3.04	78.13	22.074	31	1714
SH 2.16	0.39	97.6	9.48	4.53	5.62	10.3	0.04	ND	45.53	2.18	326.33	17.826	30	2167
SH 2.17	0.1	30.24	2.72	1.76	5.41	7.66	0.28	ND	73.21	2.53	ND	0.483	7	2570
SH 3.18	0.81	180.7	110.9	46.07	23.06	21.64	0.17	0.06	18.89	2.2	2217.97	4.83	0	0
SH 3.19	0.27	163.7	35.77	21.86	39.87	18.26	0.1	0.06	12.17	0.44	1835.32	0.129	0	0
SH 3.20	0.49	521.23	38.85	23.48	46.65	16.46	0.3	0.03	48.43	2.79	5379.52	35.229	1.5	49
SH 3.21	0.06	23.04	4.47	2.25	44.47	8.04	0.13	ND	88.87	2.77	61.75	1.425	6	267
SH 3.22	0.4	146.04	16.77	6.32	13.02	14.7	0.22	ND	56.23	2.08	833.61	27.045	30	685
SH 3.23	0.7	102.74	21.2	6.53	12.7	18.25	0.16	ND	58.82	2.07	430.21	18.152	28	907
SH 3.24	0.58	122.49	7.27	8.41	9.83	15.14	0.11	ND	64.82	1.88	188.26	18.254	32	1277

Cont. table 1:

Sa. No.	Fe%	Mn*	Zn*	Cu*	Pb*	Ni*	Cd*	Hg*	Carb.%®	TOM%®	TP*®	Mud®	Depth (m)	D. sh (m)
SH 3.25	0.73	98.71	15.47	6.29	13.28	16.7	0.26	ND	59.11	2.52	117.75	27.236	32	1760
SH 3.26	0.49	129.17	10.69	2.31	9.26	15.18	0.1	ND	57.75	6.27	104.06	16	34	2463.5
SH 3.27	0.49	65.14	5.42	4.52	18.36	12.38	0.17	ND	66.16	1.26	5.69	7.47	27	3096
SH 3.28	0.12	18.81	2.27	2.47	6.39	9.42	0.1	ND	85.64	2.51	ND	1.267	13	2976
Stdev	0.32	94.76	21.18	9.43	17.67	4.14	0.16	0.02	24.11	1.28	1376.23	12.067	13	1020
Gm	0.42	98.44	16.26	7.78	13.81	13.49	0.14	0.04	33.15	1.76	193.46	5.82	12	650
Min	0.06	13.5	2.27	1.76	2.15	7.66	0.02	ND	8.14	0.44	ND	0.109	0	0
Max	1.57	521.23	110.9	46.07	55.87	23.56	0.92	0.06	88.87	6.27	5379.52	35.229	34	3096
Avg.	0.52	126.91	22.5	10.44	20.33	14.09	0.18	0.01	41.14	2.08	757.6	13.784	15	990

Carb.% = carbonate content TOM = total organic matter TP = total phosphorus *= values ppm
D. sh.= distance from the shoreline Stdev = standard deviation Gm= Geomean Min= minimum
Max= maximum Avg.= average ND = not detected ®= Reference [22]

Table 2: The correlation coefficient among heavy metals, major, minor, mud, depth, and distance from the shoreline of marine sediments at Safaga Harbour.

	Fe	Mn	Zn	Cu	Pb	Ni	Cd	Hg	Carb.	TOM	TP	Mud	Depth	D.sh
Fe	1													
Mn	0.15	1												
Zn	0.37	0.45	1											
Cu	0.30	**0.54**	**0.96**	1										
Pb	0.21	0.38	0.35	0.42	1									
Ni	0.25	**0.53**	**0.60**	**0.59**	0.06	1								
Cd	-0.18	0.23	0.01	-0.01	0.13	0.28	1							
Hg	-0.07	0.47	**0.66**	**0.71**	0.21	**0.62**	0.07	1						
Carb.	-0.43	-0.21	**-0.52**	**-0.53**	-0.32	-0.31	0.14	-0.38	1					
TOM	-0.10	0.13	-0.11	-0.19	-0.26	0.14	0.18	-0.17	0.49	1				
TP*	-0.07	**0.79**	**0.51**	**0.54**	0.32	**0.52**	0.18	**0.68**	-0.23	-0.03	1			
Mud	0.21	0.32	-0.11	-0.13	-0.33	0.20	0.16	-0.29	0.19	0.35	0.01	1		
Depth	0.06	-0.24	-0.44	**-0.50**	**-0.56**	0.07	0.12	**-0.50**	0.45	0.45	-0.44	**0.64**	1	
D.sh	-0.23	-0.42	**-0.55**	**-0.58**	**-0.56**	-0.38	0.11	-0.44	**0.68**	0.37	-0.46	0.12	**0.54**	1

Carb. = carbonate content TOM = total organic matter TP = total phosphorus
D. sh = distance from the shoreline.

Table 3: Comparison of heavy metals in the current study with other studies of the Egyptian Red Sea coast and worldwide harbours (values in ppm unless otherwise noted).

Location	Heavy metal								Reference
	Fe (%)	Mn	Zn	Cu	Pb	Ni	Cd	Hg	
Safaga Harbour	0.06–1.57 0.52	13.5–521.23 126.91	2.27–110.9 22.5	1.76–46.07 10.44	2.15–55.87 20.33	7.66–23.56 14.09	0.02–0.92 0.18	ND–0.06 0.01	Present study
Red Sea coast	~~~~ 0.2–1.45	~~~~ 127-609	~~~~ 13.6–73.5	~~~~ 11.7–57.8	~~~~ 14.4-71	~~~~ 4.6–57.8	~~~~ 0.1–1.71	~~~~ ~~~~	[17]
Safaga area	~~~~ 1.34	~~~~ 1342.5	~~~~ 15.95	~~~~ 12.92	~~~~ 22.97	~~~~ 40.52	~~~~ 2.06	~~~~ ~~~~	[10]
Hurghada area	1.0^{-5}–1.23 0.26	0.6–221.76 49.0	0.0–49.41 12.41	0.05–23.25 4.57	0.007-9.83 1.51	0.02-71.74 7.21	0.03-0.68 0.11	0.00-0.66 0.020	[23]
Safaga Harbour	9.25–10.40 9.82	200–620 398	40–361 117	10–756 138	22–81 37	0 – 5 3	0 – 0.8 0.2	~~~~ ~~~~	[14]
El Zaitiya Harbour	0.20–4.83 2.72	18.59–314.35 182.43	69.72–414.84 180.47	11.91–272.19 67.02	10.44–375.68 62.81	ND – 34.63 19.01	~~~~ 0.02	~~~~ ~~~~	[24]
Bilbao Harbour	~~~~ ~~~~	~~~~ ~~~~	250 – 3200 ~~~~	46 – 479 ~~~~	40 – 2260 ~~~~	~~~~ ~~~~	1.7 -57 ~~~~	~~~~ ~~~~	[25]
Naples Harbour	~~~~ ~~~~	~~~~ 479.00	~~~~ 56.00	~~~~ 21.00	~~~~ 23.00	~~~~ ~~~~	~~~~ 0.20	~~~~ ~~~~	[26]
Threshold effect level	2	640	124	18.7	30.2	16	0.7	0.13	[27; 28]
Probable effect level	4	1100	271	108	112	75	4.2	0.7	[27; 28]
Shale	4.72	850	95	45	20	68	0.3	0.40	[29]

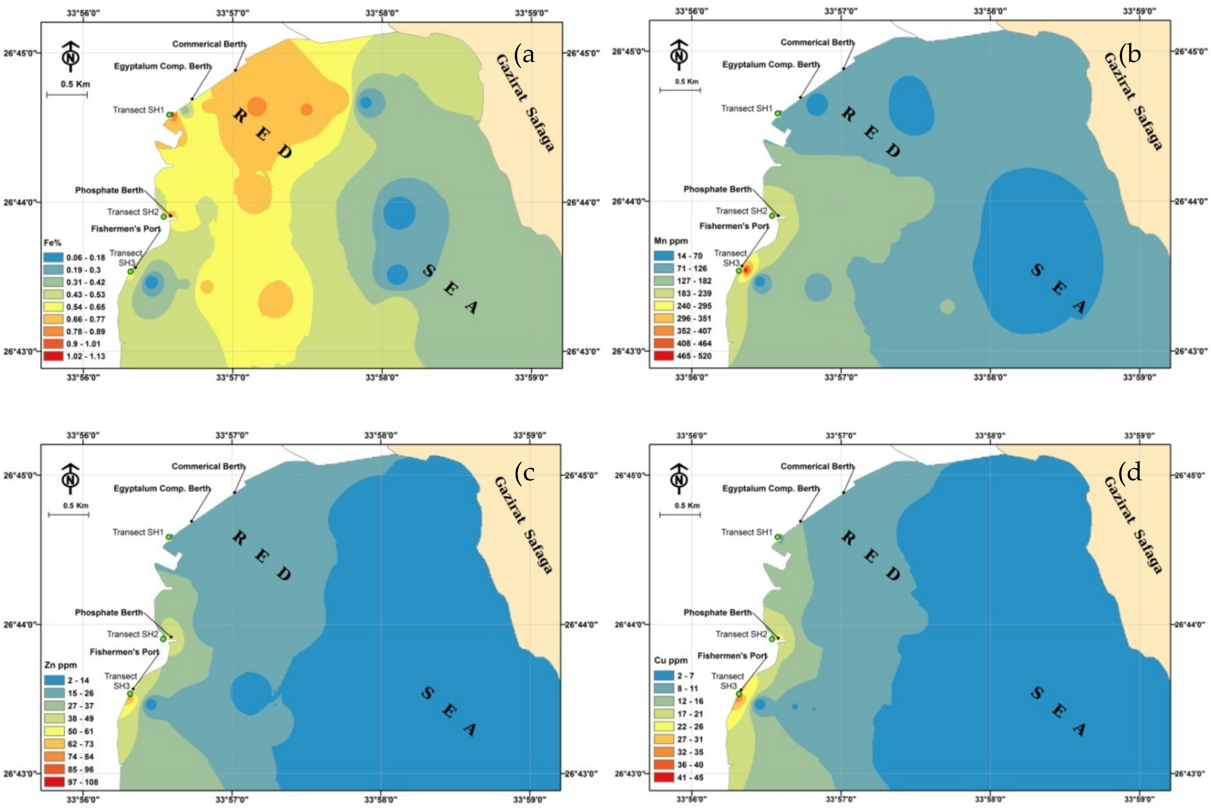
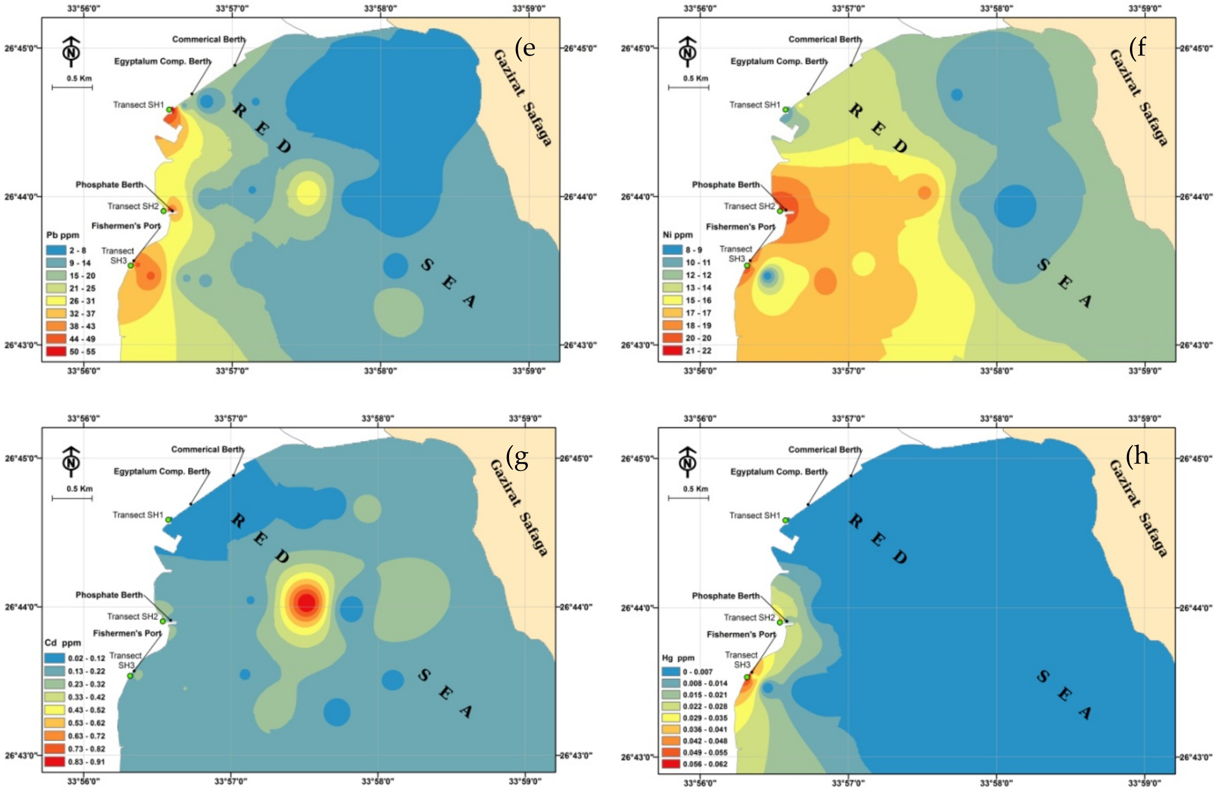


Fig. 3: Spatial distribution of Fe (a), Mn (b), Zn (c), and Cu (d) at Safaga Harbour using GIS technique.



Cont. Fig. 3: Spatial distribution of Pb (e), Ni (f), Cd (g), and Hg (h) at Safaga Harbour using GIS technique.

Principal component analysis (PCA)

PCA is a variance-focussed method that does not differentiate common and unique variance, which are incorporated into the derived components [30]. The principal component analysis results of Safaga Harbour sediments give four components that have eigenvalues > 1, with an accumulative account of 77.16%. They are illustrated in table 4 and fig. 4. The first component (PC1) is the dominant component, accounting for 38.42% of the total variance and including significant positive loadings for Hg, Cu, Zn, Ni, TP, and Mn. Hg, Cu, Zn, Ni, TP, and Mn were grouped together with negative loading for carbonate, indicating the anthropogenic source of these elements, which is due to past phosphate shipment and cement packing at the area and other human activities at Fishermen's Port.

The third component accounts for 12.37% of the total variance; it only has a strong positive loading with Fe. The negative loading of carbonate for the third component suggests an anthropogenic origin of Fe in the area, which is different than the anthropogenic source of the first component's elements. The fourth component represents 8.75% of the total variance. Cd and Pb show high positive loadings onto the fourth component with no significant loadings from other elements, indicating another anthropogenic source in the area, while the second component describes 17.61% of the total variance and has strong positive loadings for mud and TOM with weak loading for carbonate.

Table 4: Total variance explained and matrix of principal components analysis of marine sediments of Safaga Harbour.

Component	Initial Eigenvalues			Extraction Sums of Squared Loadings[a]			Rotation Sums of Squared Loadings[b]		
	Total	% of Variance	Cumulative %	Total	% of Variance	Cumulative %	Total	% of Variance	Cumulative %
1	4.611	38.424	38.424	4.611	38.424	38.424	3.982	33.185	33.185
2	2.113	17.610	56.034	2.113	17.610	56.034	2.069	17.244	50.429
3	1.485	12.372	68.406	1.485	12.372	68.406	1.729	14.407	64.836
4	1.050	8.751	77.157	1.050	8.751	77.157	1.479	12.321	77.157
5	0.796	6.633	83.790						
6	0.734	6.120	89.910						
7	0.396	3.302	93.213						
8	0.319	2.654	95.867						
9	0.228	1.903	97.770						
10	0.135	1.123	98.893						
11	0.120	1.000	99.893						
12	0.013	0.107	100.000						

Component matrix					Rotated component matrix				
Element	PC1	PC2	PC3	PC4	Element	PC1	PC2	PC3	PC4
Cu	0.913	-0.112	0.062	-0.124	Hg	0.894	-0.248	-0.191	0.005
Zn	0.879	-0.092	0.141	-0.170	Cu	0.847	-0.226	0.300	0.079
Hg	0.804	-0.024	-0.361	-0.348	Zn	0.829	-0.162	0.340	0.018
TP	0.754	0.307	-0.311	0.048	Ni	0.795	0.304	0.143	0.100
Ni	0.725	0.394	0.132	-0.240	TP	0.744	-0.008	-0.128	0.438
Mn	0.710	0.471	0.013	0.266	Mn	0.612	0.227	0.167	0.586
Carb.	-0.605	0.497	-0.278	-0.023	Mud	-0.064	0.820	0.318	0.125
TOM	-0.195	0.731	0.085	-0.138	TOM	-0.015	0.740	-0.210	0.079
Mud	-0.096	0.673	0.572	0.062	Fe	0.081	0.061	0.921	-0.049
Cd	0.119	0.513	-0.290	0.449	Carb.	-0.428	0.450	-0.547	0.078
Fe	0.304	-0.190	0.834	0.191	Cd	0.047	0.224	-0.219	0.680
Pb	0.491	-0.296	-0.157	0.702	Pb	0.142	-0.556	0.286	0.659

[a] extraction method : the principal components. [b] rotation method: orthogonal rotation with Kasier standardization.

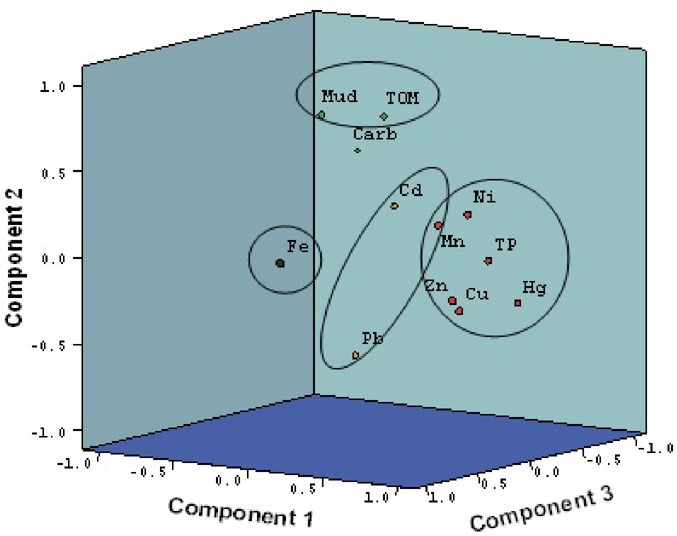


Fig. 4: Principal component analysis plot of heavy metals, TP, carbonate, TOM, and mud of the samples at Safaga Harbour.

Ecological risk assessment of heavy metals

Pollution indices are frequently used to explain the contamination situation in surface sediments in aquatic environments [31]. Six indices were applied to describe the contamination condition of surface sediments of Safaga Harbour area.

Contamination factor (CF)

The contamination factor (CF), a single index, is regarded as a simple and effective method for heavy metals contamination monitoring [32]. Hakanson [32] classified the contamination factor (CF) into four grades based on their intensities on a scale ranging from < 1 to ≥ 6 (Table 7). The average values of contamination factor (CF) for the analyzed heavy metals at Safaga Harbour decreased in the sequence of Pb > Cd > Zn > Cu > Ni > Mn > Fe > Hg (Table 5; Fig. 5). The average values of Fe, Mn, Zn, Cu, Ni, Cd, and Hg at sampling sites were below 1, which classified them at class (1), suggesting a low degree of contamination or clean site, except the calculated CF values of Pb were ranging between the first and second class with an average value of 1.02, suggesting a moderate degree of contamination (1 < CF < 3). Sample SH 3.18 is moderately contaminated with Zn and Cu, while samples SH 2.15 and SH 3.20 are moderately contaminated, and considerably contaminated, respectively with Cd. This is attributed to coal disburdening, oil spills from ships at the harbour area, cement packing, and phosphate shipment, in addition to human activities at Fishermen's Port (marine paints as Pb chloride and oily waste from the boats).

Contamination degree (C_d)

The contamination degree of Safaga Harbour sediments ranged from 0.93 to 5.42, with an average of 2.57, indicating a low degree of contamination (Table 5; Fig. 6).

Pollution load index (PLI)

As illustrated in table 5 and fig. 7, the pollution load index in the sediments of Safaga Harbour varied from 0.07 to 0.51, with a mean value of 0.24. The pollution load index values of all sediment samples are less than one. This suggests that the sediments are not polluted by heavy metals (baseline levels).

Modified degree of contamination (mC_d)

The mC_d values in the sediments of Safaga Harbour were between 0.13 and 0.77, averaging 0.37 for the studied metals, indicating nil to a very low degree of contamination (Table 5).

Enrichment factor (EF)

As shown in table 6; fig. 8, Pb was the most enriched element in the studied sediment of Safaga Harbour with an average of 16.37, followed by Cd with an average of 9.45, suggesting significant enrichment with both Pb and Cd. Additionally, the sediments of Safaga Harbour are moderately enriched with Ni (Avg. 2.72), Cu (Avg. 2.56), and Zn (Avg. 2.5). The rest of the elements have an enrichment factor < 2, such as Mn with an average of 1.7 and Hg with an average of 0.26, indicating deficiency to minimal enrichment.

Ecological risk indices

As shown from table 6 and fig. 9, the average value of ecological risk factor of Cd (17.87), Pb (5.08), Hg (1.67), Cu (1.16), Ni (1.04), Zn (0.24), Mn (0.15), and Fe (0.11) in Safaga Harbour is found to be less than 40, indicating that the sediments are low potential ecological risk. The average value of potential ecological risk index (27.32) is less than 150, indicating low ecological risk.

Table 5: The contamination factor (CF), contamination degree (C_d), pollution load index (PLI), and modified degree of contamination (mC_d) of heavy metals in the sediment samples of Safaga Harbour.

Sa. No.	CF								C_d	PLI	mC_d
	Fe	Mn	Zn	Cu	Pb	Ni	Cd	Hg			
SH 1.1	0.05	0.14	0.28	0.29	1.91	0.15	0.20	ND	3.02	0.23	0.43
SH 1.2	0.11	0.10	0.16	0.18	2.77	0.13	0.58	ND	4.02	0.25	0.57
SH 1.3	0.33	0.16	0.33	0.28	2.79	0.16	0.17	ND	4.24	0.33	0.61
SH 1.4	0.07	0.14	0.22	0.31	0.55	0.21	0.38	ND	1.88	0.22	0.27
SH 1.5	0.14	0.05	0.18	0.21	0.18	0.19	0.07	ND	1.03	0.13	0.15
SH 1.6	0.17	0.10	0.23	0.19	0.39	0.20	0.33	ND	1.60	0.21	0.23
SH 1.7	0.17	0.02	0.18	0.12	0.22	0.18	0.31	ND	1.18	0.13	0.17

Cont. table 5:

Sa. No.	CF								C_d	PLI	mC_d
	Fe	Mn	Zn	Cu	Pb	Ni	Cd	Hg			
SH 1.8	0.16	0.14	0.14	0.13	0.11	0.13	0.24	ND	1.06	0.15	0.15
SH 1.9	0.03	0.09	0.12	0.13	0.23	0.14	0.86	ND	1.60	0.14	0.23
SH 2.10	0.04	0.18	0.32	0.18	0.97	0.24	0.93	0.07	2.94	0.27	0.42
SH 2.11	0.10	0.26	0.30	0.35	0.84	0.35	0.85	0.13	3.18	0.35	0.45
SH 2.12	0.19	0.23	0.60	0.60	2.74	0.27	0.60	0.01	5.25	0.49	0.75
SH 2.13	0.11	0.19	0.18	0.17	0.47	0.25	0.51	ND	1.87	0.23	0.27
SH 2.14	0.15	0.20	0.24	0.18	0.39	0.24	0.39	ND	1.79	0.24	0.26
SH 2.15	0.10	0.17	0.17	0.15	1.51	0.26	3.05	ND	5.42	0.34	0.77
SH 2.16	0.08	0.11	0.10	0.10	0.28	0.15	0.14	ND	0.97	0.13	0.14
SH 2.17	0.02	0.04	0.03	0.04	0.27	0.11	0.94	ND	1.45	0.08	0.21
SH 3.18	0.17	0.21	1.17	1.02	1.15	0.32	0.58	0.15	4.77	0.51	0.68
SH 3.19	0.06	0.19	0.38	0.49	1.99	0.27	0.34	0.16	3.87	0.32	0.55
SH 3.20	0.10	0.61	0.41	0.52	2.33	0.24	1.00	0.07	5.29	0.50	0.76
SH 3.21	0.01	0.03	0.05	0.05	2.22	0.12	0.42	ND	2.90	0.10	0.41
SH 3.22	0.08	0.17	0.18	0.14	0.65	0.22	0.74	ND	2.18	0.23	0.31
SH 3.23	0.15	0.12	0.22	0.15	0.63	0.27	0.54	ND	2.08	0.25	0.30
SH 3.24	0.12	0.14	0.08	0.19	0.49	0.22	0.38	ND	1.62	0.19	0.23
SH 3.25	0.15	0.12	0.16	0.14	0.66	0.25	0.87	ND	2.35	0.25	0.34
SH 3.26	0.10	0.15	0.11	0.05	0.46	0.22	0.33	ND	1.43	0.16	0.20
SH 3.27	0.10	0.08	0.06	0.10	0.92	0.18	0.58	ND	2.02	0.17	0.29
SH 3.28	0.03	0.02	0.02	0.05	0.32	0.14	0.34	ND	0.93	0.07	0.13
Stdev	0.07	0.11	0.22	0.21	0.88	0.06	0.55	0.05	1.42	0.12	0.20
Min	0.01	0.02	0.02	0.04	0.11	0.11	0.07	ND	0.93	0.07	0.13
Max	0.33	0.61	1.17	1.02	2.79	0.35	3.05	0.16	5.42	0.51	0.77
Avg.	0.11	0.15	0.24	0.23	1.02	0.21	0.60	0.02	2.57	0.24	0.37

CF = contamination factor C_d = contamination degree PLI = pollution load index
mC_d = modified degree of contamination Stdev = standard deviation
Min = minimum Max = maximum Avg. = average ND = not detected

Table 6: The enrichment factor (EF), the ecological risk factor (Er), and the potential ecological risk index (RI) of heavy metals in the sediment samples of Safaga Harbour.

Sa. No.	EF							ER								RI
	Mn	Zn	Cu	Pb	Ni	Cd	Hg	Fe	Mn	Zn	Cu	Pb	Ni	Cd	Hg	
SH 1.1	2.54	5.27	5.44	35.82	2.77	3.74	ND	0.05	0.14	0.28	1.45	9.56	0.74	5.99	ND	18.21
SH 1.2	0.94	1.55	1.68	26.12	1.25	5.44	ND	0.11	0.10	0.16	0.89	13.83	0.66	17.28	ND	33.03
SH 1.3	0.49	1.00	0.85	8.39	0.49	0.51	ND	0.33	0.16	0.33	1.41	13.97	0.82	5.14	ND	22.17
SH 1.4	2.07	3.33	4.64	8.29	3.13	5.76	ND	0.07	0.14	0.22	1.55	2.77	1.05	11.55	ND	17.34
SH 1.5	0.37	1.31	1.48	1.27	1.33	0.52	ND	0.14	0.05	0.18	1.04	0.89	0.94	2.20	ND	5.45
SH 1.6	0.61	1.37	1.11	2.30	1.17	1.94	ND	0.17	0.10	0.23	0.94	1.93	0.98	9.76	ND	14.11
SH 1.7	0.10	1.08	0.70	1.31	1.09	1.87	ND	0.17	0.02	0.18	0.58	1.09	0.90	9.29	ND	12.22
SH 1.8	0.88	0.84	0.81	0.66	0.82	1.48	ND	0.16	0.14	0.14	0.66	0.54	0.67	7.27	ND	9.58
SH 1.9	3.22	4.23	4.58	8.13	4.90	30.09	ND	0.03	0.09	0.12	0.65	1.16	0.70	25.75	ND	28.50
SH 2.10	4.12	7.40	4.08	22.15	5.43	21.32	1.70	0.04	0.18	0.32	0.89	4.85	1.19	28.00	5.95	41.43
SH 2.11	2.72	3.10	3.63	8.73	3.58	8.79	1.33	0.10	0.26	0.30	1.75	4.22	1.73	25.50	10.32	44.20
SH 2.12	1.19	3.13	3.09	14.17	1.41	3.13	0.04	0.19	0.23	0.60	2.98	13.68	1.36	18.13	0.68	37.87
SH 2.13	1.74	1.64	1.52	4.30	2.23	4.59	ND	0.11	0.19	0.18	0.84	2.37	1.23	15.17	ND	20.08
SH 2.14	1.32	1.58	1.14	2.52	1.59	2.53	ND	0.15	0.20	0.24	0.88	1.93	1.22	11.63	ND	16.26
SH 2.15	1.73	1.71	1.53	15.17	2.57	30.55	ND	0.10	0.17	0.17	0.76	7.57	1.29	91.51	ND	101.57
SH 2.16	1.40	1.21	1.22	3.42	1.84	1.73	ND	0.08	0.11	0.10	0.50	1.40	0.76	4.26	ND	7.22

Cont. table 6:

Sa. No.	EF							ER								RI
	Mn	Zn	Cu	Pb	Ni	Cd	Hg	Fe	Mn	Zn	Cu	Pb	Ni	Cd	Hg	
SH 2.17	1.74	1.40	1.91	13.22	5.51	46.01	ND	0.02	0.04	0.03	0.20	1.35	0.56	28.23	ND	30.42
SH 3.18	1.25	6.84	6.00	6.76	1.86	3.39	0.88	0.17	0.21	1.17	5.12	5.77	1.59	17.35	11.98	43.36
SH 3.19	3.41	6.66	8.60	35.28	4.75	5.99	2.79	0.06	0.19	0.38	2.43	9.97	1.34	10.15	12.60	37.12
SH 3.20	5.93	3.95	5.04	22.54	2.34	9.71	0.65	0.10	0.61	0.41	2.61	11.66	1.21	30.13	5.35	52.08
SH 3.21	2.10	3.63	3.87	171.89	9.14	32.42	ND	0.01	0.03	0.05	0.25	11.12	0.59	12.58	ND	24.63
SH 3.22	2.03	2.09	1.66	7.70	2.56	8.75	ND	0.08	0.17	0.18	0.70	3.25	1.08	22.16	ND	27.63
SH 3.23	0.82	1.51	0.98	4.30	1.82	3.68	ND	0.15	0.12	0.22	0.73	3.17	1.34	16.31	ND	22.04
SH 3.24	1.17	0.62	1.52	4.01	1.81	3.07	ND	0.12	0.14	0.08	0.93	2.46	1.11	11.32	ND	16.17
SH 3.25	0.75	1.06	0.91	4.32	1.60	5.67	ND	0.15	0.12	0.16	0.70	3.32	1.23	26.15	ND	31.83
SH 3.26	1.46	1.08	0.50	4.46	2.15	3.14	ND	0.10	0.15	0.11	0.26	2.32	1.12	9.77	ND	13.82
SH 3.27	0.74	0.55	0.97	8.91	1.77	5.62	ND	0.10	0.08	0.06	0.50	4.59	0.91	17.40	ND	23.64
SH 3.28	0.85	0.92	2.11	12.28	5.33	13.17	ND	0.03	0.02	0.02	0.27	1.60	0.69	10.28	ND	12.91
Stdev	1.27	1.99	2.02	31.97	1.92	11.63	0.66	0.07	0.11	0.22	1.05	4.42	0.30	16.46	3.82	18.94
Min	0.10	0.55	0.50	0.66	0.49	0.51	0.00	0.01	0.02	0.02	0.20	0.54	0.56	2.20	ND	5.45
Max	5.93	7.40	8.60	171.89	9.14	46.01	2.79	0.33	0.61	1.17	5.12	13.97	1.73	91.51	12.60	101.57
Avg.	1.70	2.50	2.56	16.37	2.72	9.45	0.26	0.11	0.15	0.24	1.16	5.08	1.04	17.87	1.67	27.32

Table 7: Pollution classes of single and integrated indices

Index		Value	Classification	Reference
CF		Cf< 1	Low degree of contamination	[32]
		1 ≤ Cf< 3	Moderate degree of contamination	
		3 ≤ Cf< 6	Considerable degree of contamination	
		Cf ≥ 6	Very high degree of contamination	
C_d		Cd < 8	Low degree of contamination	
		8 ≤ Cd < 16	Moderate degree of contamination	
		16 ≤ Cd < 32	Considerable degree of contamination	
		Cd ≥ 32	Very high degree of contamination	
PLI		0	Perfection	[33]
		0 < PLI < 1	Baseline levels	
		PLI > 1	Progressive deterioration of site	
mC_d		mCd<1.5	Nil to a very low degree of contamination	[34]
		1.5 ≤ mCd < 2	Low degree of contamination	
		2 ≤ mCd < 4	Moderate degree of contamination	
		4 ≤ mCd < 8	High degree of contamination	
		8 ≤ mCd < 16	Very high degree of contamination	
		16 ≤ mCd < 32	Extremely high degree of contamination	
		mCd ≥ 32	Ultra-high degree of contamination	
EF		EF < 2	Deficiency to minimal enrichment	[35]
		2 ≤ EF < 5	Moderate enrichment	
		5 ≤ EF < 20	Significant enrichment	
		20 ≤ EF < 40	Very high enrichment	
		EF ≥ 40	Extremally high enrichment	
Ecological Risk Indices	**ER**	Er< 40	Low potential ecological risk	[32]
		40 ≤ Er< 80	Moderate potential ecological risk	
		80 ≤ Er< 160	Considerable potential ecological risk	
		160 ≤ Er< 320	High potential ecological risk	
		Er ≥ 320	Very high ecological risk	
	RI	RI < 150	Low ecological risk	
		150 ≤ RI < 300	Moderate ecological risk	
		300 ≤ RI < 600	Considerable ecological risk	
		RI ≥ 600	Very high ecological risk	

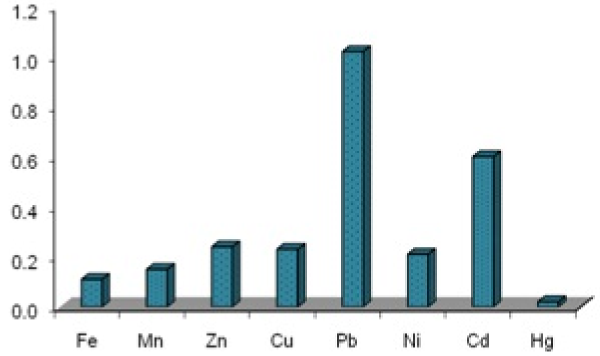


Fig. 5: Average values of contamination factor of sediments at Safaga Harbour.

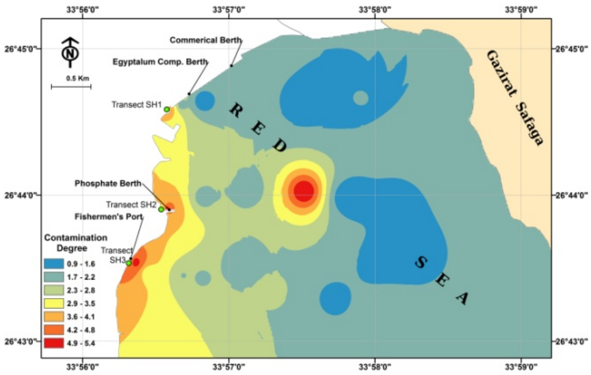


Fig. 6: Spatial representation of contamination degree at Safaga Harbour.

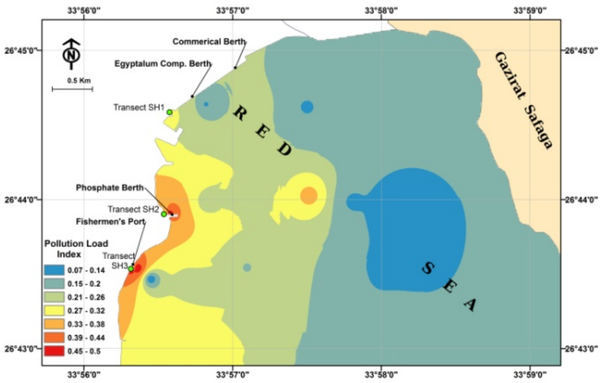


Fig. 7: Spatial representation of pollution load index at Safaga Harbour.

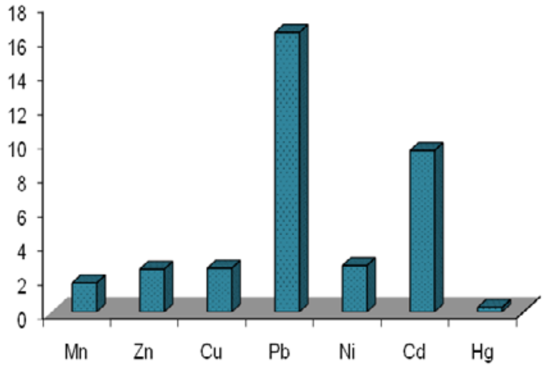


Fig. 8: Average values of enrichment factor of sediments at Safaga Harbour

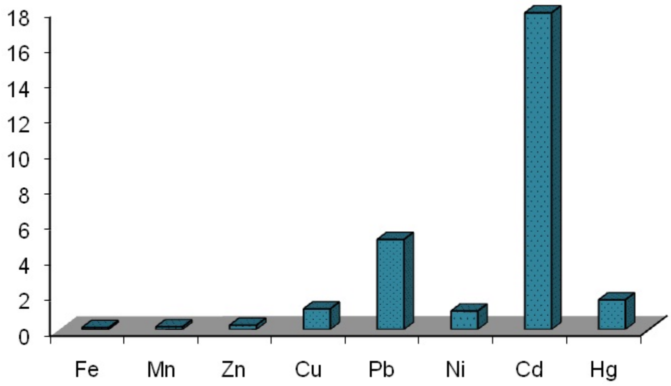


Fig. 9: Average values of ecological risk factor of sediments at Safaga Harbour

IV. Conclusions and recommendations

The high concentration of Mn, Zn, Cu, Ni, and Hg are localized in the southern region of Safaga Harbour area, close to the shoreline. Mn, Zn, Cu, and Hg contents recorded an average value of 126.91, 22.5, 10.44, 14.09, and 0.01 ppm, respectively. This is due to the impact of human activities that have been operating in the Safaga Harbour region for more than two decades, such as phosphate shipment, in addition to human activities in the Fishermen's Port area. The beach and intertidal areas show the highest values of Pb at Safaga Harbour. Pb content recorded an average value of 20.33 ppm. This is attributed to coal disburdening, oil spills from ships at the harbour area, cement packing, and phosphate shipment, in addition to human activities at Fishermen's Port (marine paints as Pb chloride and oily waste from the boats). Iron showed a different spatial distribution than the other heavy metals, where Fe showed high values in the area close to the harbour and continues as well in the deep area between the shoreline and Gazirat Safaga. Fe recorded 0.52% as an average. This can be attributed to the landfilling and dredging operations in the harbour area. Cd recorded an average value of 0.18 ppm. The occurrence of Cd in the sediments of the study area is natural, probably due to the formation of cadmium carbonates, where its concentrations are within the background value. In general, comparing the data of heavy metals from this study with guidelines showed that the average values of the studied heavy metals were lower than the threshold effect level.

The principal component analysis results of Safaga Harbour sediments give four components. The first component accounted for 38.42% of the total variance and included significant positive loadings for Hg, Cu, Zn, Ni, TP, and Mn, with a negative loading for carbonate, indicating an anthropogenic source of these elements due to past phosphate shipment and cement packing at the area and other human activities at Fishermen's Port. The third component accounted for 12.37%, it only has a strong positive loading with Fe. The negative loading of carbonate for the third component suggests an anthropogenic origin of Fe in the area, which is different than the anthropogenic source of the first component's elements. The fourth component represents 8.75% of the total variance. Cd and Pb show high positive loadings onto the fourth component with no significant loadings from other elements, indicating another anthropogenic source in the area.

The average values of six indices that have been applied to the results of heavy metals of the study area suggest that the sediments of the area under study aren't polluted by heavy metals, except for enrichment factor results, which suggest that the sediments of Safaga Harbour area are significantly enriched with Pb and Cd.

Conducting more studies in the area is recommended to monitor the environmental risks resulting from human activities to protect the marine environment from pollution. Additionally, environmental awareness is needed among boat operators, tourists, and the public.

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