

A Comparison of Pollution, Environmental Hazards, Sedimentology, and Geochemistry, in Five Economic Harbors Along the Egyptian Coast of Mediterranean Sea

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Abstract

Heavy metal pollution and its environmental and human risks have become one of the most important global environmental problems. In the current study, the potential heavy metals ecological risks and their pollution status were assessed in five important harbors (Sidi Krir, Dekhila, Western, Damietta, and Port Said) along the Egyptian coast of the Mediterranean Sea. Twenty-six sediment samples were collected from five harbors, where eight heavy metals (Fe, Mn, Zn, Cu, Ni, Cr, Pb and Cd) were identified as well as their texture and geochemistry. To gain deeper insights into the human and ecological hazards of the heavy metals, thirteen ecological indices, sediment quality guidelines and multivariate analysis as well as two pathways of exposures to non-carcinogenic and carcinogenic risk of heavy metals for children and adults were evaluated. The data shown that Sidi Kriri harbor recorded the lowest values for heavy metals, for Cu, while Western Harbor had the highest average for Zn. Multivariate analysis revealed the contribution of heavy metals to sediment contamination and the geochemical characteristics as well as nearby sources of pollution. Geo-accumulation index, Contamination factor, Toxic units, sum of toxic units, sediment modified hazard quotient, and sediment hazard quotients reflected the significant contribution of Cd to sediments along all harbors. Non-carcinogenic hazard risk index (*H*) values along the harbors gave the order: Western> Port Said> Damietta> Dekhila> Sidi Krir. Also, *TLCR* values for children and adults indicated the irregularly high abundance of heavy metals in harbor sediments that may cause adverse public health effects.

Introduction

Heavy metals are the main man-made pollutants in the global coastal and marine environment. Due to potential toxicity, multiple sources, and cumulative pollution, pollution of the coastal environment is one of the environmental issues that arouse the attention of the scientific community (El Barjy et al. 2020). It was pointed out that more than 99% of the heavy metals entering the marine water system are stored in the sediment in various ways, that is, the sediment can be used as a large heavy metal storage pool (Shen et al. 2019). Sediment's heavy metals originate from both natural and human sources (Deng et al. 2020). Heavy metals in marine systems can be released into the water column under appropriate parameters and affect the ecosystem. Over time, the further development of human activities has increased the toxicity of heavy metals and integrated them into the food chain by transferring them from sediments to the marine environment. Thus, the accumulation of heavy metals in marine organisms and finally in human consumers has become an issue of concern in modern society as they threaten their health.

Several conventions and international organizations have been established heavy metals-based indices to assess marine sediment pollution, and a variety of methods have been used to evaluate heavy metal pollution and its potential environmental hazards in sediments. These methods include the enrichment factor (*EF*), contamination factor (*C_F*), and geoaccumulation index (*I_{geo}*). Enrichment factor (*EF*), Contamination factor (*C_F*), degree of contamination (*C_d*) and pollution load index (*PLI*) methods. Although these methods cannot provide information about the toxicity of heavy metals, they cannot fully reflect the overall toxicity of heavy metals (Liu et al. 2019). Therefore, a potential ecological risk index (*PERI*) method was proposed to compensate for this shortcoming, and it has become a popular method for evaluating heavy metal pollution in marine sediments.

The Sediment Quality Guidelines (*SQGs*) is necessary to detect contaminated sediment hotspots and the potential impact of contaminated sediments on benthic organisms (Enuneku 2018). By comparing the concentration of sediment pollutants with the criteria for quality matching, sediment pollution can be estimated (MacDonald et al. 2000). These guidelines can also help clarify sediment quality.

Two criteria were developed: the low and median range effects (*ERL/ERM*) and the threshold/probable effect level (*TEL/PEL*). The low range (*ERL* or *TEL*) values were reported as a pollutant contaminant with a relatively low impact on biological communities. Under this concentration, there would be rare adverse effects upon on sediment-dwelling animals. On the other hand, *ERM* and *PEL* values represent contaminant concentrations above which adverse effects are likely to occur (MacDonald et al. 1996; Long and MacDonald 1998). These *SQGs* were developed based on sediment toxicity information collected for freshwater and saltwater sediments throughout the USA and were developed in a manner consistent with the TELs and PELs for freshwater sediments (Smith et al. 1996). Human health risk assessment of potentially toxic heavy metals provides an indication of the risk level due to pollutant exposure, and it is based on the characterization or quantification of the risk level either as carcinogenic or a non-carcinogenic risk (Cherf et al. 2016).

The current research plan was to sample sediments from five harbors, which are named: Sidi Krir Harbor, Dekhila Harbor, Western Harbor, Damietta Harbor, and Port Said Harbor(1) to identify the spatial distributions of some heavy metals in the sediments; (2) to state the metal pollution status using some established guidelines and pollution indices; (3) to follow heavy metals ecotoxicity by different ecological indices; (4) to estimate the impact of heavy metals on human health; (5) to estimate the potential sources of heavy metal contamination by using the multivariate statistical analysis.

Materials And Methods

Area of study

Twenty-six sediment samples were tested from Sidi Krir (A), Dekhila (B), Western (C), Damietta (D), and Port Said (E) Harbors located along the Egyptian Mediterranean Sea coast.

Sidi Krir Harbor (A) is located on the west coast of Alexandria City. It is a typical carbonate province with an open coastal environment. It lies between Latitudes 31.05° and 31.09° N and Longitudes 29.58° and 29.70° E (Fig. 1). The near shore seabed is characterized by a relatively gentle slope, while the seabed is steep and the continental shelf is very narrow or missing (Abdel-Halim et al. 2016). The shore is mostly sandy, with a relatively wider beach. There are various activities in the area such as: a power plant that use tar instead of natural gas for a long time, the Arab Petroleum Pipe Company SUMED (Suez, Mediterranean pipeline), and some tourist villages that may dispose of waste directly into the sea without treatment, resulting in serious pollution in the area.

Dekhila Harbor (B) is located on the western side of El-Mex Bay (Fig. 1). It is a semi-enclosed basin constructed in 1986 for the export of manufactured iron and steel and the import of coal (Heneash 2015). It also plays an important role in the export and import of other goods such as minerals, ores, fertilizers, salts and grain. The surface area of the harbor is about 12.5 km² and the water depth ranges from 4 to 20 m. The harbor's water is exposed to several sources of wastewaters coming from the El-Mex Bay through El-Umoum drain.

Western Harbor (C) is considered one of the most important and largest harbors in the Mediterranean (Fig. 1). The length of the Western Harbor is 7 km and the maximum width is 2 km (Saad et al. 2003). The depth of its water ranges from 5.5 to 14.0 m and its region is divided into internal and external mouths of 200 acres and 600 acres respectively. It is a shallow and semi-enclosed basin that directly receives variable volumes of drainage from the Nubariya Canal (\approx 9000 m³/day) and El-Umoum drainage. Due to the prevailing winds the drainage waters of Nubariya Canal and El-Umoum drain enters WH area. The harbor also suffers from intense marine activities, including the import of fertilizers, coal, cement, and export of oil. Harbor (C) is under pressure from various pollutants from different external and internal sources. The external pollution originates from household, industrial and agricultural waste. In addition, a large amount of untreated sewage and industrial waste are also dumped directly into Western Harbor from multiple outlets. The internal pollution originates from different shipping wastes other than discharges generated during the loading and unloading of imported and exported industrial raw materials.

Damietta Harbor (D) is a marine harbor located west of Damietta City on the coast of Nile Delta in Egypt (El-Gharabawy et al. 2011). It was constructed in 1982 for about 10 km west to Damietta outlet of the Nile River. It is semi-closed water body with an area of about 11.8 x 10⁶ m², and it is situated between Latitudes 31.29° N and Longitudes 31.45° E (Fig. 1). The harbor is mainly affected by loading/unloading operations, municipal and agricultural waste from Damietta Governorate. It is mainly affected by human activities including fishing.

Port Said Harbor (E) is located on the northern entrance of the Suez Canal and is considered one of the most important Egyptian ports. Due to its privileged location at the entrance of the largest international shipping corridor (Suez Canal) and in the middle of the largest commercial shipping line connecting Europe to the east and the largest transit port in the world. Its total area about 3,000,800 m², with water surface is 1.733.800 m² and land surface area is 1.267.095 m². It is situated between Latitudes 31.15° N and Longitudes 32.18° E (Fig. 1). Most of the days of the year and the prevailing winds are moderate to moderate northwesterly winds, with 50 cm tides. Damietta and Port Said are exposed to agricultural drains contaminated with hazardous industrial wastes, domestic sewage, organic matter, fertilizers and pesticides, in addition to oil pollution from ships and oil terminal (Soliman et al. 2015).

Sampling and elemental analysis

26 surface sediments samples were taken from A (Sites 1-5), B (Sites 6-10), C (Sites 11-16); D (Sites 17-21) and E (Sites 22-29) using Ekman grab sampling tool during winter 2018 (Fig. 1). The collected sediment samples were transported to the National Institute of Oceanography and Fisheries in an ice box. In the laboratory, samples were stored in polypropylene bags and kept in the freezer at (-20 °C) processing and analysis. Each of the frozen sediments were spread separately on glass plates and dried at room temperature. Each of the sediment samples was frozen dried, then grind with a pestle and mortar and sift to pass a 63 μ m mesh sieve. A portion of each sediment sample was washed and dried at 105 °C for mechanical analysis (Folk 1974). The total organic carbon (TOC) content was determined by oxidation (Loring and Rantala 1992). Total carbonates were estimated as described by Molnia (1974). The total, inorganic, and organic phosphorus contents (TP, IP and OP) were determined (Murphy and Riley 1962; Aspila 1976). Fine powder sediment samples were digested in closed Teflon vessels with a mixture of concentrated HNO₃, HClO₄, and HF acids (3: 2: 1 v/v, respectively; Oregoni and Aston 1984). Heavy metals concentrations were measured in the sediment solution digested using a Flame-Atomic Absorption Spectrophotometer (FAAS, Shimadzo 6800, with Autosampler 6100). Na, K, and Li concentrations were measured using a flame photometer (JENWAY PEP7). Calcium and magnesium levels were volumetrically determined (APHA-AWWA-WPCF 1999). Total boron concentration was determined by curcumin colorimetric method (Bingham 1982). Fluoride was extracted following the fusion procedure (Jeffery 1975). Fluoride ion concentration was determined by a colorimetric procedure for zirconium alizarin red S. (Anselm and Robinson 1951; Masoud et al. 2004). Colorimetric determination of both boron and fluoride was performed by UNICO UV-2000 spectrophotometer.

Quality assurance

The accuracy of the chemical analysis was verified with a sediment reference material (IAEA-405, International Atomic Energy Agency, Austria), which was analyzed with sediment samples during analysis. Results indicated good agreement between the reference material and analytical levels with recovery rates for heavy metals selected from the standard reference material of 95.5–100.2%.

Environmental risk assessment of heavy metals

Some indices (EF , I_{geo} , CF , C_d , mC_d , PLI , RI , TRI , TUs , $mPELQ$, $mERMQ$, HQ_{sed} and mHQ_{sed}) were applied to verify the geological and anthropogenic sources of heavy metals in the different harbors examined (Table 1). Variation in pollution and ecological risk indices results from the difference in the applicability of these indices to sediment pollutants (Omran 2016).

Table 1 The applied risk assessment indices

Pollution indicators	Procedures of calculation	Definition of parameters	References
Enrichment factor (EF)	$EF = \frac{C_i \text{ sediment}}{(\text{Median } C_i \text{ Sediment} + 2 \times MAD C_b)}$	Where, C_i sediment and Median C_b Background were concentration and median concentration of sediments and background of the determined heavy element, respectively. MAD was the median absolute deviation from median.	Khalil et al. 2016
Geoaccumulation index (I_{geo})	$I_{geo} = \log_2 [C_i / (1.5 \times B_i)]$	Where, C_i is the measured concentration of metal (i) in the sediments, B_i is the geochemical background concentration of the metal (earth crust, and 1.5 is introduced to minimize the effects of possible variations in the background values.	Müller (1969)
Contamination factor (CF), Degree of contamination (C_d), and modified degree of contamination (mC_d)	$CF_i = \frac{C_i}{C_b}$ $C_d = \sum_{i=1}^n CF_i$ $mC_d = \frac{\sum_{i=1}^n CF_i}{n}$	Where, n is the number of heavy metals, CF_i is the contamination factor of the heavy metal in the sediment sample and C_b is the concentration of the metal in the earth crust .	Ashayeri and Keshavarzi (2019)
Pollution load index (PLI)	$PLI = (CF_1 \times CF_2 \times CF_3 \times \dots \times CF_n)^{1/n}$ $PLI \text{ for zone} = \sqrt[n]{\text{station 1} \times \text{station 2} \dots \times \text{station m}}$	Where CF is the contamination factor for each of the n metal and m number of stations in each zone	Ganugapenta et al. (2018)
Potential ecological risk factor (E_r) and potential ecological risk index (RI)	$E_r = Tr_i \times CF_i$ $RI = \sum_{i=1}^n E_r^i$	Where, toxic-response factor (Tr_i) for Cd, Cu, Pb, Ni, Cr, Zn, Mn are 30, 5, 5, 5, 2, 1, 1, respectively, and CF_i is the contamination factor. Where RI is the requested potential ecological risk index for the environment and E_r is the potential ecological risk factor for a given element i.	Hakanson (1980); Ibrahim et al. 2019
Toxic risk index (TRI) and integrated (ΣTRI)	$TRI_i = \sqrt{\left(\frac{C_i}{TEL}\right)^2 + \left(\frac{C_i}{PEL}\right)^2} / 2$ $TRI = \sum_{i=1}^n TRI_i$	C_i , TEL and PEL are concentration, threshold and probable level effects of each heavy metal in sediment sample	Elsagh et al. (2021)
Toxic units (TUs) and sum of toxic units (ΣTUs)	$\Sigma TUs = \sum_{i=1}^n \left(\frac{C_i}{PEL_i}\right)$	toxic unit (TUs) is defined as the ratio of each determined trace metal concentration to its PEL value	Pederson et al. (1998)
Mean PEL and ERM quotients	$m - ERM - Q \text{ or } m - PEL - Q$ $= \left(\sum_{i=1}^n [C_i / (ERM_i \text{ or } PEL_i)] \right) / n$	C_i is the concentration, ERM_i is the threshold effect level, and PEL is the probable effect level of each heavy metal	Long et al. (2000); El Nemr and El-Said (2017)
Sediment modified hazard quotient (mHQ_{sed})	$mHQ_{sed} = \left[C_i \left(\frac{1}{TEL_i} + \frac{1}{PEL_i} + \frac{1}{SEL_i} \right) \right]^{1/2}$	Where, C_i is the concentration of the heavy metal, and TEL_i , PEL_i , and SEL_i are the threshold effect level, probable effect level, and severe effect level for i metal, respectively.	Macdonald et al. (2000); El-Alfy et al. 2020
Sediment hazard quotients (HQ_{sed})	$HQ_{sed} = \frac{C_i}{SQG}$	Where, C_i is the observed concentration of a metal in sediment and SQG is the sediment quality guideline (Urban and Cook, 1986). The SQG adopted for calculating the HQ_{sed} in this study was the threshold effects level (TEL)	El-Alfy et al. 2020

Human health risk assessment

Exposure to toxic heavy metals may be of great concern to humans who live near polluted aquatic ecosystems. There are two pathways of exposure to heavy metals in sediments, called ingestion (Ing), and dermal ($Derm$). These exposures can be calculated using equations below equations (Kusin et al. 2018):

$$CDI_{Ing} = \frac{C_{sed} \times IngR_{sed} \times ED \times EF \times CF}{BW \times AT}$$

$$CDI_{Derm} = \frac{C_{sed} \times SA \times AF \times EF \times ABS \times ED \times CF}{BW \times AT}$$

The exposure factors used in the calculation of chronic daily intake (CDI) are given (Table 2). The potential non-carcinogenic risk of heavy metal concentrations in sediments is characterized by the use of the hazard quotient (HQ). According to US Environmental Protection Agency, the hazard quotient (HQ) is defined as the ratio of the chronic daily intake or dose (CDI ; mg/kg/day) to reference dose (RfD ; mg/kg/day; USEPA 2012) as shown (Kusin et al. 2018;):

$$HQ = \frac{CDI}{RfD}$$

Table 2
The exposure factors and their identified values of human health assessment equations based on (USEPA 2011).

Exposure factors	Identify value
C_{sed}	Heavy metal concentration (mg/kg)
ED	Exposure duration of adult (35 years) and child (6 years)
EF	Exposure frequency (312 days/year)
BW	Body weight of adult (70 kg) and child (15 kg)
AT	Averaging time of adult and child (365 X ED)
$IngR_{sed}$	Ingestion rate of adult (100 mg/kg) and child (200 mg/kg)
CF	Conversion factor (1 X 10^{-6} kg/mg)
SA	Skin exposed area of adult (6032 cm ²) and child (2373 cm ²)
AF	Skin adherence factor for sediment of adult (0.07 mg/cm ²) and for child (0.2 mg/cm ²)
ABS	Dermal absorption factor (0.001)
LCR	Lifetime cancer risk (mg/kg/day)

The total hazard quotient (THQ) of heavy metals (i) in the sediment harbors for children and adults is calculated (El-Sadaawy et al. 2013; Liu et al. 2020):

$$THQ = \sum HQ_i = HQ_{Fe} + HQ_{Mn} \dots \dots HQ_{Cd}$$

HI is a combination of THQ 's traditional exposure pathways with the same detrimental effect. HQ values less than 0.2 are allowed, while value greater than 0.2 not and THQ values <1 show no exposure risk. Similarly, an HI of greater than unity from various pathways is considered unacceptable which means that the exposed population may experience adverse health effect and risk management measures should be implemented while HI of less than unity is considered negligible (Kusin et al. 2018):

$$HI = \sum THQ_{ing} + THQ_{derm}$$

According to HI values, no significant risk of non-carcinogenic will be expected if the value is less than one ($HI < 1$). However, if HI value exceeds one ($HI > 1$), there is a possibility of non-carcinogenic risk effects that tend to increase as the HI value increases.

On the other hand, the health risk for carcinogenic heavy metals expressed through incremental excess lifetime cancer risk ($IELCR$) was determined by estimating the total value of cancer risks for each of the exposure pathways (Table 2). Where, the cancer slope factor (CSF) values for Cd, Cr and Pb are 6.3, 0.5, 0.0085 and 1.5 mg/kg/day (USEPA 2012). Where, LADD is lifetime average daily dose and incremental excess lifetime cancer risk ($IELCR$) can be calculated from the following equation (Johnbull et al. 2019):

$$IELCR = LADD \times CSF$$

The sum the carcinogenic effect from exposure to carcinogenic pollutants gives the cumulative target risk (CTR) (Johnbull et al. 2019), while, $TLCR$ represents the sum of CTR in this equation (Li et al. 2021):

$$CTR = \sum_i LELCR_i$$

$$TLCR = \sum CTR_{Ing} + CTR_{Derm}$$

The acceptable threshold value for total lifetime cancer risk ($TLCR$) is between 1.0E-06 and 1.0E-04 that does not cause adverse human health risks (USEPA 2012; Johnbull et al. 2019; Li et al. 2021). Whereas, there may be significant public health risks above 1.0E-04 which makes the decision makers take notice.

Principal component analysis (PCA)

The statistical analysis of the physico-chemical and heavy metals characterization of sediments was performed by the SPSS-19 program. Principal component analysis (PCA) can assess the relationship between examined heavy metals and can also explore the hypothetical sources of heavy metals from both natural and anthropogenic origins (Bhardwaj et al. 2017).

Results And Discussion

Sediment characterization

The grain size data reveal that the sediments in Sidi Krir Harbor (A) composed of different types of sand fractions (coarse, medium, fine). The mean size ranges between 0.45 Φ and 2.59 Φ with average value 1.54 Φ (Table 3). The mean size in Dekhila Harbor (B) fluctuates from 3.33 Φ (very fine sand) to 6.19 Φ

(fine silt) with an average value 4.68 Φ . The occurrence of fine sediments here may be due to the dominance of terrigenous fine grain size sediments. The inclusive graphic mean size (MZ Φ) of the Western Harbor (C) ranges between 2.08 Φ (fine sand) and 6.22 Φ (fine silt) with the average value 4.34 Φ . It was found that, the majority of sediments consist mainly of silt fractions covering the bottom. In Damietta Harbor (D), the mean size ranges from 5.75 to 6.17 Φ . In this harbor the majority of sediments covering the bottom are silt (fine, and medium). The mean size in Port Said Harbor (E) varies between 3.00 (very fine sand) and 7.04 (very fine silt). However, the differences in grain size distribution can be attributed to the bottom configuration and dominant current regime.

Table 3
Sediment characterization of sediments of studied harbors

Sediment	SidiKrir Harbor				Dekhila Harbor (B)				Western Harbor (C)				Damietta Harbor (D)			
	Min.	Max.	Av.	SD	Min.	Max.	Av.	SD	Min.	Max.	Av.	SD	Min.	Max.	Av.	S
Sand (%)	99.8	100.0	99.9	0.1	5.9	57.9	32.5	24.8	24.1	78.6	39.3	22.2	4.0	39.4	17.6	1.
Silt (%)	0.0	0.4	0.1	0.2	31.3	72.6	52.5	19.1	15.6	67.1	45.3	17.6	29.2	87.7	53.0	2.
Clay (%)	0.0	0.0	0.0	0.0	8.6	25.4	15.0	6.7	5.8	18.6	15.4	5.4	8.4	46.8	29.5	1.
Mean (Φ)	0.45	2.59	1.54	0.8	3.33	6.16	4.68	1.2	2.08	6.22	4.34	1.5	5.75	6.17	6.0	0.
Sorting (\emptyset)	0.8	1.2	1.0	0.2	0.8	3.0	2.1	0.9	2.05	3.31	2.58	0.4	1.15	2.57	2.0	0.
Skweness	-0.3	0.2	0.0	0.2	-0.4	0.4	0.1	0.3	-0.2	0.3	0.1	0.2	-0.5	0.3	-0.1	0.
Kurtosis	0.8	1.6	1.0	0.3	1.0	2.2	1.3	0.5	0.9	2.0	1.3	0.4	0.7	2.2	1.3	0.
A (%)	14.7	22.2	17.94	2.7	49.4	67.9	57.9	8.3	56.8	65.9	61.21	3.9	40.3	54.6	48.33	6.
TOC (%)	0.1	0.2	0.1	0.1	2.4	4.0	3.1	0.7	1.7	5.6	4.5	1.5	1.0	1.7	1.4	0.
TCO ₃ (%)	84.0	99.6	92.5	7.3	79.4	88.6	82.9	4.1	20.1	90.5	66.1	24.0	11.1	20.2	16.0	3.
TSiO ₃ (%)	0.0	16.0	8.0	7.0	11.4	20.6	17.2	4.1	9.5	79.9	33.9	24.0	79.8	89.0	84.0	3.
TP (μ g/g)	30.0	121.0	62.0	40.0	250.0	933.0	640.0	312.0	649.0	913.0	771.0	87.0	671.0	914.0	769.0	9.
IP (μ g/g)	16.0	92.0	38.0	32.0	205.0	743.0	484.0	247.0	482.0	882.0	634.0	149.0	648.0	710.0	680.0	2.
OP (μ g/g)	11.0	42.0	24.0	12.0	45.0	215.0	155.0	71.0	31.0	244.0	138.0	87.0	16.0	204.0	89.0	7.
Ca (mg/g)	169.1	373.7	298.6	83.9	367.4	709.7	580.1	129.6	292.0	595.3	501.9	111.8	109.2	346.7	213.0	9.
Mg (mg/g)	240.5	482.6	385.4	98.7	402.0	736.8	625.1	128.9	370.6	745.2	606.8	155.8	93.5	435.8	234.4	1.
Na (mg/g)	7.7	21.3	14.3	5.1	25.3	30.2	28.2	1.8	15.3	19.1	17.2	1.5	18.6	37.7	26.1	7.
K (mg/g)	0.0	0.2	0.1	0.1	0.8	1.2	1.1	0.2	0.8	1.8	1.6	0.4	2.3	3.3	3.0	0.
Li (μ g/g)	0.8	15.3	3.7	6.5	115.9	165.9	137.7	20.3	18.6	173.6	94.2	59.1	33.8	49.9	40.7	6.
B (mg/g)	2.3	5.7	3.4	1.5	4.7	14.1	8.0	4.4	3.5	6.9	5.0	1.4	3.0	4.1	3.5	0.
SO ₄ (mg/g)	1.9	7.4	4.1	2.0	17.7	29.6	23.2	4.3	19.1	79.6	33.3	23.3	4.4	17.5	10.2	5.
Cl (mg/g)	0.4	0.5	0.5	0.1	2.0	2.5	2.3	0.2	2.6	5.2	3.8	1.2	1.7	4.5	2.8	1.
F (mg/g)	0.31	0.56	0.42	0.10	0.18	0.57	0.51	0.16	0.37	0.62	0.51	0.09	0.13	0.55	0.27	0.

In Sidi Kirir Harbor (A), the classification of sediments varies from moderately to poorly sorted Φ (Table 3). Whereas, in Dekhila Harbor (B), the sediments characteristics range between poorly sorted (0.80 Φ) and very poorly sorted (3 Φ). Poor sediments or ting mainly caused by the crushing the calcareous shells into fragments. At Western Harbor (C), the entire sediments are very poorly sorted. It varies between 2.05 Φ and 3.31 Φ with average value 2.58. The sediments in Damietta (D) and Port Said (E) harbors vary from poorly sorted (1.15 and 0.71 Φ , respectively) to very poorly sorted (2.57 and 2.52 Φ , respectively). It was suggested that poorly sorted sediments indicate a variable or disturbance during sedimentation (Wigley 1961). The main factors controlling sorting are the range of the particle size of materials the supplied to environments, the types of deposition and the current characteristics (Yang and Sh 2019).

The percentage of water content (A %) well reflects the sediment texture of the examined sediment samples, and the variation in all different samples is relatively slight, while there is significant variation between the five studied harbors studied (Table 3). The harbor of Sidi Kirir scores the lowest average A (17.94%), while the highest average is determined for the harbors of Dekhila and Western (57.90 and 61.21%, respectively). Harbors of Damietta and Port Said show relatively similar percentages of 48.33 and 46.08, respectively. For Dekhila Harbor, the displays results show good correlation between A % and each of TP % ($r=0.9647$, $p\leq0.008$), IP ($r=0.9830$, $p\leq0.003$), Fe ($r=0.9580$, $p\leq0.010$), Mn ($r=0.8957$, $p\leq0.040$), and Zn ($r=0.9560$, $p\leq0.011$). A% Damietta Harbor gives a weak correlation with TOC% ($r=0.8800$, $p\leq0.049$), while, Port Said Harbor explores good correlations between A % and each of TOC% ($r=0.9326$, $p\leq0.021$), TCO₃ ($r=0.9865$, $p\leq0.002$), and Cl ($r=0.9412$, $p\leq0.017$). In contrast, A % does not specify any relationship to the sediment components of Sidi Kirir and Western harbors. These correlations could be related to the uptake of the previously mentioned parameters at the inner surfaces as well as their condensation in the capillaries of the small pores.

Sorting(ϕ) of the sediment indicates the fluctuation in the degree of kinetic energy and the effect of sedimentation system on the grain size characteristics (El-Said et al. 2014). It ranges from poorly sorted to very poorly indicating troubled conditions. Most of the sediments are observed from poorly sorted in Sidi Krir to very poorly locate in Western Harbor, Damietta and Port Said Harbor (Table 3).

Skewness values give information about the symmetry or asymmetry of the frequency distribution of the sediment, and the sign of skewness correlates with environmental energy (Bhattacharya et al. 2016).

Kurtosis plays a vital role in sediment characterization in different environments as explained by Duane (1964) It is also working as on internal sorting or distribution. Friedman (1962) suggested that very high or low values of kurtosis mean that a portion the sediment has achieved sorting elsewhere in a high-energy environment. Almost all studied samples are leptokurtic. It has been suggested that carbonate sands tend to be exclusively leptokurtic or peaked (Pikey et al. 1967). This is related to the dominance of the carbonate sands (El-Said et al. 2014).

Among the examined harbors sediments, the organic carbon content (TOC%) show high values in both the Dekhila and Western harbors (Table 3). TOC% at Dekhila Harbor ranges between 2.4 and 4.0%, while, the higher value is limited to station 3, which includes agricultural drainage, sewage, and industrial wastewater from Lake Mariout through El Umoum drain, heavy ship traffic, export, and import activities. And the high values of TOC% (1.74 - 5.63%) are recorded in most of the Western Harbor stations, which are severely affected by agricultural runoff from the El-Mahmoudiya and Noubaria canals and are also affected by household waste. Generally, the low organic carbon content in most harbor sediments is due to reduced bioactivity and good aeration of bottom sediments, as most of the sediment organic matter is oxidized and washed out. The distribution of total organic carbon in the studied harbor sediments is strongly influenced by the amount of CaCO_3 .

The total silicate content ranges between the maximum (84.0%) value in Damietta and the minimum in Sidi Krir Harbor (8.0%; Table 3). Total silicate contents show the opposite trend to the carbonate contents along the area of investigation.

The data presented reflect those sediments of Sidi Krir Harbor show the lowest average TP, IP and OP contents (62.0, 38.0 and 24.0 $\mu\text{g/g}$) among the other studied harbors (Table 3). OP content ranges from 11 to 42 $\mu\text{g/g}$ with an average value (24 $\mu\text{g/g}$), representing 39% of the TP content. The correlation matrix yields high modulus values for TP&TOC% and IP&TOC% ($r = 0.9881$, $p \leq 0.002$ and $r = 0.9901$, $p \leq 0.001$, respectively), indicating the autolysis of dead cells of benthic organisms and their activities using phosphorus content (Pakzad et al. 2014).

The TP in the sediment harbors of Western Harbor and Damietta have higher average values (771.0 and 769.0 $\mu\text{g/g}$, respectively) than the other examined harbors. TP, IP and OP content of Dekhila Harbor varies from 250 to 933, 205.0 to 743.0 and 45 to 215 $\mu\text{g/g}$, respectively, where, IP and OP that count by 76 and 24%, respectively of TP. The positive correlations between TP&Silt% ($r = 0.9875$, $p \leq 0.002$) and IP&Silt ($r = 0.995$, $p \leq 0.000$) indicate that sediments with smaller grain size (clay and silt) have a greater ability to adsorb P (Jin et al. 2006; Kapanen 2008). Additionally, the presented data reflects the possible adsorption of phosphate with Fe, Mn, and Zn compounds (TP & Fe; $r = 0.9526$, $p \leq 0.012$, TP & Mn; $r = 0.9157$, $p \leq 0.029$ and TP & Zn; $r = 0.9332$, $p \leq 0.021$, respectively). Also, these relations are agreement with the correlations of Fe & Mean% ($r = 0.9355$, $p \leq 0.019$), Mn & Mean% ($r = 0.8860$, $p \leq 0.045$), Zn & Mean% ($r = 0.9673$, $p \leq 0.007$, Fe & A% ($r = 0.9580$, $p \leq 0.010$), Mn & A% ($r = 0.8957$, $p \leq 0.040$), and Zn & A% ($r = 0.9560$, $p \leq 0.011$).

In Western Harbor sediments, the values of TP show high values ranging from 649.0 to 913 $\mu\text{g/g}$. IP contents are between 482 and 882 $\mu\text{g/g}$ and represented 82% of the TP, while OP varies between 31 and 244 $\mu\text{g/g}$. Data reveal a significant positive association between TP & Zn ($r = 0.8994$, $p \leq 0.015$), IP & Ni ($r = 0.9401$, $p \leq 0.005$) and OP & Pb ($r = 0.8521$, $p \leq 0.031$) which reflects the potential adsorption of phosphate forms with their compounds. Also, the relationship of TP and F ($r = 0.893$, $p \leq 0.017$) indicates the formation of fluorapatite ($\text{Ca}_5(\text{PO}_4)_3\text{F}$) (El-Said et al. 2015).

The average concentrations of TP, IP and OP in Damietta Harbor are 769.0, 680.0, and 89.0 $\mu\text{g/g}$, respectively. The relationships TP&Sit% ($r = 0.8863$, $p \leq 0.045$) and IP&Sit% ($r = 0.9534$, $p \leq 0.012$) show a significant positive association. Mn in the present work reflects high correlations between TP and OP ($r = 0.9553$, $p \leq 0.011$ and $r = 0.9856$, $p \leq 0.002$, respectively). While, IP shows negative significant relationships with B and SO_4 ($r = -0.9816$, $p \leq 0.003$ and $r = -0.8837$, $p \leq 0.047$, respectively). Average concentrations of TP, IP and OP for Port Said Harbor are 620, 550 and 65 $\mu\text{g/g}$ respectively and IP content represents about 90% of the TP. It is observed that TP and IP show a positive correlation with F ($r = 0.9249$, $p \leq 0.024$ and $r = 0.9283$, $p \leq 0.023$, respectively). In general, TP contents in surface sediments of all studied harbors are much significantly higher than those of the Sidi Krir Harbor. This could be because this harbor is relatively remote from the mainland with fewer human impacts such as agricultural activities, so fewer land-based sources of phosphorus would be expected.

Ca (580.1 ± 129.6 mg/g), Mg (625.1 ± 128.9 mg/g), Na (28.2 ± 1.8 mg/g), B (8.0 ± 4.4 mg/g), F (0.5 ± 0.2 mg/g) and Li (137.7 ± 20.3 $\mu\text{g/g}$) show the highest average contents at Dekhila Harbor (B) (Table 3). The Ca values determined in this study are relatively similar to those recorded along the Egyptian coast of Mediterranean Sea, but the Mg values detected are higher than those obtained at the Egyptian Mediterranean Sea coast (El-Said et al. 2010). The relationship between Ca and Mg in Dekhila Harbor and Sidi Krir Harbor (A) ($r = 0.9757$, $p \leq 0.005$ and $r = 0.9806$, $p \leq 0.003$, respectively) may attributed to the formation of aragonite and high Mg calcite (El-Said et al. 2021). The lowest Ca (213.0 ± 98.8 mg/g), and Mg (234.4 ± 142.4 mg/g), average contents are recorded at Damietta Harbor (D). The values recorded for Na (7.7 - 37.7 mg/g) and K (0.0 - 4.9 mg/g) in the current study are lower those recorded for the contaminated Egyptian Lake Mariout (18.33 - 39.25 mg/g and 0.91 - 5.99 mg/g, respectively) (El-Said et al. 2020). Minimum Cl (0.5 ± 0.1 mg/g), K (0.1 ± 0.1 mg/g), B (3.4 ± 1.5 mg/g), SO_4 (4.1 ± 2.0 mg/g) and Li (3.7 ± 6.5 $\mu\text{g/g}$) contents reflect the minimum amounts of pollutants at Sidi Krir Harbor (A). Relationship between Cl-TOC% ($r = 0.9999$, $p \leq 0.000$) Cl-IP ($r = 0.9901$, $p \leq 0.001$) and Cl-TP ($r = 0.9881$, $p \leq 0.002$) at Sidi Krir Harbor and chloride relationships of Cl-TOC% ($r = 0.9329$, $p \leq 0.021$), $\text{TCO}_3\%$ ($r = 0.8973$, $p \leq 0.039$) and Cl-K ($r = 0.9274$, $p \leq 0.023$) are likely related to the water-soluble chloride compounds released and leached during the process of mineralization and weathering in Port Said (Harlove and Aranovich 2018). The highest average fluoride concentration (0.51 ± 0.16 mg/g) is recorded at Dekhila Harbor (B), while the lowest (0.22 ± 0.04 mg/g) is determined at Port Said Harbor (E). The highest recorded average fluoride content is within the amount of fluoride reported in ocean sediments (0.45 - 1.1 mg/g) (El-Said et al. 2010; 2016). The average amount of fluoride detected in Damietta Harbor (D) is

relatively similar to that previously determined in it (0.25 ± 0.31) (El-Said et al. 2016), whereas, the average value of fluoride recorded in Port Said is lower than that reported previously in this region (0.49 ± 0.10) (El-Said et al. 2016).

Heavy metals distribution

The average concentration of heavy metals along the harbors examined indicates that their regions are predominantly Fe and Mn, with the exception of the Sidi Kriri Harbor which is predominantly Fe and Cu (Table 4). Among the heavy metals identified in the harbors, the harbor of Sidi Kriri shows the lowest heavy metal values, with the exception of Cu, which ranks second after the Western Harbor. Along the harbors, cadmium shows the lowest values ranging between 1.06 and 29.99 $\mu\text{g/g}$ in harbors of Damietta and Western, respectively. Generally, the sediment quality guidelines (*SQGs*) indicate that most of the heavy metals identified (Cu, Ni, Cr, Pb and Cd) in the studied harbors rang between *TEL* and *PEL* values, with the exception of average Ni in harbors of Dekhila and Port Said, which is more than *ERM* values and Cd contents which are relatively similar to the *ERM*.

Table 4
Heavy metals concentration ($\mu\text{g/g}$) of sediments of studied harbors

Harbor	Station number	Fe	Mn	Zn	Cu	Ni	Cr	Pb	Cd
Sidi Krir	1	212.9	27.6	57.17	43.29	3.29	3.96	11.44	2.97
	2	185.6	7.7	6.11	20.02	4.25	3.79	9.08	1.45
	3	115.1	9.8	15.42	51.73	3.10	3.52	9.19	1.79
	4	257.2	33.1	21.31	79.22	4.25	4.22	3.35	1.83
	5	153.4	3.1	3.54	61.03	3.17	3.52	4.53	1.81
	Minimum	115.1	3.10	3.54	20.02	3.10	3.52	3.35	1.45
Maximum	257.2	33.14	57.17	79.22	4.25	4.22	11.44	2.97	
Average	184.9	16.27	20.71	51.06	3.61	3.80	7.52	1.97	
S.D	54.5	13.26	21.60	21.89	0.59	0.30	3.43	0.58	
Dekhila	6	5507.7	147.5	61.84	0.00	3.33	26.92	7.83	1.98
	7	6867.2	188.4	57.59	8.77	206.14	4.29	12.31	4.07
	8	10569.7	275.5	176.86	3.59	24.40	10.49	19.99	3.74
	9	8237.7	236.0	82.37	43.80	21.35	8.93	4.08	5.00
	10	10493.5	254.2	183.46	26.18	19.06	46.43	25.70	3.91
	Minimum	5507.7	147.48	57.59	0.00	3.33	4.29	4.08	1.98
Maximum	10569.7	275.50	183.46	43.80	206.14	46.43	25.70	5.00	
Average	8335.2	220.32	112.43	16.47	54.86	19.41	13.98	3.74	
S.D	2225.5	51.86	62.58	18.28	84.96	17.35	8.84	1.10	
Western	11	6633.4	209.5	208.47	886.98	54.29	14.96	17.48	4.05
	12	9555.9	285.8	267.43	72.49	10.81	45.88	104.67	3.17
	13	8606.4	313.4	290.48	114.64	70.83	99.32	14.65	5.38
	14	6929.1	282.6	278.83	159.20	8.04	4.33	124.80	3.37
	15	11312.1	273.3	133.57	101.05	6.51	73.72	12.82	5.50
	16	11103.4	349.4	215.05	66.35	3.87	544.78	129.92	29.99
Minimum	6929.1	273.26	133.57	66.35	3.87	4.33	12.82	3.17	
Maximum	11312.1	349.43	290.48	159.20	70.83	544.78	129.92	29.99	
Average	9501.4	300.90	237.07	102.75	20.01	153.60	77.37	9.48	
S.D	1821.1	30.98	64.64	37.32	28.52	221.49	58.86	11.51	
Damietta	17	18212.6	840.9	104.44	28.96	127.34	97.94	9.30	1.23
	18	17305.8	917.7	134.40	50.64	151.53	79.23	111.55	8.96
	19	17513.6	553.9	87.48	32.34	134.99	84.27	8.50	1.06
	20	17829.3	1280.0	93.73	29.51	158.29	84.34	8.70	1.87
	21	17995.5	796.9	96.72	37.44	175.44	83.73	9.01	2.04
	Minimum	17305.8	553.85	87.48	28.96	127.34	79.23	8.50	1.06
Maximum	18212.6	1280.03	134.40	50.64	175.44	97.94	111.55	8.96	
Average	17771.4	877.88	103.36	35.78	149.52	85.90	29.41	3.03	
S.D	364.5	262.79	18.39	8.96	19.08	7.06	45.92	3.34	
Port Said	22	17015.4	1205.3	127.82	47.02	138.49	149.76	30.31	3.35
	23	16795.2	1001.9	138.35	54.16	114.42	107.54	40.16	2.16
	24	16967.8	1338.1	108.12	34.74	135.15	73.55	4.19	2.15
	25	15551.9	615.3	63.85	6.57	76.75	126.25	3.37	1.50

Harbor	Station number	Fe	Mn	Zn	Cu	Ni	Cr	Pb	Cd
	26	18048.9	1176.8	105.38	27.20	150.77	174.57	11.72	1.94
Minimum		15551.9	615.35	63.85	6.57	76.75	73.55	3.37	1.50
Maximum		18048.9	1338.10	138.35	54.16	150.77	174.57	40.16	3.35
Average		16875.8	1067.49	108.70	33.94	123.11	126.33	17.95	2.22
S.D		889.3	279.69	28.58	18.54	29.03	38.78	16.48	0.69
Sediment quality guidelines (SQGs)									
TEL				124	18.7	15.9	52.3	30.2	0.68
PEL				271	108	42.8	160	112	4.2
ERL				150	34	30	81	46.7	1.2
ERM				410	270	50	370	218	9.6

The correlation matrix for the studied parameters for each harbor shows that the heavy metals examined contribute to the sediment contamination and the geochemical properties of the sediments. In Sidi Krir Harbor this contribution is shown in the correlations of Cr-Fe ($r=0.9685$, $p\leq 0.007$), Cr-Mg ($r=0.9033$, $p\leq 0.036$), Cd-Zn ($r=0.9505$, $p\leq 0.013$), Cd- Li ($r=0.9451$, $p\leq 0.015$), and Cu-Na ($r=-0.9433$, $p\leq 0.016$). In Dekhila Harbor Fe-K ($r=0.9146$, $p\leq 0.030$), Mn-K ($r=0.9301$, $p\leq 0.022$), Ni-B ($r=0.9456$, $p\leq 0.015$), Ni-Cl ($r=-0.9675$, $p\leq 0.007$), Cd-Ca ($r=0.9798$, $p\geq 0.003$), and Cd-Mg ($r=0.9748$, $p\geq 0.005$) are obtained. In Western Harbor, heavy metals accumulation in sediments due to pollution sources is demonstrate by the following correlations of Zn-Li ($r=0.8430$, $p\geq 0.035$), Zn-F ($r=0.8519$, $p\geq 0.031$), Cd-Cr ($r=0.9934$, $p\geq 0.000$), and Pb-B ($r=-0.9553$, $p\geq 0.003$). In Damietta Harbor, the relationships of Zn-Pb ($r=0.9456$, $p\geq 0.015$), Zn-Cd ($r=0.9406$, $p\geq 0.017$), Cd-Pb ($r=0.9924$, $p\geq 0.001$), Zn-Ca ($r=0.9024$, $p\geq 0.036$), Zn-Mg ($r=0.9241$, $p\geq 0.024$), Zn-K ($r=0.9487$, $p\geq 0.014$), Pb-K ($r=0.9218$, $p\geq 0.026$), and Cd-K ($r=0.9497$, $p\geq 0.013$) are obtained. In Port Said, there are many correlations between Ni-Fe ($r=0.9468$, $p\geq 0.015$), Ni-Mn ($r=0.9217$, $p\geq 0.026$), Zn- Cu ($r=0.9902$, $p\geq 0.001$), Zn-Li ($r=0.9349$, $p\geq 0.020$), Cr-Na ($r=0.9211$, $p\geq 0.026$), Cd-Li ($r=0.8879$, $p\geq 0.044$), Cd-F ($r=0.9355$, $p\geq 0.019$), Cd-K ($r=0.9673$, $p\geq 0.007$), and Cd-Cl ($r=0.8916$, $p\geq 0.042$). The large amount of heavy metals may be related to the wastewater evacuation of phosphate fertilizers and untreated industrial pollutants, along with shipping activities. These correlations coincide with the high significant multiple regression equations (Table 5).

Table 5
Multiple regression analyses of heavy metals and different geochemical properties in the examined harbors

Harbor	Multiple regression equation	R
Sidi Krir	Fe = -191.7 + 0.40 Cr + 0.56 Mg - 0.15 Na	0.9998523
	Mn = - 233.6 + 1.90 Cr - 0.48 Ni - 0.69	0.9996286
	Zn = -38.22 + 1.07 Cd - 0.31 F + 0.14 B	0.9999672
	Cu = 28.41 - 0.92 Na + 0.38 A% + 0.08 Ni	1.0000000
	Ni = 3.96 - 0.94 Clay % + 0.11 Ca + 0.02 TP	1.0000000
	Cr = 43.11 + 0.98 Fe - 0.18 F - 0.16 Sand %	0.9999997
	Pb = 1.59 + 0.79 Na + 0.57 Zn - 0.14 Mg	0.9999990
	Cd = 2.00 + 1.69 Li - 0.77 IP - 0.03 Fe	0.9999995
	Dekhila	Fe = 12302.6 - 1.08 Sand % + 0.34 Ni - 0.11 SO4
Mn = - 30.65 + 1.28 Fe - 0.34 Pb + 0.11 SO4		0.9999979
Zn = - 95.73 + 0.56 Mean + 0.43 Pb + 0.13 TSiO3%		0.9999788
Cu = 42.63 - 0.93 F + 0.54 Cr + 0.19 Cd		0.9989686
Ni = 583.4 - 1.19 Cl + 1.02 A% + 0.73 Sand %		0.9999819
Cr		not significant
Pb = 5.38 + 1.27 Zn - 0.66 OP + 0.13 Cr		0.9999796
Cd = - 1.0 + 0.91 Ca + 0.19 Cu + 0.08 Cr		0.9999981
Western		Fe = 24718.2 - 1.01 K + 1.11 F - 0.73 Zn - 0.14 Silt %
	Mn = 117.56 - 0.68 Cu + 0.57 Mean + 0.41 Fe + 0.14 IP	0.9999757
	Zn = - 148.1 + 0.14 Na + 0.84 Tp - 0.39 B - 0.07 Cr	0.9999963
	Cu = 702.0 - 0.97 Mn + 0.71 Mean + 0.43 Li + 0.29 Sorting	0.99998544
	Ni = - 245.1 + 0.97 IP + 0.50 Mg + 0.26 Sorting + 0.11 A %	0.9999963
	Cr = - 226.1 + 0.92 Cd + 0.20 Mn - 0.10 Cl + 0.05 Cu	0.9999998
	Pb = 263.2 - 0.54 B + 0.48 Cr - 0.54 Li - 0.16 Zn	0.9999976
	Cd = 12.5 + 1.08 Cr - 0.22 Mn + 0.11 C - 0.05 Cu	0.9999998
	Dameitta	Fe = 9773.0 + 0.75 Cr + 0.59 TSiO3%
Mn = 518.2 + 0.87 OP + 0.20 Ca - 0.10 Clay %		0.99999726
Zn = 320.1 + 0.76 K - 0.77 IP + 0.62 A%		0.99997148
Cu = 22.3 + 0.96 Cd + 0.41 Cl - 0.25 Silt %		0.99996917
Ni		not significant
Cr = 368.5 - 1.23 Mean + 0.62 Mn + 0.10 F		0.99999789
Pb = 31.4 + 1.08 Cd - 0.14 A % - 0.02 F		1
Cd = - 2.12 + 0.93 Pb + 0.13 A % + 0.02 F		1
Port Said		Fe = 15733.2 + 1.08 Silt % - 0.009 Ca - 0.06 Li
	Mn = 1521.3 - 1.10 Sand % - 0.19 SO4 - 0.10 Sorting	0.99999988
	Zn = - 25.0 + 0.96 Cu + 0.16 Fe - 0.06 Clay %	0.99999972
	Cu = 16.9 + 1.04 Zn - 0.16 Fe + 0.07 Clay %	0.9999997
	Ni = 73.4 + 1.13 Silt % - 0.31 SO4 + 0.06 OP	0.99999999
	Cr = - 109.3 + 0.77 Na + 0.49 B - 0.17 Mean	0.99992905
	Pb = 5.27 + 1.27 Cu - 0.60 Mean + 0.11 Na	0.99999901
	Cd = 0.29 + 0.93 K + 0.22 OP + 0.13 Sand %	0.99999847

The cluster of heavy metals grouping and the geochemical parameters analyses also demonstrate the great coordination of these among themselves and with other parameters in each harbor (Fig. 2). The main processes affecting the distribution of heavy metals in sediments are dispersion, precipitation and sedimentation and chemical reactions (Amankwaa et al. 2021).

Principle component analysis (PCA) is applied to heavy metals and geochemical results to identify potential factors and sources of pollutants in sediments from the studied harbors (Amankwaa et al. 2021). Fig. 3 demonstrates loading factors for the various studied parameters including heavy metals to sediments in the harbors examined after Varimax rotation. The obtained PCs explain the different percentages of each harbor, reflecting the difference in sediment properties and the contributions of different heavy metals. In most harbors, the results identified two PCs of eigenvalues greater than 1, with the exception of Western Harbor displaying three PCs. About 73.45, 80.52, 86.07, 76.58 and 78.25% of the total variance in the sediments data sets represent the Sidi Krir, Dekhila, Western, Damietta and Port Said harbors respectively.

Box Whisker plots for the various detected heavy metals (Fe, Mn, Zn, Cu, Ni, Cr, Pb and Cd) in the sediments of the investigated harbors are represented (Fig. 4). However, the box represents the minimum (Q_0 or 0%, lowest data point excluding any outliers), maximum (Q_4 or 100%, highest data point excluding any outliers), Median (Q_2 or 50%, the middle value of the dataset of each heavy metal. First quartile (Q_1 or 25%, the lower quartile) is the median of the lower half of the dataset. Third quartile (Q_3 or 75%, the upper quartile) is the median of the upper half of the dataset. Box Whisker plot for Sidi Krir Harbor shows great variability in Fe, Mn, Zn, and Cu contents. Amongst the studied heavy metals, Fe concentration varies greatly along the sediments of Sidi Krir, Dekhila, and Western harbors.

Pollution and ecological indices

Enrichment factor (EF)

The enrichment factor using the median background of the studied heavy metals in each harbor values gives minimal enrichment for all the determined elements. ($EF < 2$; Khalil et al. 2016).

Geo-accumulation index (I_{geo})

Almost all harbors examined show that 100% of their stations are uncontaminated by all examined heavy metals ($I_{geo} \leq 0$), except for Cd (Table 6). Cd appears to contribute significantly to the sediment pollution in all stations in the studied harbors and I_{geoCd} ranges from moderately to severe to severely polluted. High I_{geoCd} values are observed in the sediments at Dekhila, Western, Damietta and Port Said harbors.

Table 6
Overall pollution status using different risk indices in each of the studied harbors

Risk indices	Sidi Krir	Dekhila	Western	Dameitta	Port Said	Most polluted station	Overall pollution status
EF_{Fe}	0.35-1.00	0.40-1.00	0.47-0.95	0.92-1.00	0.79-1.00		No enrichment
EF_{Mn}	0.13-1.00	0.36-1.00	0.48-0.99	0.39-1.00	0.27-1.00		No enrichment
EF_{Zn}	0.09-1.00	0.44-1.00	0.29-0.91	0.76-1.00	0.32-1.00		No enrichment
EF_{Cu}	0.17-1.00	0.00-1.00	0.41-0.94	0.73-1.00	0.07-1.00		No enrichment
EF_{Ni}	0.81-1.00	0.06-1.00	0.43-0.89	0.64-1.00	0.30-1.00		No enrichment
EF_{Cr}	0.82-1.00	0.09-1.00	0.03-0.84	0.84-1.00	0.32-1.00		No enrichment
EF_{Pb}	0.16-1.00	0.14-1.00	0.08-0.71	0.52-1.00	0.12-1.00		No enrichment
EF_{Cd}	0.57-1.00	0.26-1.00	0.41-0.89	0.30-1.00	0.43-1.00		No enrichment
$I_{geo Fe}$	-ve	-ve	-ve	-ve	-ve		Unpolluted
$I_{geo Mn}$	-ve	-ve	-ve	-ve-0.25	-ve-0.31	Stations 20, 22, 24, and 26	Unpolluted to moderately polluted
$I_{geo Zn}$	-ve	-ve	-ve-0.61	-ve	-ve	Station 11-14, and 16	Unpolluted to moderately polluted
$I_{geo Cu}$	-ve	-ve	-ve-3.08	-ve	-ve	Station 11, 13 and 14	Unpolluted to strongly polluted
$I_{geo Ni}$	-ve	-ve-1.46	-ve	0.76-1.23	0.03-1.01	Stations 7, and 17- 26	Unpolluted to moderately polluted
$I_{geo Cr}$	-ve	-ve	-ve-1.86	-ve	-ve-0.22	Station 16 and 26	Unpolluted to moderately polluted
$I_{geo Pb}$	-ve	-ve-0.10	-ve-2.44	-ve-2.22	-ve-0.74	Stations 10, 12, 14, 16, 18, 22 and 23	Unpolluted to moderately polluted
$I_{geo Cd}$	2.69-3.72	3.14-4.47	3.82-7.06	2.23-5.32	2.74-3.90	All stations	Moderately to strongly polluted to Extremely polluted
CF_{Fe}	0.00-0.01	0.15-0.29	0.18-0.32	0.48-0.51	0.43-0.50	All stations	No contamination
CF_{Mn}	0.00-0.05	0.20-0.38	0.29-0.49	0.77-1.78	0.85-1.86	Stations 17-18, 20-24, and 26	No to moderate contamination
CF_{Zn}	0.03-0.45	0.45-1.44	1.05-2.29	0.69-1.06	0.50-1.09	Stations 8, 10-16, 18, and 23	No to moderate contamination
CF_{Cu}	0.29-1.13	0.04-0.63	0.95-12.67	0.41-0.72	0.09-0.77	Stations 11	No to very high contamination
CF_{Ni}	0.04-0.06	0.04-2.75	0.05-0.94	1.70-2.34	1.02-2.01	Stations 7,18,20, 21 and 26	Moderate contamination
CF_{Cr}	0.035-0.04	0.04-0.46	0.04-5.45	0.79-0.98	0.74-1.75	Station 16, 22-23, and 25-26	No to very high contamination
CF_{Pb}	0.27-0.92	0.33-2.06	1.03-10.39	0.68-8.92	0.27-3.21	Station 8, 10-16, 18, and 22-23	No to very high contamination
CF_{Cd}	9.65-19.79	13.21-33.34	13.21-199.90	7.06-59.75	10.00-22.33	All stations	very high contamination
C_d	10.82-21.90	15.04-35.88	33.92-219.23	12.79-75.03	14.44-31.92	All stations	moderate degree to very high degree of contamination
mC_d	1.35-2.74	1.88-4.48	4.24-27.40	1.60-9.38	1.80-3.99	Stations 7-16, 17-18, 19-24, and 26	low degree of contamination to extremely high degree of contamination
PLI	0.09-0.19	0.30-0.88	0.89-1.86	0.98-2.12	0.70-1.59	Station 18	Unpolluted to Heavily polluted
$PLIs$	0.13	0.54	1.19	1.27	1.24	Western, Damietta, and Port Said	No to progressive deterioration

Risk indices	Sidi Krir	Dekhila	Western	Dameitta	Port Said	Most polluted station	Overall pollution status
<i>RI</i>	297.8-963.9	234.6-1852.9	411.9-6054.1	234.6-1852.9	269.4-466.8	Station 15	High to very high risk
<i>TRI_{Zn}</i>	0.02-0.36	0.36-1.15	0.84-1.82	0.55-0.84	0.40-0.87	Station 13	No toxic risk
<i>TRI_{Cu}</i>	0.77-3.04	0.12-1.68	2.55-34.04	1.11-1.94	0.25-2.08	Station 11	Very high toxic risk
<i>TRI_{Ni}</i>	0.15-0.20	0.16-9.78	0.18-3.36	6.04-8.32	3.64-7.15	Station 7	Low toxic risk
<i>TRI_{Cr}</i>	0.05-0.06	0.06-0.66	0.06-7.75	1.13-1.39	1.05-2.48	Station 16	Low toxic risk
<i>TRI_{Pb}</i>	0.08-0.28	0.10-0.62	0.31-3.15	0.21-2.70	0.08-0.97	Station 16	No toxic risk
<i>TRI_{Cd}</i>	1.73-3.55	2.37-5.98	3.79-35.84	1.27-10.71	1.79-4.00	Station 16	Very high toxic risk
$\sum TRI$	2.93-6.06	3.53-15.59	10.98-49.60	10.78-23.48	7.93-15.76	All stations, except stations 2-3, and 5-6	No toxic risk to very high toxic
<i>TUs</i>	0.76-1.52	1.02-6.22	3.47-13.20	4.62-8.13	3.27-6.15	Stations 7, 11, 13, 14, 16-24 and 26	No toxic risk to more than moderate toxic ecosystem
<i>m-ERM-Q</i>	0.07-0.13	0.09-0.92	0.29-1.04	0.63-0.96	0.42-0.77	Station 16	Most stations are of 21% being biotoxic
<i>m-PEL-Q</i>	0.12-0.25	0.17-0.92	0.57-2.20	0.70-1.27	0.50-0.95	Station 16	Rang from 9–21% being bio toxic
<i>HQ_{sedZn}</i>	0.03-0.46	0.46-1.48	1.08-2.34	0.71-1.08	0.51-1.12	Station 13	No to moderately hazards
<i>HQ_{sedCu}</i>	1.07-4.24	0.17-2.34	3.55-47.43	1.55-2.71	0.35-2.90	Station 11	Potentail to very high hazards
<i>HQ_{sedNi}</i>	0.20-0.27	0.21-12.96	0.24-4.45	8.01-11.03	4.83-9.48	Station 7	Potentail to very high hazards
<i>HQ_{sedCr}</i>	0.07-0.08	0.08-0.89	0.1-10.42	1.51-1.87	1.41-3.34	Station 16	Potentail to high hazards
<i>HQ_{sedPb}</i>	0.11-0.38	0.14-0.85	0.42-4.30	0.28-3.69	0.11-0.33	Station 16	Potentail to moderate hazards
<i>HQ_{sedCd}</i>	2.13-4.37	2.91-7.36	4.66-44.10	1.56-13.18	2.21-4.92	Station 16	Moderate to high hazards
<i>mHQ_{sedZn}</i>	0.21-0.86	0.86-1.54	1.32-1.94	1.07-1.32	0.91-1.34	station 13	No low to moderate severity of contamination
<i>mHQ_{sedCu}</i>	1.20-2.39	0.47-1.77	2.18-7.98	1.44-1.91	0.69-1.97	station 11	No to extreme severity of contamination
<i>mHQ_{sedNi}</i>	0.56-0.65	0.58-4.53	0.62-2.66	3.56-4.18	2.76-3.87	station 7	Very low to extreme severity of contamination
<i>mHQ_{sedCr}</i>	0.35-0.38	0.38-1.26	0.39-4.33	1.65-1.84	1.59-2.45	Station 16	No to extreme severity of contamination
<i>mHQ_{sedPb}</i>	0.39-0.73	0.43-1.09	0.77-2.45	0.63-2.27	0.39-1.36	Station 16	No to considerable severity of contamination
<i>mHQ_{sedCd}</i>	1.62-2.32	1.89-3.01	2.39-7.36	1.38-4.03	1.65-2.46	Station 16	Low to extreme severity of contamination

Contamination factor (CF), contamination degree (Cd) and modified degree of contamination (mCd)

The *CF* of all the heavy metals studied in the harbors examined reflects that Fe is the only heavy metal showing a low level of contamination ($CF_{Fe} < 1$), while Cd shows the very high contamination ($CF_{Cd} > 6$) (Table 6). Most of the Damietta (sites: 17-18 and 20-21; 80% of sites) and Port Said (sites: 22-24 and 26; 80% of sites) harbors stations suffer moderately from Mn pollution ($1 < CF_{Mn} < 3$), while three other harbors examined have low Mn contamination ($CF_{Mn} < 1$). Most the stations studied in the examined harbors give CF_{Zn} values of low contamination level ($CF_{Zn} < 1$), except for Western Harbor sites showing moderate zinc contamination ($1 < CF_{Zn} < 3$). Half of Western Harbor sites have moderate Cu contamination (sites 13-15; $1 < CF_{Cu} < 3$), while site 11 shows the highest percentage of Cu contamination ($CF_{Cu} > 6$) among the sites examined. Almost of the stations in inspected harbors have low Ni contamination ($CF_{Ni} < 1$) with the exception of site 7 in Dekhila and sites 17-21 in Damietta (100% of sites) and sites 22-24 and 26 in Port Said harbor (80% of sites) which show medium Ni pollution ($1 < CF_{Ni} < 3$). Almost all harbor stations give a low degree of Cr contamination ($CF_{Cr} < 1$), except for station 16 (Western Harbor), and stations 22, 23, 25 and 26

(Port Said) are affected by moderate Cr pollution ($1 < CF_{Cr} < 3$). Western Harbor is the most Pb contaminated site, however, half of the sites (sites: 23, 14 and 16) show $CF_{Cu} > 6$, along with station 18 (Damietta Harbor), while the other sites range from low to Pb contamination. The C_d and mC_d values reflect that the harbors range from low to very high pollution areas. The C_d values are taken in descending order for Western Harbor (33.9-219.0) > Damietta Harbor (12.8-75.0) > Dekhila (15.0-35.9) > Port Said (14.4-31.9.2) > Sidi Krir (10.8-21.9). The mC_d values are taken in descending order: Western Harbor (4.2-27.4) > Damietta Harbor (1.6-9.4) > Dekhila (1.9-4.5) > Port Said (1.8-4.0) > Sidi Krir (1.4-2.7).

Pollution load index (PLI)

The PLI values are calculated for stations at each harbor and for each harbor zone (Ganugapenta et al. 2018). The PLI values range from unpolluted (< 0.7) especially along Sidi Krir and Dekhila to heavily polluted (< 3) at Damietta Harbor (St 18); Fig. 5) The PLI for the zone gives the decreasing order: Damietta (1.27) > Port Said (1.24) > Western (1.19) > Dekhila harbors (0.54) > Sidi Krir (0.13) (Table 6 and Fig. 5), pointing out that the Western, Damietta and Port Said harbors are the most affected by heavy metal areas along the other harbors that were examined (exceed the baseline of pollutants > 1) (Goher et al. 2014).

Toxic risk index (TRI) and integrated TRI ($\sum TRI$)

The high TRI_{Cu} , TRI_{Ni} and TRI_{Cd} values distinguished in the investigated harbors refer to the industrial and other anthropogenic sources, especially in Western and Damietta harbors (Table 6 and Fig. 5). It was reported that Cu, Ni and Cd are obtained from anthropogenic activities (Al Naggar et al. 2018). Almost all the stations along the studied harbors range from low ($\sum TRI < 5$) to very high toxic ($\sum TRI > 20$) (Table 6 and Fig. 5). The high $\sum TRI$ values recorded in Western, Damietta and Port Said harbors reflect that these harbors are of considerable and very high toxic risk.

Toxic units (TUs) and sum of toxic units ($\sum TUs$)

The TUs and $\sum TUs$ of each heavy metal and studied harbor are illustrated (Fig. 5). Most of the studied sites (sites 7, 11, 13, 14, 16-24 and 26) show that $\sum TUs$ exceed 4 amount for the moderate toxicity, i.e. significant mortality can be observed (Zhang et al. 2016). Higher values of TU_{Ni} (sites 7, and 17-26) and TU_{Cu} (site 11) along the investigated region may be associated with the significant environmental toxicity contribution due to the liquid hydrocarbons' sources and cargo activity (Yee 2010). The higher TU_{Cd} values shown for Damietta and Port Said harbors probably reflect the oil pollution from the shipping activities and oil refining and gas liquefaction and other petrochemical industrial projects (El-Asmar et al. 2014; Al Naggar et al. 2018).

Mean ERM (m-ERM-Q) and mean PEL (m-PEL-Q) quotients

Amongst the harbors studied, Sidi Krir shows the lowest quotient values of $m-ERM-Q$ (0.07-0.13) and $m-PEL-Q$ (0.12-0.25), representing 9–21% being bio toxic with least potential adverse effects marine on the environment (Table 6). Given the $m-ERM-Q$ values, most of the stations in the harbors examined have 21% of adverse biotoxic effects on the marine ecosystem, whereas, the high $m-PEL-Q$ quotients reflect that about 49% of the potential biotoxicity may occur in Damietta and Port Said harbors. The variability of biotoxicity from one harbor to another may be related to the sediment texture; i.e., the high sediment contamination with heavy metals especially in silty clay sediments as previously reported (Long et al. 2000). However, the highest $m-ERM-Q$ and $m-PEL-Q$ quotients are recorded in the harbors of lower carbonate and higher sand, silt and clay % (Table 3).

Sediment modified hazard quotient (mHQ_{sed})

According to the mHQ_{sed} , Western Harbor is shown to be highly hazardous for contamination ($2.5 > mHQ_{sed} > 3$) with values of Cu, Ni, and Cd (Table 6). The harbors of Damietta and Port Said show severe Ni contamination ($mHQ_{sed} > 3.5$) and for other metals it ranges from low ($mHQ_{sed} < 0.5$) to moderate contamination ($1.5 > mHQ_{sed} > 2$).

Sediment hazard quotients (HQ_{sed})

In Table 6, along the harbors studied, most stations in Western Harbor range from medium to high risk with Cu (3.5-47.4), Pb (0.4-4.3) and Cd (4.7-44.1), except Cr which gives HQ_{sed} values (0.1-10.4) that ranges from potential to high risk. Stations in the harbors of Damietta (HQ_{sedNi} : 8.0-11.0) and Port Said (HQ_{sedNi} : 4.8-9.5) exhibit moderate Ni risks, while only station 7 at Dekhila Harbor gives high risk with Ni (HQ_{sedNi} = 13.0).

Human health risk assessment

The CDI values presented for specific heavy metals for children are higher than those for adults along the studied area due to the same consumption of heavy metals for child, lower exposure time and lower body weight resulting in higher CDI values. For Fe, the chronic daily intake (CDI_{Fe}) of the child (5.3E-03- 5.1E-01, av. 2.9E-01 mg/Kg-day) and adult (2.3E-04- 2.2E-02, av. 1.2E-02 mg/Kg-day) in the harbors studied. The CDI_{Fe} takes a child and adult in the order of harbors: Damietta (5.1E-01 and 2.2E-02, respectively) > Port Said (4.8E-01 and 2.1E-02, respectively) > Western (2.6E-01 and 1.1E-02, respectively) > Dekhila (2.4E-01 and 1.0E-02, respectively) > Sidi Krir (5.3E-03 and 2.3E-04, respectively) considering that the chronic toxicity of oral sediment ingestion to adults in all harbors causes no hemosiderosis and cirrhosis symptoms (0.7-1.4 mg/Kg-day) (USEPA 2006). All other harbors (CDI_{Fe}) for adults appear lower than those reported in dietary intake and biochemical indices for adult (0.15-0.27 mg/Kg-day) (USEPA 2006). For Mn, the chronic daily intake (CDI_{Mn}) of the child (4.6E-04-3.0E-02, av. 1.4E-02 mg/Kg-day) and adult (2.0E-05-1.3E-03, av. 6.2E-04 mg/Kg-day) in the harbors studied is less than tolerable upper intake level for adult age ≥ 19 years (11 mg/Kg-day) (ATSDR 2012a). (CDI_{Zn}) of children and adults is lower than those recorded for gastrointestinal symptoms (0.16 and 0.05 mg/Kg-day) (ATSDR 2005a). For Cu, CDI_{Cu} shows lower than reported for no-observed-adverse-effect level (NOAEL, 0.0272 mg/Kg-day) and lowest-observed-adverse effect level (LOAEL, 0.0731 mg/Kg-day) causing increased nausea vomiting, and/or abdominal pain. Based on the appropriate daily nickel dose recorded for food using a 70 Kg body weight reference (0.0024 mg/Kg-day) (ATSDR 2005b), the CDI_{Ni} harbors values have lesser values for Ni toxicity. CDI_{Cr} for child and adult

along the harbors also sets lower values than those reported for oral chromium (VI) compounds intermediate duration (MRL, 0.005 mg/Kg-day) (ATSDR 2008). The CDI_{Pb} for children and adults along the harbors studied are of higher values than those reported for the Pb reference dose (RFD of tetraethyl lead, 1×10^{-7} mg/Kg-day) (ATSDR 2020) that may pose health risks. All CDI_{Pb} values for children (2.1×10^{-4} - 1.9×10^{-3} mg/Kg-day) and adults (9.2×10^{-6} - 8.2×10^{-5} mg/Kg-day) belonging to the harbors examined have values lower than those specified for lead toxicity (ATSDR 2020). CDI_{Cd} values for children (av. 1.2×10^{-4} mg/Kg-day) and adults (av. 5.2×10^{-6} mg/Kg-day) show lower amounts than those recorded for renal system toxicity symptoms (2.1×10^{-3} mg/Kg-day) (ATSDR 2012c).

HQ values of children are higher than those for adults and show amounts of less than 0.2, reflecting no risk of ingestion and dermal contact with sediment (Fig. 6). THQ values appear approximately below unity except for the harbors of Western (2.6), Port Said (2.5), and Damietta (2.3). Non-carcinogenic hazard risk index (H) for children and adults shows amounts more than unity and the harbors are said to be not polluted with heavy metals, except for children in the Western (3.2), Port Said (2.9), Damietta (2.6) harbors (Fig. 7). Non-carcinogenic hazard risk index (H) values along the harbor take the order: Western > Port Said > Damietta > Dekhila > Sidi Krir.

CTR_{Ing} and CTR_{Derm} values for children and adults show values beyond 1.0×10^{-4} (Figure 7). Also, TLCR values for children and adults indicate the non-uniformly high abundance of heavy metals in the harbors sediments that possibly cause adverse public health effects. This explores that it is necessary to monitor heavy metals involving many industries, agriculture, and wastewaters for exposure risks.

Conclusions

The impact of anthropogenic heavy metal pollution in the sediments of five economic harbors along Egyptian Mediterranean Sea, was evaluated using multivariate statistical analysis techniques and ecological indices (EF , I_{geo} , CF , C_d , mC_d , PLI , RI , TRI , TUs , $mPELQ$, $mERMQ$, HQ_{sed} and mHQ_{sed}) to investigate negative environmental impact as well as the geological and anthropogenic sources of heavy metals in the examined harbors. Sediment properties were identified by grain size, sorting, skewness, Kurtosis, water content, besides their geochemistry by determining TOC %, TCO_3 %, $TSiO_3$ %, TP, IP, OP, Ca, Mg, Na, K, Li, B, SO_4 , Cl, and F. The results reflected that the distribution of total organic carbon in the studied harbor sediments was strongly influenced by the amount of $CaCO_3$.

Sediment quality guidelines (SQGs) indicated that most of the identified heavy metals (Cu, Ni, Cr, Pb and Cd) in the studied harbors ranged between TEL and PEL values, except for average the Ni in the harbors of Dekhila and Port Said, which was more than ERM values and Cd contents which were relatively similar to the ERM . Heavy metals contamination was associated with the evacuation of wastewater from phosphate fertilizers and untreated industrial pollutants, along with shipping activities.

The statistical analyses reflected those sediments with smaller grain sizes (clay and silt) had a greater capacity to adsorb P and indicated the formation of fluorapatite ($Ca_5(PO_4)_3F$). These analyses also referred to the formation of aragonite and high Mg calcite.

Amongst the ecological indices, contamination degree (C_d) and modified degree of contamination (mC_d) gave the descending order: Western Harbor > Damietta Harbor > Dekhila > Port Said > Sidi Krir. Given the values of median range effect quotient ($m-ERM-Q$), most of the stations in the harbors examined had 21% of the adverse biotoxic effects on the marine ecosystem, while the levels of probable effect quotient ($m-PEL-Q$) showed that about 49% of the potential biotoxicity was reflected in the harbors of Damietta and Port Said.

HQ values of children were higher than those for adults and showed amounts of less than 0.2, reflecting the lack of risk of ingestion and dermal contact with sediment. While, values of THQ were less than unity except for Western, Port Said and Damietta harbors which reflect expected pollution.

Therefore, it is critical to identify the differences in heavy metals in harbor sediments and their potential environment and public health risks, which allow the management makers to review, assess, manage and provide information, and make a better decision on environmental management of harbors.

Declarations

Declaration of interest

Declarations of interest: none

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Figures

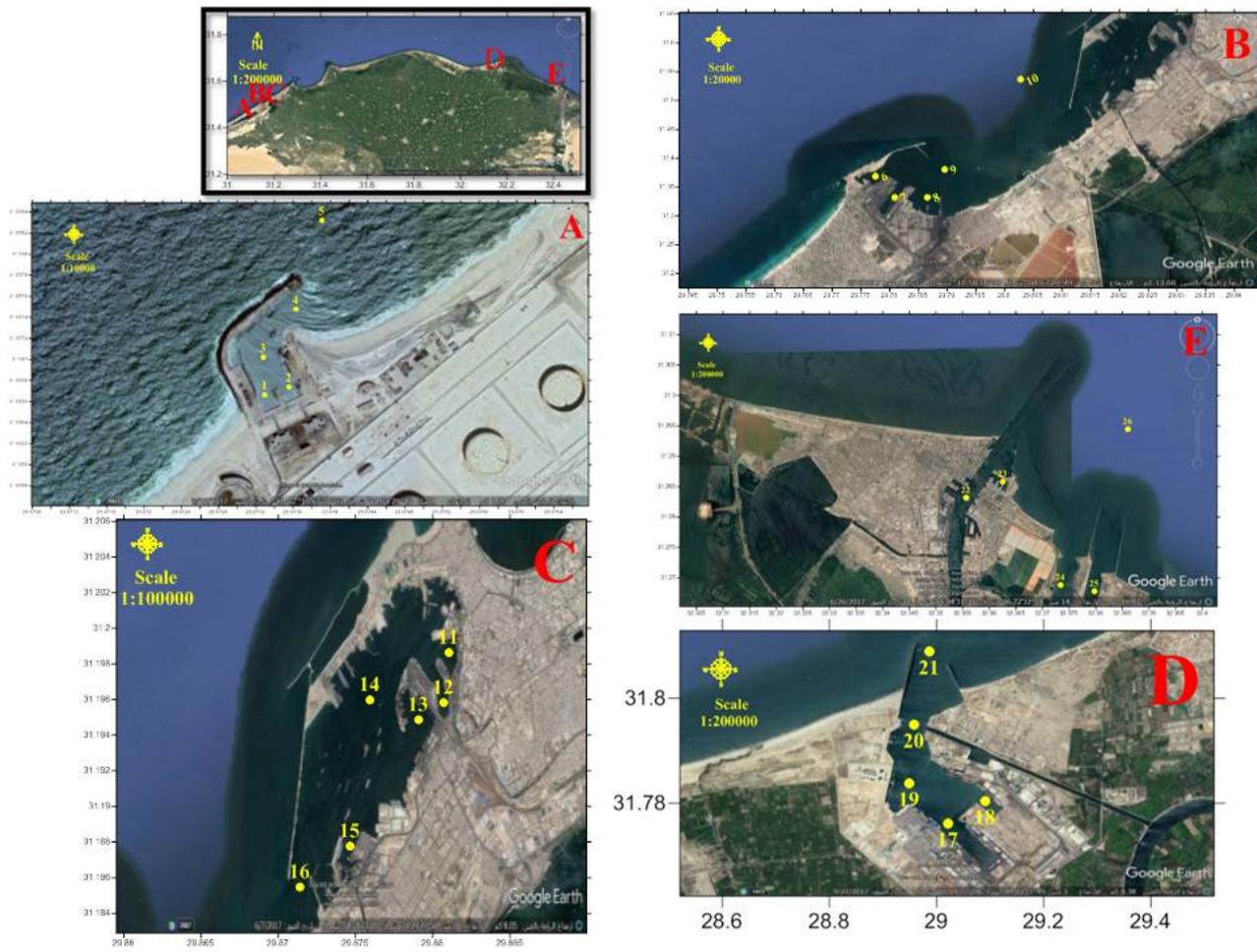


Figure 1

Sampling sites of the studied harbors

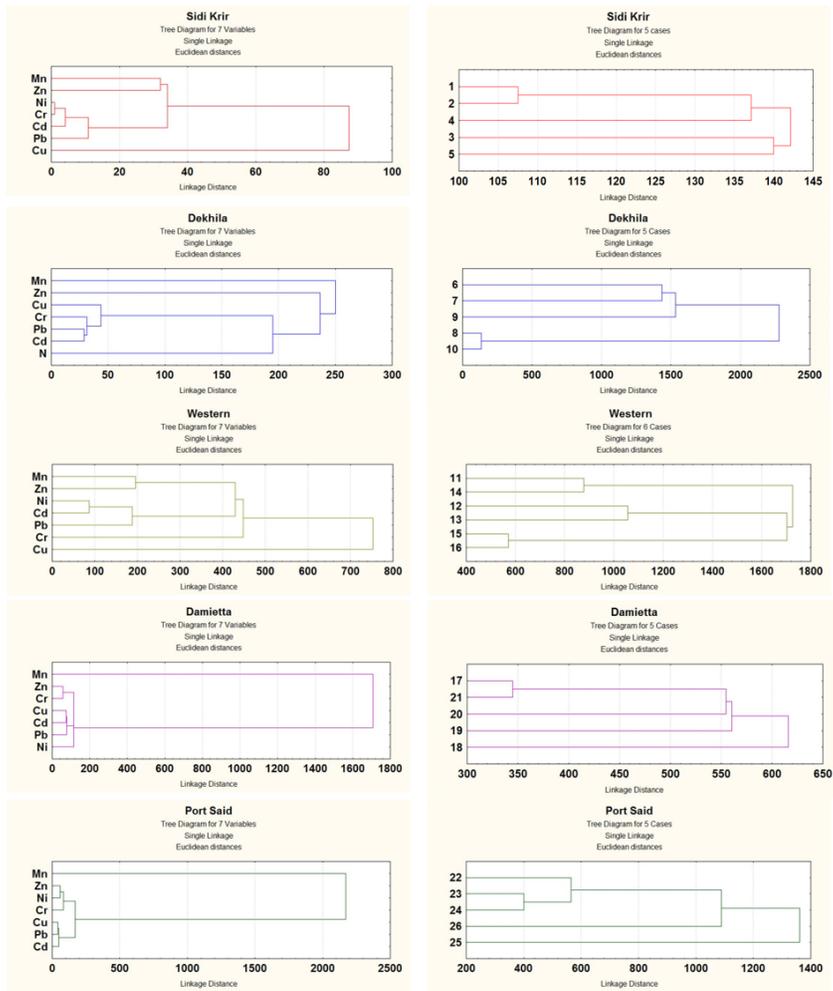


Figure 2

Tree diagram clusters analysis of studied heavy metals among themselves and with geochemical parameters along studied stations in the investigated harbors

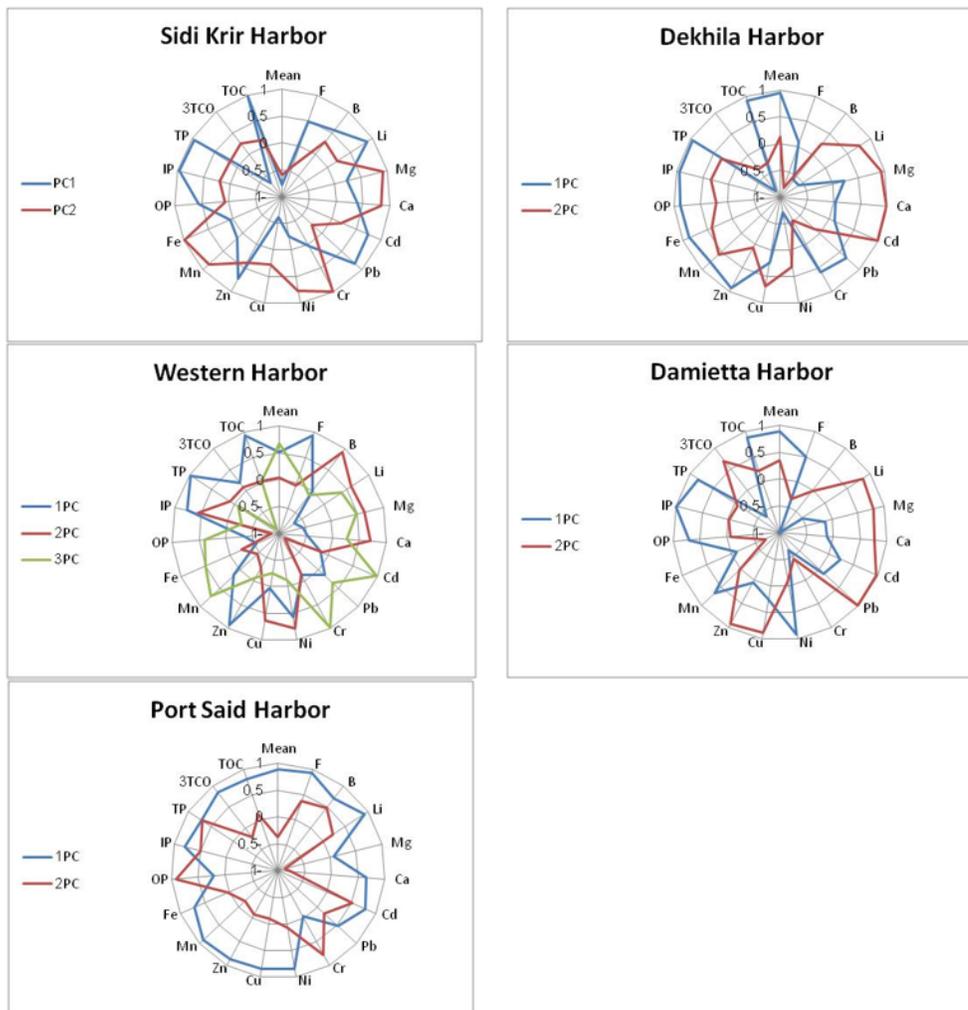


Figure 3

Factor loadings of the principle components for the studied harbors

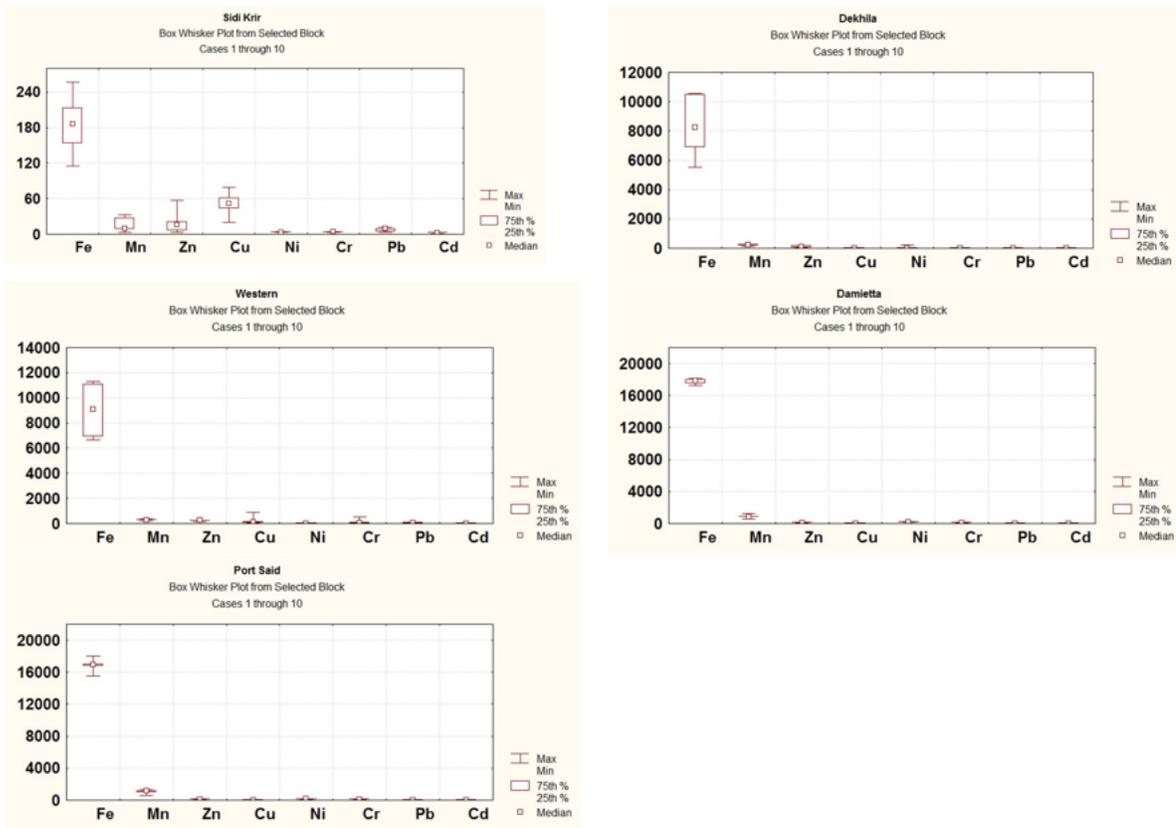


Figure 4
Box Whisker plots of the examined heavy metals in the studied harbor sediments

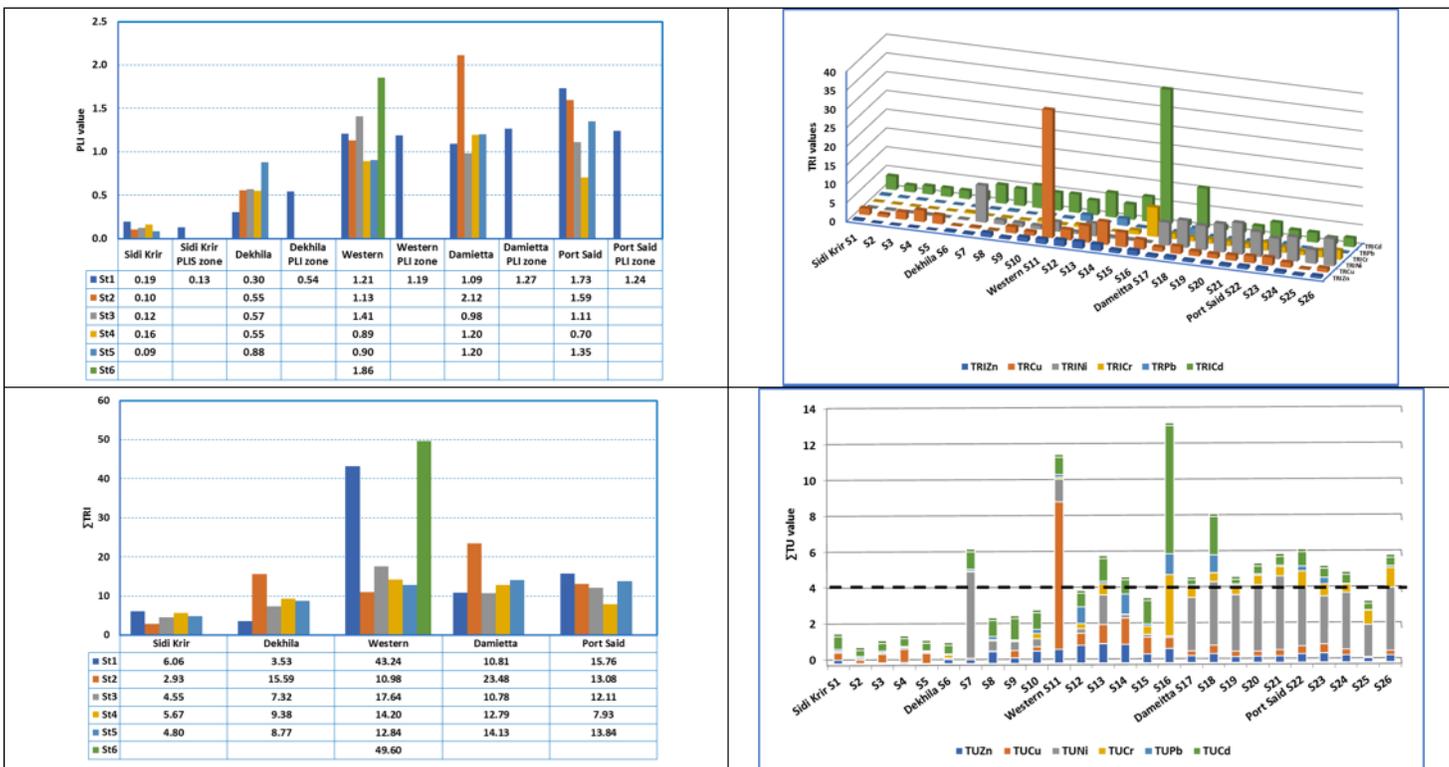


Figure 5
 PLI , TRI , ΣTRI and ΣTU s values for all harbor zone sediments examined

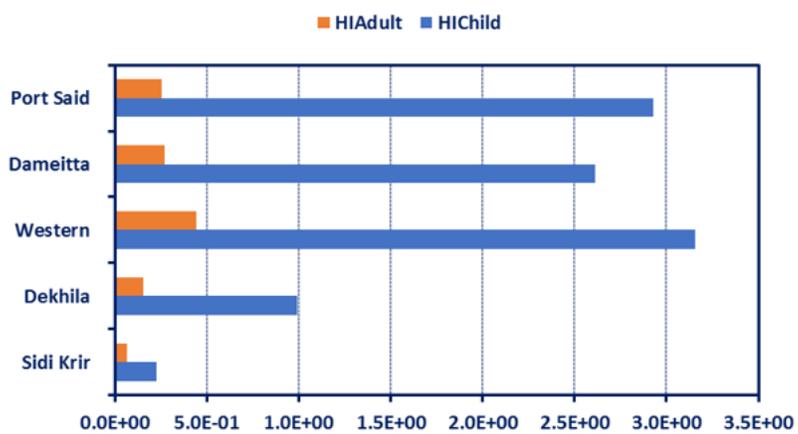
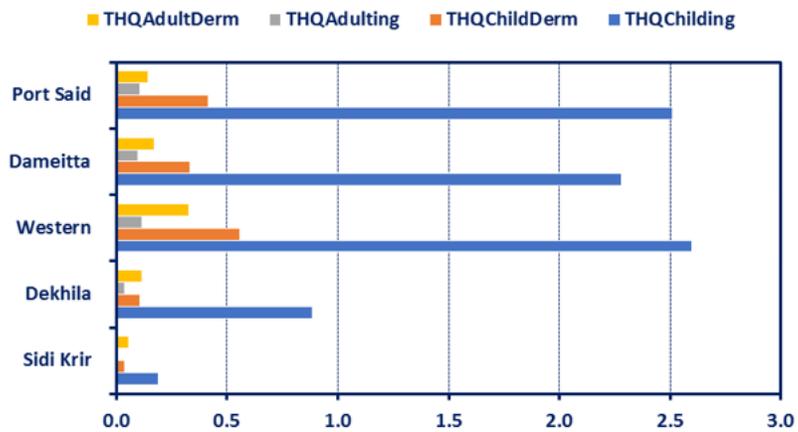


Figure 6

THQ and HI for ingestion of children and adults and dermal contact with sediment

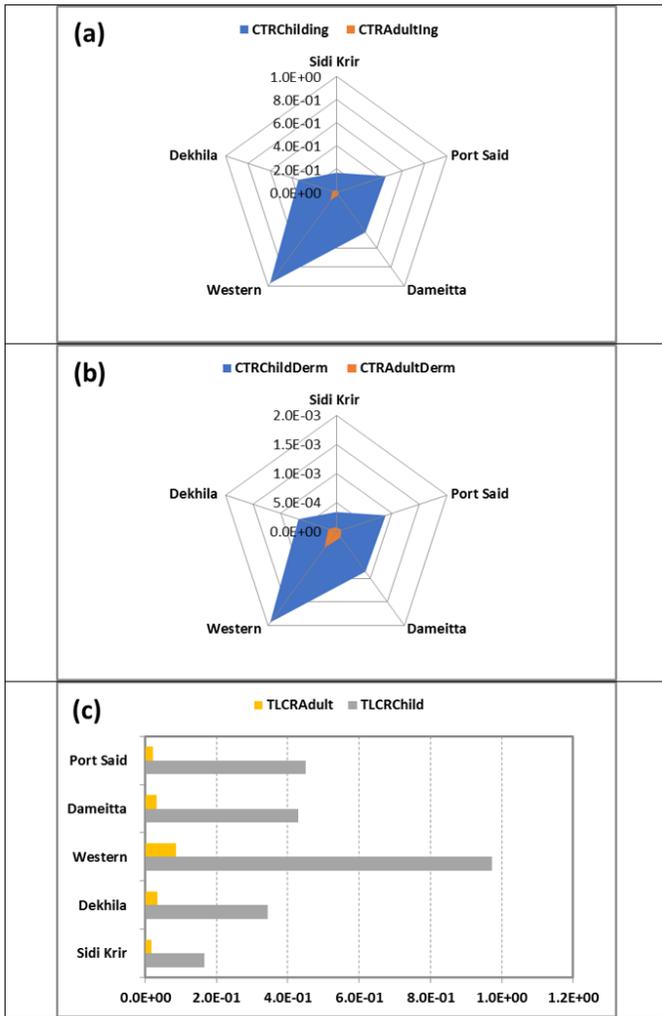


Figure 7

Cumulative target risk (a) of ingestion (b) of dermal contact (c) total lifetime cancer risk for adults and children of different heavy metals.