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 showed that Sidi Krri 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 (HI) 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), and geoaccumulation index (Igeo). Enrichment factor (EF), Contamination factor (C), degree of contamination (Cgeo) 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 (PER) 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 (Chep 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 31.05º and 31.09º N and Longitudes 29.58º and 29.70º 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 (= 9000 m²/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 primarily 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 (Sites11-16), 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 ºC) processing and analysis. Each of the frozen sediments was spread 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 µm mesh sieve. A portion of each sediment sample was washed and dried at 105 ºC for mechanical analysis (Folk 1986). The collected sediments were freeze-dried, then grind with a pestle and mortar and sift to pass a 63 µm 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; Oregioni 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 PE7). Calcium and magnesium levels were volumetrically determined (APHA-AWWA-WPCF 1999). Total boron concentration was determined by curcumin colorimetric method (Bingham 1999). Total boron concentration was determined by curcumin colorimetric method (Bingham 1992). 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, Igeo, CF, Cgeo, mCgeo, PLI, RI, TRI, TUs, mPELQ, mERMQ, HQsed and mHQsed) 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**
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):

\[
CDI_{\text{Ing}} = \frac{C_{\text{sed}} \times \text{Ing}_{\text{sed}} \times ED \times EF \times CF}{BW \times AT}
\]

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

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 $\times$ $ED$) |
| $IngR_{sed}$     | Ingestion rate of adult (100 mg/kg) and child (200 mg/kg) |
| $CF$             | Conversion factor ($1 \times 10^{-6}$ 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):

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

$HI$ 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):

$$CTR = \sum IELCR_i$$

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

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 $\Phi$ and 2.59 $\Phi$ with average value 1.54 $\Phi$ (Table 3). The mean size in Dekhila Harbor (B) fluctuates from 3.33 $\Phi$ (very fine sand) to 6.19$\Phi$
(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 (M20Φ) of the Western Harbor (C) ranges between 2.08 Φ (fine sand) and 6.22Φ (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 | Sidi Krir Harbor | Dekhila Harbor (B) | Western Harbor (C) | Damietta Harbor (D) |
|---------------------------|------------------|--------------------|--------------------|--------------------|
| Sand (%)                  | 99.8             | 100.0             | 99.9               | 1.5               |
| Silt (%)                  | 0.0              | 0.4               | 0.1                | 0.0               |
| Clay (%)                  | 0.0              | 0.0               | 0.0                | 0.0               |
| Mean (ϕ)                  | 2.59             | 1.54              | 0.8                | 0.8               |
| Sorting (ϕ)               | 0.8              | 1.2               | 1.0                | 0.8               |
| Skewness                  | -0.3             | 0.2               | 0.0                | -0.4              |
| Kurtosis                  | 0.8              | 1.6               | 1.0                | 0.3               |
| A (%)                     | 14.7             | 22.2              | 17.94              | 2.7               |
| TOC (%)                   | 0.1              | 0.2               | 0.1                | 0.2               |
| TCO2 (%)                  | 84.0             | 99.6              | 92.5               | 1.1               |
| TSiO3 (%)                 | 0.0              | 16.0              | 8.0                | 7.0               |
| TP (µg/g)                 | 30.0             | 121.0             | 62.0               | 40.0              |
| IP (µg/g)                 | 16.0             | 92.0              | 38.0               | 32.0              |
| OP (µg/g)                 | 11.0             | 42.0              | 24.0               | 12.0              |
| Ca (mg/g)                 | 169.1            | 373.7             | 298.6              | 83.9              |
| Mg (mg/g)                 | 240.5            | 482.6             | 385.4              | 98.7              |
| Na (mg/g)                 | 7.7              | 21.3              | 14.3               | 5.1               |
| K (mg/g)                  | 0.0              | 0.2               | 0.1                | 0.1               |
| Li (µg/g)                 | 0.8              | 15.3              | 3.7                | 6.5               |
| B (mg/g)                  | 2.3              | 5.7               | 3.4                | 1.5               |
| SO4 (mg/g)                | 1.9              | 7.4               | 4.1                | 2.0               |
| Cl (mg/g)                 | 0.4              | 0.5               | 0.5                | 0.1               |
| F (mg/g)                  | 0.31             | 0.56              | 0.42               | 0.10              |

In Sidi Krir 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 Krir 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 ≤ 0.008), IP (r = 0.9830, p ≤ 0.003), Fe (r = 0.9580, p ≤ 0.010), Mn (r = 0.8957, p ≤ 0.040), and Zn (r = 0.9560, p ≤ 0.011). A% Damietta Harbor gives a weak correlation with TOC% (r = 0.8800, p ≤ 0.049), while, Port Said Harbor explores good correlations between A % and each of TOC% (r = 0.9326, p ≤ 0.021), TCO3% (r = 0.9865, p ≤ 0.002), and Cl% (r = 0.9412, p ≤ 0.017). In contrast, A % does not specify any relationship to the sediment components of Sidi Krir 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(Ø) 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 an 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 DekaHila and Western harbors (Table 3). TOC% at DekaHila 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 Nubaria 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 CaCO₃.

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 µg/g) among the other studied harbors (Table 3). OP content ranges from 11 to 42 µg/g with an average value (24 µg/g), representing 39% of the TP content. The correlation matrix yields high modulus values for TP&TOC% and IP&TOC% (r = 0.9881, p ≤ 0.002 and r = 0.9991, p ≤ 0.011, 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 µg/g, respectively) than the other examined harbors. TP IP and OP content of DekaHila Harbor varies from 250 to 933, 205.0 to 743.0 and 45 to 215 µg/g, respectively, where, OP and TP that count by 76 and 24%, respectively of TP. The positive correlations between TP&Sil% (r = 0.9875, p ≤ 0.002) and IP&Sil% (r = 0.995, p ≤ 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 ≤ 0.012, TP & Mn; r=0.9157, p≤ 0.029 and TP & Zn; r=0.9332, p≤ 0.021, respectively). Also, these relations are agreement with the correlations of Fe & Mean% (r = 0.9355, p ≤ 0.019), Mn &Mean% (r = 0.8860, p ≤ 0.045), Zn&Mean% (r = 0.9673, p ≤ 0.007, Fe&A% (r = 0.9580, p ≤ 0.010), Mn&A% (r = 0.8957, p ≤ 0.040), and Zn&A% (r = 0.9560, p ≤ 0.011).

In Western Harbor sediments, the values of TP show high values ranging from 649.0 to 913 µg/g. IP contents are between 482 and 882 µg/g and represented 82% of the TP, while OP varies between 31 and 244 µg/g. Data reveal a significant positive association between TP&Zn (r = 0.8949, p≤ 0.015), IP&Ni (r = 0.9401, p≤ 0.005) and OP&Pb (r = 0.8521, p≤ 0.031) which reflects the potential adsorption of phosphate forms with their compounds. Also, the relationship of TP and F (r = 0.893, p≤ 0.017) indicates the formation of fluorapatite (Ca₅(PO₄)₃F) (El-Said et al. 2015).

The average concentrations of TP, IP and OP in Damietta Harbor are 769.0, 680.0, and 89.0 µg/g, respectively. The relationships TP&Sit% (r = 0.8863, p≤ 0.045) and IP&Sit% (r = 0.9534, p≤ 0.012) show a significant positive association. Mn in the present work reflects high concentrations between TP and OP (r = 0.9553, p≤ 0.011 and r = 0.9856, p≤ 0.002, respectively). While, OP shows negative significant relationships with B and SO₄ (r = -0.9816, p≤ 0.003 and r = -0.8837, p≤ 0.047, respectively). Average concentrations of TP IP and OP for Port Said Harbor are 620, 550 and 65 µg/g respectively and IP content represents about 76% and 24%, respectively of TP. The positive correlations between TP&Silt% (r = 0.9875, p ≤ 0.002) and IP&Silt% (r = 0.995, p ≤ 0.000) which reects the potential adsorption of phosphate forms with their compounds. Also, the relationship of TP and F (r = 0.9249, p≤ 0.024 and r = 0.9283, p≤ 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±20.3 µg/g) show the highest average contents at DekaHila 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. 2018). The relationship between Ca and Mg in DekaHila Harbor and Sidi Krir Harbor (A) (r = 0.9757, p≤ 0.005 and r = 0.9806, p≤ 0.003, respectively) may attributed to the formation of aragonite and high Mg calcite (El-Said et al. 2021). The lowest Ca (213.0±198.8 mg/g), and Mg (234.4±142.4 mg/g), average contents are recorded at Damietta Harbor (D). The values recorded for Na (7.3±37.7 mg/g) and K (0.3±4.9 mg/g) in the current study are lower those recorded for the contaminated Egyptian Lake Mariout (8.33-39.25 mg/g and 0.91-5.99 mg/g, respectively) (El-Said et al. 2020). Minimum Cl (0±0.1 mg/g), K (0.1±0.1 mg/g), B (3.4±1.5 mg/g), SO₄ (4.1±2.0 mg/g) and Li (3.7±6.5 µg/g) contents reflect the minimum amounts of pollutants at Sidi Krir Harbor (A). Relationship between Cl-TOC% (r = 0.9999, p≤ 0.000) CI-IP (r = 0.9901, p≤ 0.001) and CI-TP (r = 0.9981, p≤ 0.002) at Sidi Krir Harbor and chloride relationships of Cl-TOC% (r = 0.9329, p≤ 0.021), TCO₃% (r = 0.8873, p≤ 0.039) and CI-K (r = 0.9274, p≤ 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 DekaHila 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 µg/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.
| 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 | PEI | ERL | ERM |
|-----|-----|-----|-----|
| 124 | 108 | 30  | 410 |
| 150 | 34  | 81  | 270 |
| 150 | 34  | 81  | 410 |

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 ($r=0.9505$, $p \leq 0.015$), 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 ($r=0.8430$, $p \leq 0.035$), Zn-Cu ($r=0.9934$, $p \leq 0.000$), and Pb-B ($r=0.9553$, $p \leq 0.003$). In Damietta Harbor, the relationships of Zn-Pb ($r=0.9456$, $p \leq 0.015$), Zn-Cd ($r=0.9406$, $p \leq 0.017$), Cd-Pb ($r=0.9924$, $p \leq 0.001$), Zn-Ca ($r=0.9024$, $p \leq 0.036$), Zn-Mg ($r=0.9241$, $p \leq 0.024$), Zn-K ($r=0.9487$, $p \leq 0.014$), Pb-K ($r=0.9218$, $p \leq 0.026$), and Cd-K ($r=0.9497$, $p \leq 0.013$) are obtained. In Port Said, there are many correlations between Ni-Fe ($r=0.9468$, $p \leq 0.015$), Ni-Mn ($r=0.9217$, $p \leq 0.026$), Zn-Cu ($r=0.9902$, $p \leq 0.001$), Zn-Li ($r=0.9349$, $p \leq 0.020$), Cr-Na ($r=0.9211$, $p \leq 0.026$), Cd-Li ($r=0.8879$, $p \leq 0.044$), Cd-F ($r=0.9355$, $p \leq 0.019$), Cd-K ($r=0.9673$, $p \leq 0.007$), and Cd-Cl ($r=0.8916$, $p \leq 0.042$). 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                | 0.996286 |
|           | 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             | 1.000000 |
|           | Ni = 3.96 - 0.94 Clay % + 0.11 Ca + 0.02 TP          | 1.000000 |
|           | Cr = 43.11 + 0.98 Fe - 0.18 F - 0.16 Sand %          | 0.999997 |
|           | Pb = 1.59 + 0.79 Na + 0.57 Zn - 0.14 Mg              | 0.999990 |
|           | Cd = 2.00 + 1.69 Li - 0.77 IP - 0.03 Fe              | 0.999995 |
| Dekhila   | Fe = 12302.6 - 1.08 Sand % + 0.34 Ni - 0.11 SO4      | 0.9999345 |
|           | Mn = -30.65 + 1.28 Fe - 0.34 Pb + 0.11 SO4           | 0.999979 |
|           | 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              | 0.998686 |
|           | Ni = 583.4 - 1.19 Cl + 1.02 A% + 0.73 Sand %         | 0.999819 |
|           | Cr                                                     | not significant |
|           | Pb = 5.38 + 1.27 Zn - 0.66 OP + 0.13 Cr              | 0.999796 |
|           | Cd = -1.0 + 0.91 Ca + 0.19 Cu + 0.08 Cr              | 0.999981 |
| Western   | Fe = 24718.2 - 1.01 K + 1.11 F - 0.73 Zn - 0.14 Silt % | 0.9999497 |
|           | Mn = 117.56 - 0.68 Cu + 0.57 Mean + 0.41 Fe + 0.14 IP | 0.999757 |
|           | 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 | 0.9998544 |
|           | 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%                  | 0.9951192 |
|           | Mn = 518.2 + 0.87 OP + 0.20 Ca - 0.10 Clay %         | 0.9999726 |
|           | Zn = 320.1 + 0.76 K - 0.77 IP + 0.62 A%              | 0.9997148 |
|           | Cu = 22.3 + 0.96 Cd + 0.41 Cl - 0.25 Silt %          | 0.9996917 |
|           | Ni                                                     | not significant |
|           | Cr = 368.5 - 1.23 Mean + 0.62 Mn + 0.10 F            | 0.9999978 |
|           | 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       | 0.99999579 |
|           | Mn = 1521.3 - 1.10 Sand % - 0.19 SO4 - 0.10 Sorting  | 0.9999988 |
|           | Zn = -25.0 + 0.96 Cu + 0.16 Fe - 0.06 Clay %         | 0.9999972 |
|           | Cu = 16.9 + 1.04 Zn - 0.16 Fe + 0.07 Clay %          | 0.999997 |
|           | Ni = 73.4 + 1.13 Silt % - 0.31 SO4 + 0.06 OP         | 0.9999999 |
|           | Cr = -109.3 + 0.77 Na + 0.49 B - 0.17 Mean           | 0.9992905 |
|           | Pb = 5.27 + 1.27 Cu - 0.60 Mean + 0.11 Na            | 0.9999901 |
|           | Cd = 0.29 + 0.93 K + 0.22 OP + 0.13 Sand %           | 0.9999847 |
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}≤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 | Damietta | 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     | -ve0.25  | -ve0.31  | Unpolluted to moderately polluted |
| $I_{geo Zn}$ | -ve      | -ve     | -ve0.61 | -ve      | -ve      | Station 11-14, and 16 | Unpolluted to moderately polluted |
| $I_{geo Cu}$ | -ve      | -ve     | -ve3.08 | -ve      | -ve      | Station 11, 13 and 14 | Unpolluted to strongly polluted |
| $I_{geo Ni}$ | -ve      | -ve1.46 | -ve     | 0.76-1.23| 0.03-1.01| Stations 7, 17-26     | Unpolluted to moderately polluted |
| $I_{geo Cr}$ | -ve      | -ve1.86 | -ve     | -ve0.22  | -ve      | Station 16 and 26     | Unpolluted to moderately polluted |
| $I_{geo Pb}$ | -ve      | -ve0.10 | -ve2.44 | -ve2.22  | -ve0.74  | Stations 10, 12, 14, 16, 18, 22 and 23 | Unpolluted to moderately polluted |
| $I_{geo Cd}$ | -ve      | -ve0.45 | -ve2.75 | -ve2.26  | -ve0.74  | Stations 17-18, 20-24, and 26 | 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| 1.05-2.99| 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 | Very high contamination |
| $CF_{Pb}$    | 0.27-0.92| 0.33-2.06| 1.03-10.59| 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| 1.60-9.98| 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 |

*Overall pollution status using different risk indices in each of the studied harbors.*
The contamination factor (CF), contamination degree (Cd) and modified degree of contamination (mCd) are given in 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 show moderate Cu contamination (1 < CF< 3), while three other harbors examined have low Mn contamination (CF< 1). Most of the stations studied in the examined harbors show low contamination level (CF< 1), except for Western Harbor sites showing moderate zinc contamination (1 < CF< 3). Half of Western Harbor sites have moderate Cu contamination (sites 13-15, 1 < CF< 3), while site 11 shows the highest percentage of Cu contamination (CF> 6) among the sites examined. Almost of the stations in inspected harbors have low Ni contamination (CF< 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< 3). Almost all harbor stations give a low degree of Cd contamination (CF< 1), except for station 16 (Western Harbor), and stations 22, 23, 25 and 26.
(Port Said) are affected by moderate Cr pollution (1<CF<3). Western Harbor is the most Pb contaminated site, however, half of the sites (sites: 23, 14 and 16) show CF>6, along with station 18 (Damietta Harbor), while the other sites range from low to mild Pb contamination. The Cr and mCd values reflect that the harbors range from low to very high pollution areas. The Cd 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 mCd 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) (Gohar et al. 2014).

Toxic risk index (TRI) and integrated TRI (ΣTRI)

The high TRIcr, TRI Ni, and TRICd 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 (ΣTRI<5) to very high toxic (ΣTRI>20) (Table 6 and Fig. 5). The high ΣTRI values recorded in Western, Damietta and Port Said harbors reflect that these harbors are of considerable and very high toxic risk.

Toxic units (TU) and sum of toxic units (ΣTU)

The TUs and ΣTUs 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 ΣTUs exceed 4 amount for the moderate toxicity, i.e. significant mortality can be observed (Zhang et al. 2016). Higher values of TU Cu (sites 7, 17-26) and TUCd (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 TUCd 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 (mHQsed)

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

Sediment hazard quotients (HQsed)

In Table 6, along the harbors studied, most stations in Western Harbor range from high to medium risk with Cu (3.5-47.4), Pb (0.4-4.3) and Cd (4.7-44.1), except Cr which gives HQsed values (0.1-10.4) that ranges from potential to high risk. Stations in the harbors of Damietta (HQsedNi, 8.0-11.0) and Port Said (HQsedNi, 4.8-9.5) exhibit moderate Ni risks, while only station 7 at Dekhila Harbor gives high risk with Ni (HQsedNi= 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_c) 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_c 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_c) 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_m) of the child (4.6E-03-4.0E-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_c) 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_c 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_c values have lesser values for Ni toxicity. CDI_c for child and adult
along the harbors also sets lower values than those reported for oral chromium (VI) compounds intermediate duration (RFD, 0.005 mg/Kg-day) (ATSDR 2008). The CDI_{inf} for children and adults along the harbors studied are of higher values than those reported for the Pb reference dose (RFD of tetraethyl lead, 1X10^-7 mg/Kg-day) (ATSDR 2020) that may pose health risks. All CDI_{inf} values for children (2.1E-04 - 1.9E-03 mg/Kg-day) and adults (9.2E-06 - 8.2E-05 mg/Kg-day) belonging to the harbors examined have values lower than those specified for lead toxicity (ATSDR 2020). CDI_{inf} values for children (av. 1.2E-04 mg/Kg-day) and adults (av. 5.2E-06 mg/Kg-day) show lower amounts than those recorded for renal system toxicity symptoms (2.1E-03 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 (HI) 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 (HI) 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 1.0E-04 (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_{geo}, PLI, RI, TRI, TUs, mPEL, mERMQ, HQ_{sed} and mLHQ_{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, skwenes, 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_{geo}) and modified degree of contamination (mC_{geo}) 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, $\sum$ TRI and $\sum$ TUs 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.