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# Estimation of metal pollutant levels in bottom sediments from Rosetta to Damietta promontories

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## Abstract

The concentration of heavy metals; Cd, Cu, Fe, Mn, Ni, Pb and Zn, total organic carbon and carbonate content were studied in sediment of twenty one locations from continental shelf between Rosetta to Damietta promontories during 2008. The mean grain size ranged between medium sand and very fine silt. The TOC ranged between 0.15% and 1.79 % while total carbonate varied between 7% and 85 %. The total metals concentration fluctuated between 0.26 -1.51 $\mu g\ g^{-1}$ for Cd, 8.52 – 46.67 $\mu g\ g^{-1}$ for Cu, 942 - 15703 for Fe, 71- 956 $\mu g\ g^{-1}$ for Mn, 3.23 - 65.79 $\mu g\ g^{-1}$ for Ni, 13.59 - 43.7 $\mu g\ g^{-1}$ for Pb, and 33.03 -119 $\mu g\ g^{-1}$ for Zn. For various metals different normalizing methods were used, enrichment factor $(EF)_{crustal}$, contamination factor ($C_f$), metal pollution index (MPI), as well as geoaccumulation index (*I*geo), to compensate the influence of natural variability in sediment mineralogy. The results indicate that Cd and Cu still much lower than ERM, while Pb and Zn levels never exceeded the ERL revealing that there is no adverse effect on biota. While, Ni level exceeded ERM by of 29% of the investigated sites indicating that this metal could cause an adverse effect on local community.

*Keywords*: Heavy metals, Grain size, Sedimentation, Rosetta and Damietta, Degree of contamination

## 1. Introduction

The Nile Delta shelf comprises a unique depositional environment, in which sedimentation is controlled by waves, currents, tides and river discharge. Since the building of Aswan High Dam (1964), an imbalance between the two major forces affecting the shore (erosion and accretion) has occurred. As a result of this, a strong decrease in the amount of sediments accreted. The shoreline of Nile Delta is typically a smooth wide circulate coast. The beach and backshore are enriched by significant amounts of heavy minerals. The delta coast has a gentle slope varying from 1:50 to 1:100 and a smooth wide beach face (Frihy, 1996). Several studies on the Nile Delta has been carried out; among them, are the studies of sedimentary processes in the Nile Delta sponsored by UNESCO, 1973 and 1976, Frihy (1975), Anwar *et al.* (1981), El-Fishawi and El-Askary (1981), Inman and Jinkins(1984), Moufaddal (1995) and AboZed (1996). The geochemistry of the continental shelf sediments off the Nile Delta suffers but so a little attention from scientists that only few published papers could be hardly found in literature e.g. Saad *et al.* (1980), Salem (1981), Abouldahab (1985), El-Sayed *et al.* (1988), El-Sayed and Rifaat (1993). These studies focused on metal enrichment in sediments of the near shore marine environment of the Nile cone due to human activities. On the other hand, the study of Rifaat *et al.* (1992) gave detailed study on metal partitioning and behavior of some metals in Nile shelf yet was not considered due to the relatively few samples collected.

On the other hand, the sediments are important sources for assessment of man-made contamination in aquatic systems (GAUR *et al*, 2004). According to Jardim (2004) sediments contamination causes very noxious effects to the whole ecosystem.

The present study deals with the area from Rosetta to Damietta between Latitude 31° 58' 50" and 32° 11' 37" N Longitude 31° 33' 44"and 32 º 07' 43" E. The water depths sampling range between 10 and 100 meters (Table 1 and Figure 1).

The aim of this research is to determine the concentration levels of the seven heavy metals, Cd, Cu, Fe, Mn, Ni, Pb and Zn in the surface sediments of the study area to differentiate between the natural and anthropogenic input of heavy metals on the area by using crustal enrichment factor $(EF)_{crustal}$, contamination factor ($C_f$), metal pollution index (MPI), as well as, geoaccumulation index (*I*geo).

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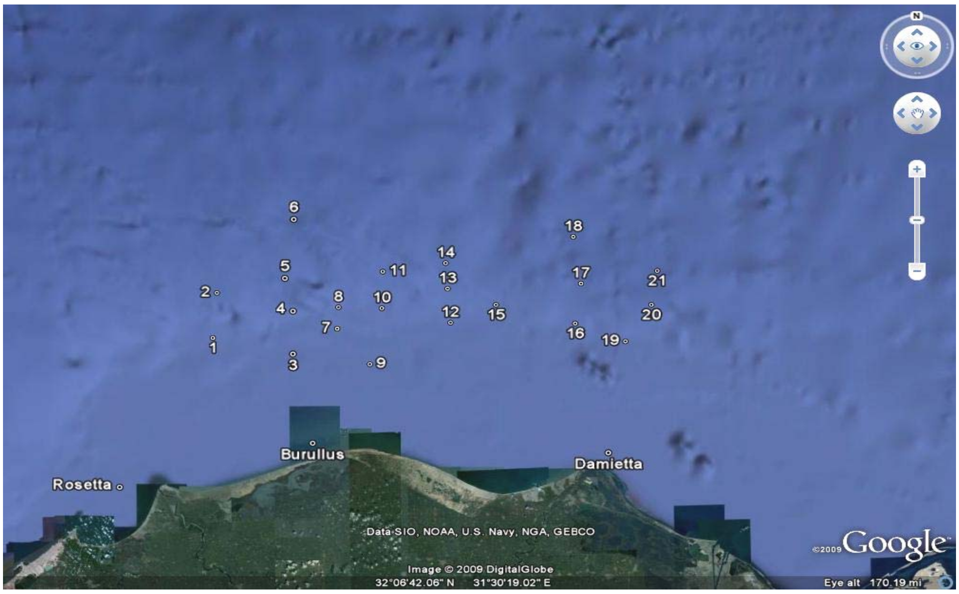

Figure 1: Satellite image of Nile Delta Coast showing locations of collected sediment samples.

Table 1: Location, latitude and longitude of stations.

| Location | Station Number | Longitude | Latitude |
|---|---|---|---|
| **Rosetta** | 1 | 30° 33' 44" | 31° 57′ 52" |
| | 2 | 30° 34' 05" | 31° 07′ 21" |
| | 3 | 30° 51' 00" | 31° 55′ 03" |
| | 4 | 30° 50' 55" | 32° 04′14" |
| | 5 | 30° 49' 05" | 32° 10' 54" |
| | 6 | 30° 51' 02 " | 32° 22' 52" |
| **Burullus** | 7 | 30° 00' 02" | 32° 00' 36" |
| | 8 | 31° 00' 20" | 32° 04' 57" |
| | 9 | 31° 06' 52" | 31° 53' 21" |
| | 10 | 31° 09' 29" | 32° 04' 41" |
| | 11 | 31° 09' 47" | 32° 12' 07" |
| **Abukhashaba** | 12 | 31° 23' 56" | 31° 01' 38" |
| | 13 | 31° 23' 25" | 32° 08' 32" |
| | 14 | 31° 23' 04" | 32° 13' 43" |
| **Baltim** | 15 | 32° 33' 33" | 32° 05' 10" |
| **Between Baltim and Damietta** | 16 | 31° 50' 11" | 32° 01' 10" |
| | 17 | 31° 51' 33" | 32° 09' 15" |
| | 18 | 31° 50' 06" | 32° 18' 46" |
| **Damietta** | 19 | 32° 00' 30" | 32° 57' 24" |
| | 20 | 32° 06' 21" | 32° 04' 44" |
| | 21 | 32° 07' 43" | 32° 11' 37" |

## 2. Materials and methods

Twenty one surface sediment samples were collected recently in 2008 from continental shelf area between Rosetta and Damietta (Table 1 and Figure 1).

The samples were analyzed according to Folk (1974) to determine the mean grain size and the proportions of sand, silt and clay using a standard sieving and pipette techniques. The total organic carbon (TOC) content was determined by oxidation with 1N $K_2Cr_2O_7$ acidified with concentrated $H_2SO_4$ and titration with 0.5 N Fe $(NH_4)_2(SO_4)_2$, [Loring & Rantala, 1992]. Total carbonates and silicate were estimated as described by Molnia (1974).

The concentration of total metals were measured using Flame-Atomic Absorption Spectrophotometer

(FAAS, Shimadzo 6800, with Autosampler 6100) after complete digestion of sediment samples with mixture of concentrated $HNO_3$, HF and $HClO_4$ (3 : 2 : 1 v/v) according to Oregioni and Aston (1984).

For quality control, triplicate samples and standard reference material (SD-M-2/TM). Marine sediments, National Research Council, Canada) were used, with each batch of samples analysis. Ten replicates of the SRM were digested with the same procedure as the samples. Recovery ratios of heavy metals in the SRM were 96.5-104.23% (Table 2).

Table 2: Heavy metal concentrations (µg/g dry weight) in reference materials analyzed together with sediment samples.

| Metal | Certified values | Found values | Standard deviation | Recovery (%) |
|---|---|---|---|---|
| **Cd** | 0.113 | 0.101 | 0.026 | 104.2373 |
| **Cu** | 32.7 | 33.011 | 0.827 | 100.9421 |
| **Fe** | 27100.0 | 26231.861 | 126.362 | 96.691 |
| **Mn** | 12100.0 | 2305.256 | 182.718 | 101.668 |
| **Ni** | 56.1 | 54.875 | 1.392 | 97.76765 |
| **Pb** | 22.8 | 24.263 | 0.521 | 101.9903 |
| **Zn** | 74.8 | 76.206 | 1.492 | 101.845 |

## 3. Results and discussion

### 3.1. Grain size distribution

The grain size of the sediment provides important clues to the sediment provenance, transport history and depositional conditions Bui, *et al*., (1990).

Table 3 summarizes the results of grain size analysis. It was noticed that these sediment are widly different in their grain size characteristics, generally comprising an admixture of sand, silt and clay. It is clear that the sediment type in coastal area in front off Rosetta is mainly silty clay changed to silt far from the coast. In front of Abu Khashaba (st. 12-14), the sediments composed of sand near the coast while the mean increase toward the deeper station and reach to sandy clayey silt. At Baltim (st.15), the bottom is mainly clayey silt whereas, at Damietta (st. 19, 20 and 21), it changes to silt. The mean grain size ranges between 1.07 Φ (medium sand) and 6.8Φ (very fine silt) at Rosetta (st. 5 & 1). The change of the graphic mean size is attributed to the difference in the sorting values between erosion and accretion period and the admixture with shell fragments. The mean grain size generally decreases with depth at Rosetta while unlike the case at Burullus and Abu Khashaba.

### 3.2. Total organic carbon (TOC)

The organic carbon content of any sediment represents a direct measure of its organic richness (Hunt, 1972). In general the TOC are low, ranging between 0.15% recorded in Burullus (st.11) and 1.79 % at Rosetta (st.1) (Table 4).

The fine-grained nature of sediments, as well as, the high organic production in the overlying waters explains the high content of organic matter in nearshore sediments (st. 1).

It is noted that TOC showed positive correlation with mean grain size and clay %, where r = 0.5 & 0.67 respectively (Table 9), which could be attributed to the effect of drainage water loaded with considerable amount of fine particles.

### 3.3. Total carbonate content ($TCO_3$)

From Table 4 it was noticed that, the bottom sediments are relatively low in carbonate content near the coastal area; it varies between 7% at Rosetta st. (1) and 85 % at Burullus st. (10 & 11). Generally, $TCO_3$ increases with depth, at 50 and 100 meters, it reach about 80 % in front of Rosetta (st.5 & 6) and also at Burullus (st. 10 & 11). High carbonates content are found in deeper areas, while the lower contents are found in areas subjected to the direct winnowing effects of water. Also, this can be attributed to the inverse relationship between the amount of terrigenous mud and carbonate content. It seams that the richness in the carbonate content resulted from two factors: the eroded carbonate-rich coastal materials and the mixing of sediments with shell fragments of gastropods, lamellibranchs and other calcareous debris (El-wakeel and El-Sayed, 1978). Carbonate content correlates negatively with mean grain size (Table 9), where r = -0.55. This indicating that carbonate components tend to be concentrated in coarse grained sediment. The high carbonate content recorded at stations 10, 11 and 17.

Table 3: Sand, silt, clay %, mean and type of sediment samples in the investigated area.

| Station Number | Sand % | Silt % | Clay % | Mean(Φ) | Significant | Sediment type |
|---|---|---|---|---|---|---|
| **1** | 3.71 | 40.05 | 56.25 | 6.80 | Fine silt | Silty clay |
| **2** | 6.42 | 93.40 | 0.19 | 5.36 | Medium silt | Silt |
| **3** | 40.57 | 35.54 | 23.88 | 5.22 | Medium silt | Clayey silty sand |
| **4** | 91.18 | 4.12 | 4.70 | 2.41 | Fine sand | Sand |
| **5** | 75.75 | 22.24 | 1.98 | 1.07 | Medium sand | Silty sand |
| **6** | 78.63 | 9.82 | 11.55 | 1.38 | Medium sand | Clayey sand |
| **7** | 51.74 | 46.76 | 1.50 | 4.36 | Medium silt | Silty sand |
| **8** | 10.37 | 88.01 | 1.62 | 4.46 | Coarse silt | Sandy silt |
| **9** | 0.00 | 98.68 | 1.32 | 4.51 | Coarse silt | Silt |
| **10** | 61.40 | 35.65 | 2.95 | 3.92 | Very fine sand | Silty sand |
| **11** | 79.87 | 15.98 | 4.15 | 3.64 | Coarse silt | Silty sand |
| **12** | 84.20 | 14.13 | 1.67 | 1.93 | Medium sand | Silty sand |
| **13** | 95.54 | 0.89 | 3.56 | 2.86 | Fine sand | Sand |
| **14** | 17.83 | 43.47 | 38.7 | 5.83 | Medium silt | Sandy clayey silt |
| **15** | 6.13 | 52.24 | 41.64 | 6.08 | Fine silt | Clayey silt |
| **16** | 5.44 | 85.05 | 9.51 | 5.32 | Medium silt | Silt |
| **17** | 93.43 | 4.51 | 2.06 | 1.47 | Medium sand | Sand |
| **18** | 41.23 | 56.4 | 2.37 | 3.80 | Very fine sand | Sandy silt |
| **19** | 26.83 | 38.88 | 34.29 | 5.88 | Medium silt | Sandy clayey silt |
| **20** | 22.33 | 74.61 | 3.07 | 4.76 | Coarse silt | Sandy silt |
| **21** | 9.19 | 87.09 | 3.72 | 5.84 | Medium silt | Silt |

Table 4: Total organic carbon, total carbonate and % silicate of sediment samples in the investigated area.

| Station Number | TOC% | $TCO_3$% | $TSiO_3$% |
|---|---|---|---|
| **1** | 1.79 | 7.02 | 92.98 |
| **2** | 0.40 | 7.17 | 92.83 |
| **3** | 0.83 | 15.13 | 84.87 |
| **4** | 0.28 | 13.47 | 86.53 |
| **5** | 0.68 | 76.56 | 23.43 |
| **6** | 0.67 | 79.76 | 20.24 |
| **7** | 1.09 | 18.23 | 81.76 |
| **8** | 0.23 | 13.79 | 86.21 |
| **9** | 0.24 | 8.13 | 91.86 |
| **10** | 0.52 | 85.66 | 14.34 |
| **11** | 0.15 | 85.72 | 14.28 |
| **12** | 0.81 | 20.79 | 79.21 |
| **13** | 0.37 | 10.38 | 89.62 |
| **14** | 1.35 | 14.27 | 85.72 |
| **15** | 0.95 | 19.66 | 80.34 |
| **16** | 1.43 | 10.14 | 89.85 |
| **17** | 0.46 | 82.43 | 17.56 |
| **18** | 1.28 | 40.88 | 59.11 |
| **19** | 1.45 | 14.54 | 85.46 |
| **20** | 0.86 | 17.69 | 82.31 |
| **21** | 1.29 | 13.01 | 86.99 |

## 3.4. Heavy metals

Heavy metals in marine sediments have owed to either natural and or anthropogenic origin; their distribution and accumulation are influenced by sediment texture, mineralogical composition, reduction/oxidation stat, adsorption desorption processes and physical transport. The mean concentrations of the investigated metals in the area of study are presented in Table (5) and Fig. 2.

As a matter of facts, Cadmium (Cd) found in the earth's crust and is widely spread by human activity, volcanic activities and erosion. Moreover, major sources of contaminations are the industrial production and consumption of Cd and other nonferrous metals and the disposal of waste containing Cd (Kakkar and Jaffery, 2005). Large quantities of Cd are mainly used in the production of nickel-cadmium batteries or in welding (Jarup *et al.*, 2000). In the present study, the concentration of Cd decreases in seaward direction in all sections except at station 21 recording higher value than station 20 as showed in Table 5, where (st.. 20 & 21) contain 22% and 9.19% respectively. As previously discussed by many authors that fine mud/silt/clay sediment with high organic content retain more contaminants than does relatively coarse sandy sediment, thus sites where fines are deposited are likely to exhibit an elevated loading of heavy metals (de Mora *et al.*, 2004; Kosarev and Yablonskaya, 1994). It was reported that polluted areas had Cd concentrations in the range of 2.5-13.0 µg/g (Svete *et al.*, 2001), whereas the level of Cd in unpolluted areas were within the range of 1.56-8.0 µg/g (Santamaria-Fernandez *et al.*, 2005). Thus the investigated sediments are considered unpolluted by Cadmium. So in our case it may be attributed to both grain size effect and the concentration of total organic carbon.

Copper (Cu) occurs in soft natural waters primarily as the divalent cupric ion. It may be found as a free ion or complexed with humic acids, carbonate, or other inorganic and organic molecules in water of increasing hardness. Cu is an essential element in the normal metabolism of plants, animals and human life, however in high levels, causes many diseases (Gratten *et al.*, 2003). According to Jain (2004), high percentage of copper is in immobile fraction and also found in reducible fraction (Fe-Mn oxide) and residual fraction. The Cu concentrations in the present study fluctuated between 8.52 and 46.67 with an average mean of 25.36±9.99 µg/g dry weight. Previous studies reported comparable values of copper in sediment samples for different areas. It was reported that the levels of Cu in sediments from Harbor of Ceuta (Spain) were in the range of 5-86.5 µg/g (Guerra-Garcia and Garcia-Gomez, 2005), 33-72 µg/g in Semarang Estuary, Indonesia (Takarina *et al.*, 2004) and 11.5-52.2 µg/g in El-Mex Bay, Egyptian Mediterreanean Sea (Abdallah, 2007).

Iron toxicity is due to its rapid absorption by the body, the main sources of iron and its target organs are the liver and kidneys (Pais & Benton Jones, 1997). In the present study, we found that Fe is in the range of

942 – 15703 µg/g with the highest value at station 15 and the lowest at (st. 7). The range 3000–40820 µg/g of Fe was found in some unpolluted areas (Santamaria-Fernandez *et al.*, 2005; Svete *et al.*, 2001; Alomary and Belhadj, 2007), while polluted regions had higher values in the range 51000-116000 µg/g (Buykx *et al.*, 2000; Sulivan and Taylor 2003; Svete *et al.*, 2001; Tack and Verloo 1999). Comparing these studies with the present study, one can easily find that our samples are considered unpolluted by iron.

Manganese (Mn) is the 11th element in terms of abundance in the earth crust (Anschutz *et al.*, 2005). Oxidized forms of Mn are very reactive and have a strong capacity for adsorption of trace metals and play an important role as both an electron donor and acceptor in redox processes of aquatic environments (Duman *et al.,* 2007). Mn is an essential trace metal in all forms of life. Manganese (II) ions function as cofactors for a number of enzymes in higher organisms, where they are essential in detoxification of superoxide free radicals. The element is a required trace mineral for all known living organisms. In larger amounts, and apparently with far greater activity by inhalation, manganese can cause a poisoning syndrome in mammals, with neurological damage which is sometimes irreversible. The measured concentrations of Mn in our samples were in the range of 71.00-956.15 µg/g dry weight, where (st. 7) recorded the lowest concentration and the highest was in station 11. Several studies on Mn in sediments have been conducted in several regions. Our results were within the range reported by Kontas, (2008) in Izmir Bay, Turkey (233-923 µg/g), by Griethuysen *et al.,* (2005) for Floodplain Lake, Netherlands (387-1039 µg/g) and with that observed by Kucuksezgin *et al.*, (2008) in sediments of Gediz River, Eastern Aegean, Turkey.

Nickel (Ni) is used in many industrial, including stainless steel, magnets, coinage, rechargeable batteries, electric guitar strings and special alloys. It is also widely used in many other alloys, such as nickel brasses and bronzes, and alloys with copper, chromium, aluminium, lead, cobalt, silver, and gold (Davis, 2000).

Ni plays numerous roles in the biology of microorganisms and plants, though they were not recognized until the 1970s (Hausinger, 1987). Overexposure for Ni can cause decreased body weight, heart and liver damage and skin irritation (Homady *et al.*, 2002). High Ni contents in marine sediments are usually due to human activities (Pais and Benton Jones, 1997). The concentration level in this study was ranged from 3.23µg/g at station 7 to 61.47µg/g at station 15 with an average 32.82±21.62 µg/g as shown in Table 5. The Ni concentrations of samples in study area are alike within the range observed by Sari and Catagay, (2001) for Gulf of Saros, Aegean Sea (14-60 µg/g), and that reported by Kucuksezgin *et al.*, (2008) in sediment samples of Gediz River (35-175 µg/g), and sediment samples collected from Izmir Bay (Turkey) (14.9-127 µg/g) (Kontas, 2008) but lower than reported by Aloupi and Angelidis, (2002) along the coastal sediment of Greece (70-161 µg/g).

Lead (Pb) is one of the most abundant toxic metals in the Earth's crust. It has been used since prehistoric times and has become widely distributed and mobilized in the environment. The concentration of Pb in sediment samples in our study fluctuated between 13.59 µg/g at station 17 and 43.70 µg/g at (st. 5) with average range 24.73±7.11 µg/g. The concentrations of Pb in this study was almost within the range of that reported by Benamar *et al.*, (1999) (4-69 µg/g), and that observed by Alomary and Belhadj, (2007) (0.8-54.9 µg/g) for sediments collected from Algeria. However, Jdid *et al.,* (1999) and Fernex *et al.*, (2001) reported higher values of Pb than that recorded in the present study.

Zinc (Zn) is a common metal in the human environment. High levels of Zn may cause pancreatitis, anemia, muscle pain, acute renal failure (Pais and Benton Jones, 1997). The mean concentration of Zn in the studied sediment was 66.08±21.97 µg/g where the highest Zn level was recorded at station 20 while station 19 recorded the lowest value (Table 5). Comparison of the obtained results with those reported for other Mediterranean Sea sediments reveals that the found range of Zn is comparable to those found by Bernamar *et al.*, (1999) along Algiers Bay (54-274 µg/g), Algeria, and that reported by Feldstein *et al.*, (2003) for Mediterranean Sea along Israel coast (9-95 µg/g). On the other hand, Fernex *et al.*, 2001, Caredda *et al.*, 1999 reported much higher values of Pb (29.4-509.3 and 198-3239 µg/g respectively).

To evaluate metal concentrations in sediment and their effect on the biota community in the investigated area, metal concentration was compared to the effect range low (ERL) and effect range medium (ERM) (Long *et al.*, 1995). All stations in the present study reveals a Cd concentration lower than ERL except stations 12 and 21 which recorded values higher than ERL but still much lower than ERM revealing that the there is no adverse effect on the biota on almost stations in the study area (Table 5). The Cu content exceeded the ERL value (34 µg/g) at about 19% of stations but still much lower than ERM indicating that this study area is uncontaminated by Cu. The Ni level in our description area was exceeded the ERL in about 62% of study stations and exceeded ERM in about of 29% of the investigation stations indicating that this metal may cause an adverse effect on the biota community of this area. On the other hand, Pb and Zn levels in all investigated sites were never exceeded the ERL indicating that the two metals had no adverse effect on the biota of this area.

Table 5: Average concentration of heavy metals in sediment samples collected along Egyptian Mediterranean coast and Effect Range Low (ERL), Effect Range Medium (ERM) for the investigated metals.

| **Station Number** | **Heavy metals concentration (µg/g dry weight)** | | | | | | |
|---|---|---|---|---|---|---|---|
| | **Cd** | **Cu** | **Fe** | **Mn** | **Ni** | **Pb** | **Zn** |
| **1** | 1.15 | 35.48 | 11274 | 673.58 | 65.79 | 18.93 | 69.57 |
| **2** | 1.14 | 34.05 | 12241 | 770.61 | 31.14 | 24.42 | 60.56 |
| **3** | 1.11 | 33.94 | 2324 | 628.65 | 55.61 | 33.14 | 77.50 |
| **4** | 1.09 | 12.71 | 1999 | 568.51 | 8.11 | 21.54 | 54.85 |
| **5** | 0.99 | 18.21 | 1669 | 238.46 | 4.18 | 43.70 | 59.01 |
| **6** | 0.94 | 8.52 | 1781 | 292.07 | 3.27 | 30.05 | 38.14 |
| **7** | 0.26 | 10.86 | 942 | 71.00 | 8.68 | 31.58 | 34.81 |
| **8** | 1.12 | 28.72 | 2148 | 767.29 | 50.91 | 21.11 | 96.66 |
| **9** | 1.10 | 25.59 | 2096 | 690.53 | 53.72 | 24.48 | 79.49 |
| **10** | 0.50 | 23.88 | 14205 | 529.47 | 20.85 | 21.83 | 69.59 |
| **11** | 0.58 | 18.71 | 14475 | 956.15 | 21.97 | 30.72 | 71.43 |
| **12** | 1.31 | 22.51 | 14585 | 505.86 | 16.50 | 18.74 | 51.57 |
| **13** | 0.97 | 13.52 | 13228 | 468.78 | 3.23 | 16.22 | 46.37 |
| **14** | 0.91 | 32.10 | 13030 | 530.48 | 57.01 | 18.87 | 66.99 |
| **15** | 0.76 | 13.76 | 15703 | 611.37 | 61.47 | 22.01 | 35.74 |
| **16** | 1.09 | 36.19 | 2341 | 200.90 | 49.55 | 29.70 | 86.09 |
| **17** | 0.72 | 30.39 | 1753 | 233.70 | 10.81 | 13.59 | 76.56 |
| **18** | 1.00 | 25.35 | 2106 | 473.68 | 48.76 | 17.37 | 80.68 |
| **19** | 1.39 | 31.02 | 15354 | 560.65 | 47.96 | 27.38 | 33.03 |
| **20** | 0.77 | 46.67 | 11134 | 391.86 | 38.44 | 22.88 | 119.71 |
| **21** | 1.51 | 30.40 | 14798 | 242.01 | 31.36 | 31.13 | 79.37 |
| **ERL** | **1.2** | **34.0** | **--** | **--** | **20.9** | **46.7** | **150.0** |
| **ERM** | **9.6** | **270.0** | **--** | **--** | **51.0** | **218.0** | **410.0** |

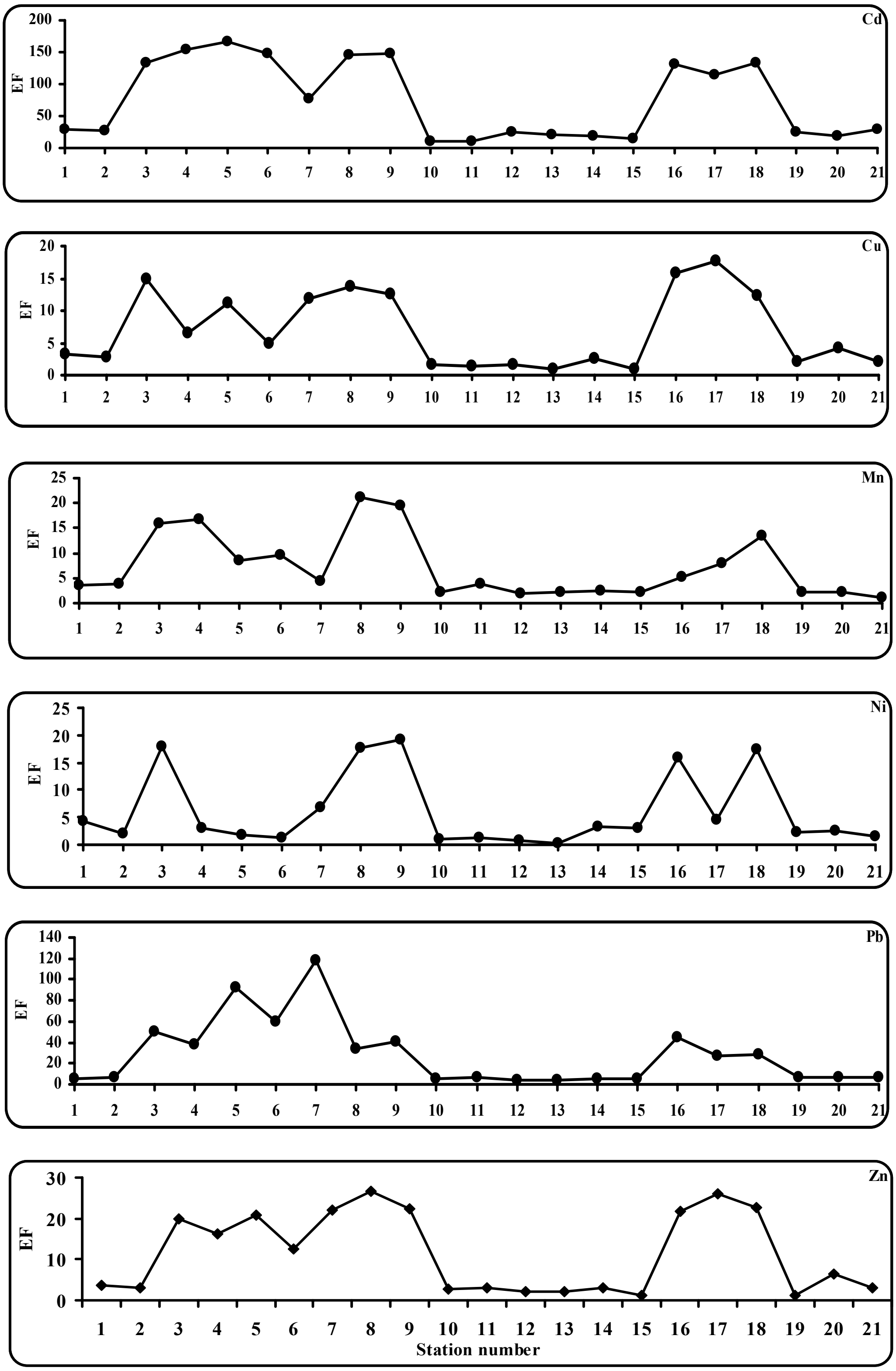

Figure 2: Enrichment factor of Cd, Cu, Mn, Ni, Pb and Zn, in the investigated sediment samples.

Natural weathering and human activities are known as metals sources for coastal environment. Therefore, for a better assessment of contamination process in the marine coastal environment, it is important to be able to distinguish between natural and human-related metal enrichments in sediments. Thus, for a meaningful comparison of metals from different stations, normalizing procedures for metals concentrations need to be used. In order to separate the natural metals concentrations from changes due to anthropogenic sources in the investigated samples and to asses the origin of each metal, the crustal enrichment factor using iron metal as reference element was used according to the following equation (Parekh *et al.*, 1989):

$$(EF)_{crustal} = \frac{[C_x / C_{Fe}]_{sample}}{[C_x / C_{Fe}]_{crust}}$$

Where $(C_x/C_{Fe})_{sample}$ is the ratio of concentrations of an element x in mg/g in analyzed sample and $(C_x/C_{Fe})_{crust}$ is the same ratio in the crustal material (natural background). The EF values were interpreted as the levels of heavy metal pollution that were suggested by Birth (2003). The proposed interpretation refers to the average concentrations of heavy metals of crustal origin provided by Martin and Meybeck, (1979) and represented the average composition of the surficial rocks exposed to weathering. Birth (2003) suggested that EF < 1 indicates no enrichment, EF= 1-3 indicates minor enrichment, EF= 3-5 indicates moderate enrichment, EF = 5-10 indicates moderately severe enrichment, EF = 10-25 indicates severe enrichment, EF = 25-50 indicates very severe enrichment and EF > 50 indicates extremely severe enrichment. In general, some sites of the investigated area, recorded minor to moderate enrichment by heavy metals while other are extremely severe enrichment. In more detail, 48%, 28.5% recorded extremely severe enrichment and very severe enrichment respectively for Cd while 38.1% and 9.5% recorded severe and very severe enrichment sites for Pb. Figure 2 revealed that 38%, 33.2%, 42.8%, and 33.3% of investigated sites were minor enriched by Cu, Mn, Ni, and Zn respectively. On the other hand, about 19.0%, 38.1%, 23.8%, 23.8%, and 38.1% of studied samples recorded severe enrichment of Cd, Cu, Mn, Ni, and Zn respectively. Enrichment in those sites is most probably due to the domestic, industrial and agricultural activities in the study area.

A common criterion to evaluate the heavy metal pollution in sediments is the geoaccumulation index *(Igeo)*, which was originally defined by Müller (1979) to determine metals contamination in sediments, by comparing current concentrations with pre-industrial levels and can be calculated by the following equation:

$$Igeo = \log_2[C_n / (1.5B_n)]$$

Where, $C_n$ is the measured concentration of the examined metal (*n*) in the sediment, $B_n$ is the geochemical background concentration of the metal (*n*), and factor 1.5 is the background matrix correction factor due to lithogenic effects. Müller (1981) has distinguished seven classes of geoaccumulation index Table 6. In the present work, $B_n$ values have been taken equal to metal concentrations of the Mediterranean background sediment according to Adamo *et al.*, (2005). According to the Müller scale, the calculated results of *Igeo* values Table 7 indicate that at most of the study stations Cd can be considered as moderately polluted (1<*I*geo<2) with the exception of stations 12. 19. 21 which fluctuated from moderately to strongly polluted (2<*Igeo*<3) (Müller, 1981). Copper, iron, manganese, lead, and Zinc fluctuated between class 1 (unpolluted) and class 2 (from unpolluted to moderately polluted) as shown in Table 7. On the other hand, the calculation of *Igeo* for nickel revealed that 42.5% of stations fall in class 1 (unpolluted), 52.5% in class 2 (from unpolluted to moderately polluted) and 5% in class 3 (moderately polluted). On the basis of the mean values of *Igeo*, sediments are enriched for metals in the following order: Cd > Ni > Cu > Zn > Pb > Mn > Fe.

The contamination factor $C_f$ was calculated to access the contamination status of sediment in the current study. Hakanson, (1980) suggested a series of contamination factor values to describe any contamination area where, $C_f < 1$: low contamination factor; $1 \leq C_f < 3$: moderate contamination factor; $3 \leq C_f < 6$: considerable contamination factor; $C_f \geq 6$: very high contamination factor. Our results revealed that (st.7) was belonged to the low contamination class, while about 19% of stations fall at the class of moderate contamination, and 76% belonged to class of considerable contamination. Although the stations 12, 19, 21 belonged to class of considerable contamination, they recorded the highest values, fluctuated between 4 and 6 Table 8, which was in agreement with data calculated from *Igeo*. All stations in the present study recorded low contamination factor for Ni, Cu, Zn. Moderated Contamination for Pb was observed in about 71% of stations in the current study while the rest of stations revealed low degree of contamination Table 8.

Metal pollution index (MPI) was used to evaluate the overall metal contamination. MPI was defined as a linear sum of the contamination factors weighted to take into account the differences in toxicity of the various metals was carried out by calculating through the equation:

$$MPI = \sum_i (W_i / W_t) \times CF_i$$

Where $CF_i$ is the contamination factor for metal *I*, $W_i$ is the weight for metal *I*, and $W_t = \sum_i W_i$. The weights of metals Zn, Cu, Pb, Ni, and Cd were established by Gonçalves *et al.*, (1992). Metal Pollution Index for the investigated stations was illustrated in Table 8. St. 7 must be classified as none contaminated stations where MPI < 1, while 14% of (st.10, 11 and 17) fluctuated between uncontaminated to low contaminated where

MPI values <2 while 62% of stations were classified to considerable contamination where MPI>2. On the other hand, (st. 12, 19, 20, & 21) were classified as serious contaminated sites (MPI>3) for the previous five metal according to the classification of Gonçalves *et al.* (1992).

Table 6: Müller's classification for the geoaccumulation index (Müller, 1981).

| **$I_{geo}$ value** | **Class** | **Quality of sediment** |
|---|---|---|
| ≤ 0 | 0 | Unpolluted |
| 0-1 | 1 | From unpolluted to moderately polluted |
| 1-2 | 2 | Moderately polluted |
| 2-3 | 3 | From moderately to strongly polluted |
| 3-4 | 4 | Strongly polluted |
| 4-5 | 5 | From strongly to extremely polluted |
| ≥ 6 | 6 | Extremely polluted |

Table 7: Geoaccumulation index ($I_{geo}$) values of heavy metals of sediment samples in the investigated area.

| Site | Cd | Cu | Fe | Mn | Ni | Pb | Zn |
|---|---|---|---|---|---|---|---|
| **1** | 1.93357 | 0.17145 | -0.20551 | -0.09314 | 1.13291 | -0.86577 | -0.27192 |
| **2** | 1.92726 | 0.11247 | -0.08679 | 0.10101 | 0.05381 | -0.49883 | -0.47205 |
| **3** | 1.88633 | 0.10748 | -2.48383 | -0.19273 | 0.89038 | -0.05806 | -0.11628 |
| **4** | 1.85912 | -1.30882 | -2.70116 | -0.33780 | -1.88719 | -0.67986 | -0.61483 |
| **5** | 1.72681 | -0.79057 | -2.96146 | -1.59124 | -2.84339 | 0.34089 | -0.50940 |
| **6** | 1.64987 | -1.88570 | -2.86775 | -1.29867 | -3.19760 | -0.19908 | -1.13890 |
| **7** | -0.22915 | -1.53649 | -3.78664 | -3.33910 | -1.78920 | -0.12763 | -1.27102 |
| **8** | 1.89610 | -0.13344 | -2.59745 | 0.09478 | 0.76299 | -0.70882 | 0.20256 |
| **9** | 1.87797 | -0.29956 | -2.63280 | -0.05728 | 0.84050 | -0.49502 | -0.07955 |
| **10** | 0.74846 | -0.39961 | 0.12789 | -0.44044 | -0.52492 | -0.66055 | -0.27143 |
| **11** | 0.95606 | -0.75131 | 0.15505 | 0.41225 | -0.44943 | -0.16747 | -0.23390 |
| **12** | 2.12102 | -0.48479 | 0.16597 | -0.50625 | -0.86250 | -0.88040 | -0.70397 |
| **13** | 1.69748 | -1.22015 | 0.02508 | -0.61608 | -3.21536 | -1.08891 | -0.85726 |
| **14** | 1.60723 | 0.02731 | 0.00333 | -0.43769 | 0.92625 | -0.87065 | -0.32653 |
| **15** | 1.34483 | -1.19529 | 0.27253 | -0.23294 | 1.03492 | -0.64844 | -1.23289 |
| **16** | 1.86054 | 0.20010 | -2.47331 | -1.83851 | 0.72392 | -0.21596 | 0.03541 |
| **17** | 1.25493 | -0.05166 | -2.89061 | -1.62033 | -1.47260 | -1.34374 | -0.13384 |
| **18** | 1.74155 | -0.31343 | -2.62593 | -0.60108 | 0.70074 | -0.99016 | -0.05809 |
| **19** | 2.20685 | -0.02234 | 0.24010 | -0.35789 | 0.67687 | -0.33332 | -1.34644 |
| **20** | 1.36737 | 0.56714 | -0.22354 | -0.87465 | 0.35765 | -0.59270 | 0.51112 |
| **21** | 2.33247 | -0.05133 | 0.18689 | -1.56992 | 0.06396 | -0.14820 | -0.08180 |

Table 8: Contamination factor, degree of contamination and the metal pollution index for the sediment samples of the investigated area.

| **Site** | **$C_f$** | | | | | **MPI** |
|---|---|---|---|---|---|---|
| | **Cd** | **Cu** | **Ni** | **Pb** | **Zn** | |
| **1** | 3.82 | 0.79 | 0.97 | 0.95 | 0.73 | 2.98 |
| **2** | 3.80 | 0.76 | 0.46 | 1.22 | 0.64 | 2.94 |
| **3** | 3.70 | 0.75 | 0.82 | 1.66 | 0.82 | 2.98 |
| **4** | 3.63 | 0.28 | 0.12 | 1.08 | 0.58 | 2.74 |
| **5** | 3.31 | 0.40 | 0.06 | 2.18 | 0.62 | 2.67 |
| **6** | 3.14 | 0.19 | 0.05 | 1.50 | 0.40 | 2.45 |
| **7** | 0.85 | 0.24 | 0.13 | 1.58 | 0.37 | 0.85 |
| **8** | 3.72 | 0.64 | 0.75 | 1.06 | 1.02 | 2.89 |
| **9** | 3.68 | 0.57 | 0.79 | 1.22 | 0.84 | 2.89 |
| **10** | 1.68 | 0.53 | 0.31 | 1.09 | 0.73 | 1.39 |
| **11** | 1.94 | 0.42 | 0.32 | 1.54 | 0.75 | 1.65 |
| **12** | 4.35 | 0.50 | 0.24 | 0.94 | 0.54 | 3.26 |
| **13** | 3.24 | 0.30 | 0.05 | 0.81 | 0.49 | 2.43 |
| **14** | 3.05 | 0.71 | 0.84 | 0.94 | 0.71 | 2.42 |
| **15** | 2.54 | 0.31 | 0.90 | 1.10 | 0.38 | 2.09 |
| **16** | 3.63 | 0.80 | 0.73 | 1.49 | 0.91 | 2.899 |
| **17** | 2.39 | 0.68 | 0.16 | 0.68 | 0.81 | 1.81 |
| **18** | 3.34 | 0.56 | 0.72 | 0.87 | 0.85 | 2.59 |
| **19** | 4.62 | 0.69 | 0.71 | 1.37 | 0.35 | 3.57 |
| **20** | 5.04 | 0.68 | 0.46 | 1.56 | 0.84 | 3.86 |
| **21** | 4.17 | 0.96 | 0.68 | 1.33 | 0.47 | 3.24 |

## 4. Conclusion

In this work, it was noticed that studied sediments are showed wide range of grain size characteristics. The sediments are composed mainly of an admixture of sand, silt and clay. The carbonate % varies between 6.19 % and 85.72 % and total organic carbon content ranges between 0.15 and 1.79 %.

In general, some sites of the investigated area have recorded minor to moderate enrichment by heavy metals while other have recorded extremely severe enrichment. In more detail, 48%, 28.5% recorded extremely severe enrichment and very severe enrichment respectively for Cd while 38.1% and 9.5% recorded severe and very severe enrichment sites for Pb. It was revealed that 38%, 33.2%, 42.8%, and 33.3% of investigated sites were minor enriched by Cu, Mn, Ni, and Zn respectively. Enrichment in those sites is most probably due to the domestic, industrial and agricultural activities in the study area.

All stations in the present study recorded low contamination factor for Ni, Cu, Zn. Moderated contamination for Pb was observed in about 71% of stations in the current study while the rest of stations revealed low degree of contamination. The geoaccumulation index ($I_{\text{geo}}$) shows that Cd moderately to extremely pollute sediments. Cu, Fe, Mn, Pb, and Zn fluctuated between unpolluted and moderately polluted. On the basis of the mean values of $I$geo, sediments are enriched for metals in the following order: Cd > Ni > Cu > Zn > Pb > Mn > Fe.

Table 9: Correlations between grain size, TOC%, TCO3%, TSiO3%, and heavy metals in sediment samples in the investigated area.

| | Sand% | Silt% | Clay% | Mean | TOC | $TCO_3$ | $TSiO_3$ | Cd | Cu | Fe | Mn | Ni | Pb | Zn |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Sand% | 1 | | | | | | | | | | | | | |
| Silt% | -0.880** | 1 | | | | | | | | | | | | |
| Clay% | -0.401* | -0.083 | 1 | | | | | | | | | | | |
| Mean | -0.861** | 0.630** | 0.591** | 1 | | | | | | | | | | |
| TOC | -0.432* | 0.118 | 0.677** | 0.503** | 1 | | | | | | | | | |
| $TCO_3$ | 0.566** | -0.439** | -0.340* | -0.553** | -0.401* | 1 | | | | | | | | |
| $TSiO_3$ | -0.566** | 0.440** | 0.340* | 0.554** | 0.401* | -1.00** | 1 | | | | | | | |
| Cd | -0.293 | 0.234 | 0.163 | 0.178 | 0.470* | -0.703** | 0.702** | 1 | | | | | | |
| Cu | -0.557** | 0.513** | 0.180 | 0.514** | 0.486* | -0.461* | 0.461** | 0.327 | 1 | | | | | |
| Fe | -0.162 | -0.002 | 0.336 | 0.421* | 0.283 | -0.237 | 0.238 | 0.136 | 0.156 | 1 | | | | |
| Mn | -0.282 | 0.200 | 0.207 | 0.341 | -0.161 | -0.316 | 0.317 | 0.149 | 0.117 | 0.358 | 1 | | | |
| Ni | -0.843** | 0.591** | 0.629** | 0.819** | 0.577* | -0.602** | 0.602** | 0.296 | 0.586** | 0.163 | 0.414 | 1 | | |
| Pb | -0.079 | 0.153 | -0.129 | 0.040 | -0.055 | 0.282 | -0.282 | 0.012 | -0.145 | -0.229 | -0.236 | -0.171 | 1 | |
| Zn | -0.361* | 0.504** | -0.257 | 0.172 | 0.073 | -0.209 | 0.208 | 0.074 | 0.727** | 0.167 | 0.112 | 0.344 | -0.119 | 1 |

Note: ** correlation is significant at the 0.01 level (1-tailed)
* correlation is significant at the 0.05 level (1-tailed)

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# تقييم مستوى المعادن فى الرسوبيات فى المنطقة الممتدة من رشيد إلى دمياط

**سوزان السيد عمر دراز - هدى حسن حافظ عهدي - منى خميس خليل - عزة خالد**

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تم دراسة بعض العناصر الثقيلة (كادميوم ، النحاس ، الحديد ، المنجنيز ، النيكل ، الرصاص ، الزنك) بجانب دراسة نسيج الرسوبيات والمواد الكربونية الكلية و الكربونات الكلية فى 21 عينة رسوبيات بحرية والتى تم جمعها من المنطقة الممتدة من رشيد إلى دمياط فى 2008 . وقد دل التحليل الحجمي للرسوبيات على أن الحجم الحبيبي يتراوح بين 1.07 (رمل متوسط الحجم) و Φ 6.8 (طمي ناعم جدا). المواد الكربونية الكلية قد تراوحت بين 1.15% إلى 1.79% بينما تراوحت الكربونات الكلية بين 7% إلى 85%. وقد دلت الدراسة على أن تركيز العناصر الثقيلة فى عينات الرسوبية موضوع الدراسة على أن العناصر: الكادميوم ، النحاس ، الحديد ، المنجنيز ، النيكل ، الرصاص والزنك قد تراوح بين 0.26-1.51 ، 8.52 – 46.67 ، 942 - 15703 ، 71 - 956 ، 2.23 – 65.79 ، 13.59 - 43.70 و 33.03 - 119 مليجرام/جرام على التوالي. وقد تم استخدام النماذج الإحصائية : عامل التراكم $(EF)_{crustal}$ درجة التلوث $(C_f)$، دليل التلوث المعدني (MPI ) بالإضافة إلى معامل التراكم الجيولوجي (*I*geo) وذلك لدراسة تأثير التغيّر الطبيعي في المحتوى المعدني للرسوبيات وتقييم حالة التلوث فى العينات موضوع الدراسة. وقد خلصت إلى أن عنصري الكادميوم والنحاس قد سجلا قيم أقل من تأثير المدى المتوسط ERM بينما عنصري الرصاص والزنك لم يتجاوزا قيم تأثير المدى المنخفض ERL وتشير النتائج أنه لا يوجد تأثير ضار على الأحياء البحرية المتواجدة فى المنطقة الدراسة. وتوضح الدراسة أن مستوى عنصر النيكل يفوق تأثير المدى المتوسط فى حوالي 29% من مجموع المحطات والتى تشير إلى تأثير النيكل على الأحياء المتواجدة فى هذه المنطقة .