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# Geochemical Study and Distribution of some Trace Metals along Coastal Zone of Abu-Qir Bay, Mediterranean Sea-Alexandria, Egypt

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**Abstract:** The current study aims to clarify the variations and distribution of some heavy metals concentrations (Chromium, Cupper, Lead, Zinc and Cadmium) among marine water and sediments of Abu-Qir Bay. Grain size analysis, as well as, total organic matter, carbonates contents and total phosphorous were determined. The concentrations of heavy metals in water were ranged from: 1.18 to 40.56, 3.04 to 6.08, 13.13 to 28.35, 1.22 to 92.47 and 0.42 to 1.36µg/l for Cr, Cu, Pb, Zn and Cd respectively. The heavy metals concentrations values in sediments were ranged between 44.68-274.2, 9.6-166.32, 53.2-159.64, 29.43- 461.88 and 0.24-4.68µg/g dry weights for chromium, Copper, Lead, Zinc and Cadmium respectively. Higher concentration values were observed in the western part of the Bay than the eastern part. An assessment of the present status of the studied area was carried out by calculating the distribution coefficient, $K_d$ and its logarithmic values log $K_d$. Copper and Chromium had highest log $K_d$ in winter near El–Maadya outlet and El-Tabia pumping station, while Zinc and Lead had higher log $K_d$ in station 1. According to toxicity guideline; concentrations of heavy metals in Abu-Qir Bay were mostly between the effect range low (ERL) and the effect range median (ERM). This indicate that there is no and/or small adverse effect on the benthic marine community and biota all over the study area. In general, the levels of metal's concentrations in water and sediments of Abu-Qir Bay were mostly within the permissible limits of both Egyptian laws 48/1982 and FAO 1985. Generally Abu-Qir Bay showed an improvement if compared with background studies as explained in literature.

**Key words:** Abu-Qir Bay · Grain Size · Organic Matter · Heavy Metals · Distribution Coefficient

## INTRODUCTION

Heavy metals are among the most common environmental pollutants and their occurrences in water, sediments and biota indicates the presence of natural or anthropogenic sources. The main natural sources of metals in water are; chemical weathering of minerals and soil leaching. The anthropogenic sources are associated mainly with industrial and domestic effluents, urban storm, water runoff, land fill, mining of coal and ore, atmospheric sources and rural areas Kabata-Pendias [1] and Biney *et al.* [2]. Water pollution by heavy metals is an important factor in both geochemical cycling of metals and in an environmental health.

The existence of heavy metals in aquatic environments leads to serious concerns about their influences on plant and animal life. Heavy metals exhibit extreme toxicity even at trace levels. Therefore Abu-Qir Bay is considered as the most polluted region due to the adverse effect of effluents from land-based sources. The data obtained from previous studies showed that, Abu–Qir Bay was suffering from risks of deterioration as a result of the increase in degradation of the coastal water quality [3- 6].

The present study and the data obtained from previous studies recommended a long-term follow-up for the physicochemical, geochemical and biological evolutions in the coastal water, sediments and biota at monthly, seasonally and annual levels are needed to identify changes occurring in a particular coastal area [7, 8].

The current study aims to clarify the variations and the distribution of five selected heavy metals (Cr, Cu, Pb, Cd and Zn) in surface water and marine sediments of Abu-Qir Bay, as well as, the impact of pollutant sources on the water quality of the Bay.

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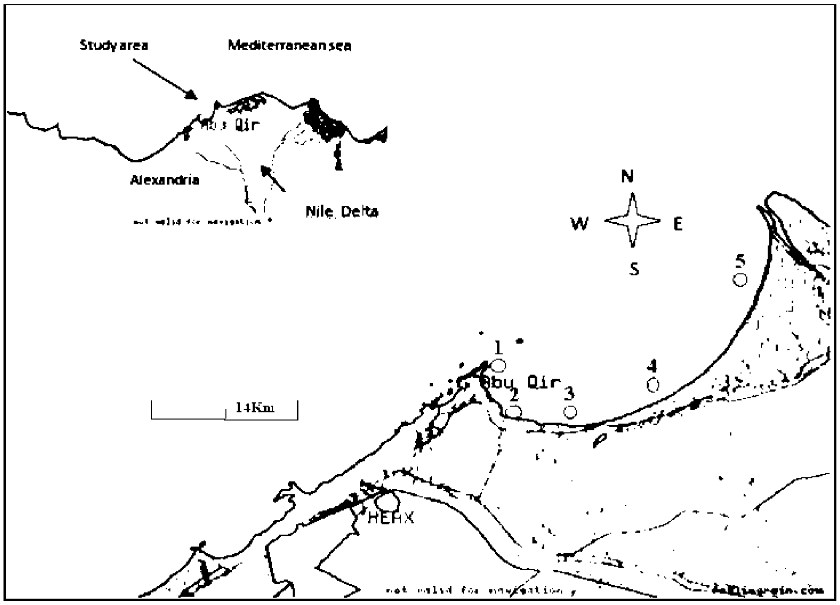


Fig. 1: Location Map showing the water and sediments sampling stations in Abu-Qir Bay

Table 1: Location of the marine sampling stations in Abu-Qir Bay

| Station No. | Latitude | Longitude |
|---|---|---|
| 1 | 31° 31¯ 76¯ ¯ | 30° 07¯ 04¯ ¯ |
| 2 | 31° 27¯ 06¯ ¯ | 30° 17¯ 50¯ ¯ |
| 3 | 31° 27¯ 31¯ ¯ | 30° 18¯ 72¯ ¯ |
| 4 | 31° 32¯ 05¯ ¯ | 30° 28¯ 42¯ ¯ |
| 5 | 31° 44¯ 38¨ | 30° 35¯ 86¯ ¯ |

**Area of Study:** Abu-Qir Bay extends between Longitude 30° 07′ and 30° 22′ E at Abu-Qir Peninsula and Latitude 31° 31′ 76′′ and 31° 44′ 38′′ north at Rosetta Branch of River Nile (Table 1 and Figure 1). It runs along a shoreline of about 50 km. The area of the Bay is about 360 km$^2$ with a maximum depth of 9 m and an average of 3.8 m; Saad and Younes [6]. Along the coast of Abu-Qir Bay there are about 22 different factories representing food processing and canning, paper mill, fertilizers, textile manufacturing and gas exhausts [8, 9]. These factories dump wastes through El-Tabia Pumping station situated at the southwestern extremity of the bay which pumps an average of about 1.5-2.0x10$^6$ m$^3$/d, also the bay receives agricultural drainage water from the coastal Lake Edku through the narrow channel El-Maadya (about 200 m long and 2 m deep) pumps about 2x10$^6$ m$^3$/d [8, 10].

## MATERIALS AND METHODS

In order to explore the impact of pollutions (industrial, agricultural and land-based sources) on Abu-Qir Bay, marine sediments and water samples were collected during two seasons (summer 2009 and winter 2010) from 5 stations, covering the bay (Fig. 1). The water depth was up to 1 m. The water samples are kept in well-stoppered polyethylene bottles until analysis. Each sediment sample collected by scuba diver using PVC tube 40 cm length and 6 cm in diameter from 5 stations. The samples were transported to the laboratory and stored frozen until analysis. All laboratory equipments and containers were washed in 10% $HNO_3$ acid solution and rinsed with double distilled water (DDW) prior each use. All reagents used were analytical reagent grade (Merck- Germany).

Water samples were filtered through 0.45µm membrane filter. The filtrate was allowed to flow through a column of Chelex-100 ion exchange resin at a rate of 5ml/min. The metals were eluted with 70ml of 2N nitric acid and 10ml DDW. The elute was collected in a silica flask and evaporated to near dryness. The residue was treated with 1ml 6N nitric acid and 10ml DDW, cooling and completed to 25ml DDW in a volumetric flask. The total concentrations of Chromium, Lead, Copper, Cadmium and Zinc were measured using Flam-Atomic Absorption Spectrophotometer (FAAS, Shimadzo 6800, with auto sampler 6100), UNEP\IAEA [11].

Sediment samples were washed with DDW and dried at 85C° in an oven, then ground in an agate mortar and sieved to pass through 63µm mesh sieve. The powder sediment samples are digested in closed Teflon vessels with a mixture of concentrated $HNO_3$, HF and $HClO_4$ (3:2:1v/v) following the method of Oregioni and Aston [12]. The samples were analyzed on a Flam-Atomic

Absorption Spectrophotometer (FAAS, Shimadzo 6800, with Auto sampler 6100). Also the sediment samples were subjected to grain size analysis using technique described by Folk [13]. Total organic carbon was determined by technique described by Loring and Rantala [14]. Total organic matter was calculated from preceding organic carbon multiplying by a factor of 1.8. Carbonate content was determined according to Molnia [15]. Total phosphorous was measured using technique mentioned by Aspila [16]. The distribution (partition) coefficients of the metals were calculated and discussed.

**Statistical Analysis:** The data analyzed statistically lead to understand aspect of chemical, physical and some of geological processes prevailing in Abu-Qir Bay, correlation coefficient were calculated between all measured variables.

## RESULTS AND DISCUSSION

**Grain Size Analysis:** The grain size varied between medium sand at stations (1 and 3), fine sand at station (2, 4) and very fine sand was shown only at station (5), Table (2). The grain size data revealed that the sediments in Abu-Qir Bay are composed of different types of sand-sized sediments. The sediment mean size in Abu-Qir bay decrease from west to east. The mean size (MZ Φ) ranges between 1.58 and 3.23 Φ. Sorting of the sediments varied from poorly sorting 40 % and moderately well sorting 60%. Pettijohn [17] found that sorting is dependent on the grain size, in that coarse sediments (gravels and conglomerates) are generally moderately to poorly sorted and fine sediments (silt and clay) are generally more poorly sorted than sand-sized sediments, which are more easily transported and sorted by wind and water.

**Total Organic Matter:** Total organic carbon and total organic matter in Abu-Qir Bay are listed in Table (2). The structure and the composition of the organic matter in the marine sediments are varying due to its origin in the aquatic environment. Phytoplankton and zooplankton are the most abundant sources of the organic material in the sediments, Grathwohl [18]. The organic matter content in sediments of Abu-Qir Bay expressed as percentage are ranged from the lowest values of 0.14%, 0.50%, 0.86% and 1.36% recorded at stations 1, 2, 3 and 4, respectively, to the highest value of 3.62% at station 5. The high percentage of organic matter might be attributed to the high amount of drainage water. The high rate of organic growth together with the organic detritus introduced by the drainage system can be considered the main source of organic matter, Masaud *et al.* [19]. The low percentages of TOM are due to the structure of the sediments in the investigated area was mainly sand i.e. has low affinity to absorb contaminates. Kuenen [20] stated that, organic matter increases with decrease of grain size and he attributed this to the presence of the protective action of clay. Wood [21] found that the small clay and silt particles with more surface areas support large bacterial population than coarse sand. Oppenheimer [22] has found that 95% of the organic matter in sands was broken down within 40 days of bacterial activation, meanwhile, 75% of organic matter is broken down in that period in clays. According to Balzer *et al.* [23], the ratio between TOM accumulation and combustion is 1:1.1.

**Total Phosphorus (TP):** Phosphorus is one of the most important nutrients for all living organisms. Two forms of phosphorus could be present in the aquatic system, dissolved and particulate. Both phosphorus and nitrogen are important elements controlling the growth and reproduction of phytoplankton. Phosphorus is necessary to all life because of its function in the storage and transfer of cell energy and in genetic systems [19, 24]. The concentration of TP in Abu-Qir Bay sediments expressed as percentage ranged between a minimum of 0.098% at station 3 and a maximum of 1.01% at stations 5. The higher value of phosphorus may be due to the decrease of decomposition of organic matter and/or the effect of drainage water coming from Rosetta branch of River Nile loaded by agricultural wastes contain phosphate fertilizers. Baturin [25] supposed that initial phosphorus content in sediments at the time of their deposition was similar to that recent surface layers, a systematic upward migration of Phosphorus take place to the surface-water interface.

Table 2: The grain size analysis and physicochemical parameters in marine sediments

| Stations | Sediment type | Mean (Φ) | Sorting | $CaCO_3$% | T O C% | TOM% | Total P% |
|---|---|---|---|---|---|---|---|
| 1 | Medium Sand | 1.58 | 1.14 | 29.02 | 0.08 | 0.14 | 0.101 |
| 2 | Fine sand | 2.09 | 0.67 | 29.76 | 0.27 | 0.50 | 0.099 |
| 3 | Fin sand | 2.03 | 0.75 | 27.4 | 0.48 | 0.86 | 0.098 |
| 4 | Fine sand | 2.07 | 0.63 | 12.0 | 0.76 | 1.37 | 0.103 |
| 5 | V. fine sand | 3.23 | 1.21 | 28.8 | 2.01 | 3.62 | 1.01 |

Table 3: concentrations of, Pb, Zn, Cr, Cu and Cd in water samples of Abu-Qir Bay during summer 2009 and winter 2010 (µg/L)

| Seasons | stations | Pb | Zn | Cr | Cu | Cd |
|---|---|---|---|---|---|---|
| Summer 2009 | 1 | 15.91 | 2.93 | NM | ND | 1.24 |
| | 2 | 18.67 | 11.63 | NM | ND | 1.27 |
| | 3 | 24.0 | 1.22 | NM | ND | 1.24 |
| | 4 | 26.28 | 2.91 | NM | ND | 1.18 |
| | 5 | 28.35 | ND | NM | ND | 1.36 |
| | Min. | 15.91 | =1.22 | ---- | ---- | 1.18 |
| | Max. | 28.35 | 11.63 | ---- | ---- | 1.36 |
| | Mean | 22.64 | 4.67 | ---- | ---- | 1.26 |
| | ±SD | 5.16 | 4.08 | ---- | ---- | 0.06 |
| Winter 2010 | 1 | 13.13 | 11.65 | 1.29 | 4.52 | 0.61 |
| | 2 | 20.21 | 20.31 | 35.35 | 6.08 | 0.63 |
| | 3 | 13.81 | 18.28 | 40.56 | 3.04 | 0.59 |
| | 4 | 15.16 | 92.47 | 7.52 | 5.17 | 0.42 |
| | 5 | 17.51 | 14.74 | 1.18 | 4.78 | 0.60 |
| | Min. | 13.13 | 11.65 | 1.18 | 3.04 | 0.42 |
| | Max. | 20.21 | 92.47 | 40.56 | 6.08 | 0.63 |
| | Mean | 15.96 | 31.49 | 17.18 | 4.72 | 0.57 |
| | ±SD | 2.60 | 30.63 | 17.20 | 0.99 | 0.08 |
| permissible limit | Law48/82 | -- | 1000 | 50 | <1000 | 10 |
| | FAO1985 | 100 | 200 | 5000 | 2000 | -- |
| | USEPA | -- | 1000 | 50 | 1000 | 10 |
| | CWQGs | 50 | 1000 | 50 | 5000 | 5 |

Law48/82: Egyptian Law for protection of the River Nile and waterways from pollution, FAO: Food and Agriculture Organization Guidelines, CWQGs 2002: Canadian Water Quality Guidelines for the protection of aquatic life and USEPA 2000: Environmental protection Agency, NM: not measured, ND: not detected.

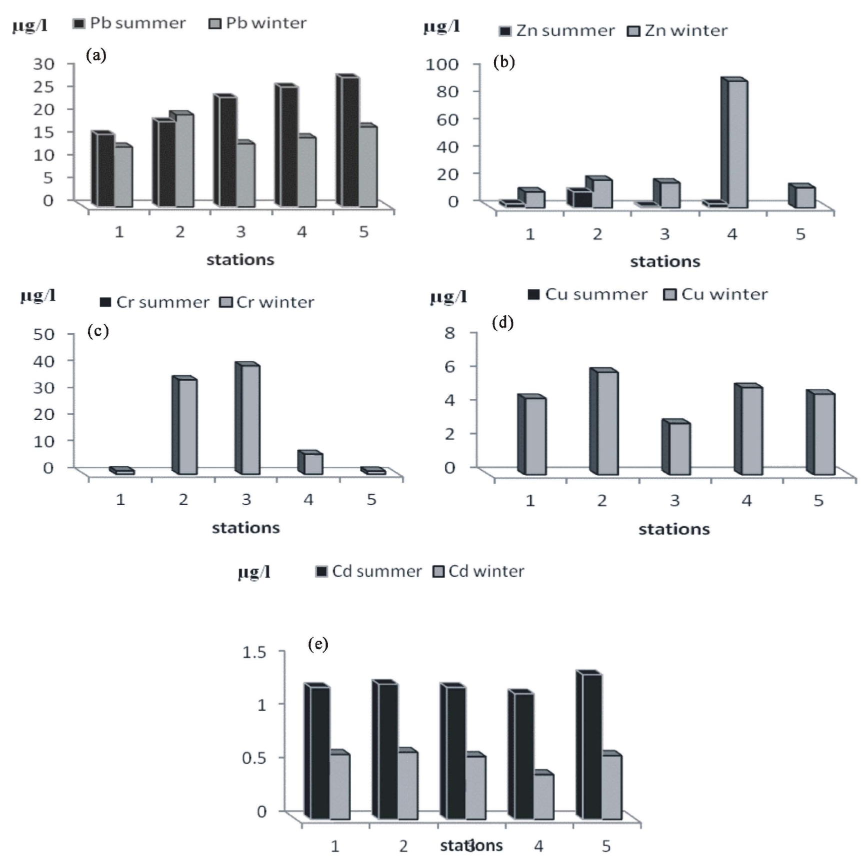


Fig. 2: Concentration of heavy metals in surface water of Abu-Qir Bay

**Total Carbonate Content ($CaCO_3$):** The carbonate content of surface sediments of Abu-Qir Bay varied from 12.0% to 29.76% at stations (4,2) respectively, Table (2). The carbonate content showed higher concentration at west side than at the east side of the bay, refers to the presence of carbonate grains derived mostly from the carbonate rich province on the shelf west of Alexandria [26]. The Carbonate Diminish might be interpreted on the basis of fluvial supply of River Nile to the study area, also could be attributed to unsuitable conditions for the flourishing of the calcareous organisms. Okbah *et al.* [27] owed the variation of carbonate content to the variability of the mineralogical components. From the present data, it is clear that, station 5 has high values for all parameters: water content, carbonate content, total organic matter and phosphorus. This might be owed to the combined effect of agricultural drainage, as well as, industrial discharge.

Heavy metal concentrations in surface water of Abu-Qir Bay: The distribution of heavy metals (Cd, Cu, Pb, Zn and Cr) in water samples of Abu-Qir Bay during summer 2009 and winter 2010 is illustrated in Figure. (2); and presented in Table (3).

**Cadmium:** Cadmium is extremely toxic to biota and living organisms, its effects on the growth rate have been observed even at low concentrations 5-10μg/l [28].

Cadmium concentrations in Abu-Qir Bay ranged from a minimum value of 1.18μg/l at station 4 to a maximum value of 1.36μg/l at stations 5 during summer. The seasonal average concentrations of Cadmium are 0.57 ±0.08 μg/l in winter and 1.26±0.06μg/l in summer, Figure (2e). The obtained results of cadmium are lower than that reported by Shriadah and Emara [29], Emara *et al.* [30], Abdallah [31] and El Zokm [32], Table (4).

**Copper:** The main sources of Copper in Abu-Qir Bay include contamination of manufacturing processes related to chemical and metals discharges of municipal wastes. The domestic sources are the major contributors of copper in the environment [33]. The present investigation revealed that copper concentration ranged from 3.04μg/l at station 3 to 6.08μg/l at station 2 in winter, with an average of 4.72±0.99μg/l (Fig. 2d). Higher copper concentration might be due to agricultural, domestic and industrial wastewaters discharged into the bay, In addition to high pH values (7.88, 7.42) El-Gohary *et al.* [34], which also seem to have influence on the concentrations of this metal in natural unpolluted water [35]. El-Nady [36] recorded mean copper concentration value of 4.17μg/l in Abu-Qir Bay. The concentrations of copper are matching with that recorded by Shriadah and Emara [29] and Abdallah [31], Table (4). Massoud and Hassan [37] found that seasonal average concentration of copper was 5.6μg/l at the estuarine mouth of the River Nile and the Mediterranean Sea. The highest seasonal average value (winter) of dissolved copper of the present study may be attributed to the presence of high amount of suspended matter during highest discharged period.

**Zinc:** Zinc is an essential trace metal for the growth of marine organism. It is one of the biologically occurred elements and is known to occur in seawater only in sub micro-molar concentrations [37 and 38]. In seawater, Zinc inter acts primary with the hydroxide and chloride ions. Van Den Berg *et al.* [39] stated that: organic complexation controls the concentration of dissolved zinc. The major sources of Zinc are the domestic wastes, municipal wastes followed by dumping and atmospheric deposition [40].

Table 4: Concentration of some heavy metals (μg/l) in Abu-Qir Bay water compared to other studies

| Location | Pb | Zn | Cr | Cu | Cd | Reference |
|---|---|---|---|---|---|---|
| Abu-Qir Bay | 15.96-22.64 | 4.67-31.39 | 17.18 | 4.72 | 0.57-1.26 | present |
| El-Max fish farm | 0.23-17.09 | 2.6-23.92 | ----- | 0.55-25.9 | 0.1-1.9 | [32] |
| Nile Delta in Egypt | < 5.0 -57.0 | 16.0-66.0 | 2.0-56.0 | 2.0-41.0 | 0.5-34.0 | [35] |
| El- Max Bay | 2.65-26.14 | 20.79-59.29 | 1.48-7.06 | 3.69-4.90 | 0.66-6.45 | [31] |
| Lake Edku | 10.0-225.0 | 11.0-126.0 | 1.0-26.0 | 14.0-49.0 | 2.0-16.0 | [19] |
| Rosetta estuary | ---- | 42.7 | ---- | 9.0 | 0.79 | [37] |
| Abu-Qir Bay | ---- | 25.5 | ---- | 4.17 | 0.23 | [36] |
| Eastern Harbor | ----- | 140.4 | ----- | 2.90 | 2.14 | [30] |
| Eastern Harbor | ------ | 170.2 | ---- | 4.84 | 1.77 | [29] |
| El-Max Bay | ----- | 40.6 | ------ | 7.4. | 3.50 | [30] |
| El- Max Bay | ------ | 55.5 | ------ | 4.89 | 1.89 | [29] |

The concentration of zinc in Abu-Qir Bay fluctuated between 1.22µg/l and 92.74µg/l at stations 3 and 4 in summer and winter respectively, with seasonal average concentrations of 4.67±4.08 µg/l and 31.49±30.63 µg/l for summer and winter respectively (Fig. 2c). Depletion of Zn concentrations in summer season may be related to the contribution of phytoplankton, pH and dissolved oxygen concentration. Massoud and Hassan [37] recorded seasonal average concentration of Zn in the estuarine mouth of Rosetta estuary was 26.9µg/l. Abdallah, [31] recorded concentration values of Zn in El-Max Bay ranged from 20.76 to 59.29µg/l with an average of 33.58µg/l, Table (4).

**Lead:** Lead concentrations in Abu-Qir Bay ranged from 13.13µg/l at station 1 in winter to 28.35µg/l at station 5 in summer with an average of 22.64 ± 5.16µg/l and 15.96±2.60µg/l for summer and winter seasons respectively (Fig. 2a). The highest concentration of lead was observed at station 5. El-Bouraie *et al.* [35] found that the concentration values of lead in River Nile were =5.0-57.0 µg/l. Abdallah [31] recorded the concentration values of lead ranged from 2.65 to 26.14µg/l in El-Max Bay. The low concentrations are probably related to high pH values (7.42, 7.88) which associated to removal of heavy metals from the aqueous phase to the solid phase, Masaud *et al.* [19]. The higher values of lead might be attributed to increase the amount of agricultural, domestic and industrial wastewater poured in Abu-Qir Bay. The elemental background concentrations recorded in Table (4).

**Chromium:** Chromium is one of the biochemically active transition metals in aquatic environment. The concentration of chromium ranged from a minimum of 1.18µg/l at station 5 to a maximum of 40.56µg/l at station 3, with an average value of 17.18±17.20µg/l. The highest values of chromium 40.56µg/l and 35.35µg/l. might be owed to the effect of El-Tabia pumping station, while the lower concentration was observed at station 5, this station is far away from the sources of pollution, Table (3) and Fig. (2c).

The present data showed that: All metal concentrations in surface water of Abu-Qir Bay were found within the permissible limits of both Egyptian Law,48/1982 and FAO [41, 42]. The different concentration values of metals in water might be depending on seasonal variations and types of discharges. The concentrations of selective heavy metals reveal decreasing in the order: Pb>Zn>Cr>Cu>Cd. Comparing the data obtained from the present study with the other surrounding regions (Eastern Harbor, El-Max Bay and Lake Edku), most heavy metal concentrations in Abu-Qir Bay were lower than that reported in other regions in the literature Table (4). This indicates that Abu-Qir Bay showed an improvement relative to some of the previous studies.

**Heavy Metals Concentrations in Marine Sediments of Abu-Qir Bay:** Heavy metals measurements in sediment play an important role in assessing the pollution status of environment [43]. Metal pollutants enter the environment from industrial mining effluent, combustion of fossil fuels, discharge of sewage, fertilizer and pesticide residue. The heavy metals acting as sinks and sources of contamination in aquatic system. Many of heavy metal concentrations in fine grained sediments which act as a transport agent in the water column are at least three orders of magnitude higher than the same metals in the surrounding water, El-Bouraie *et al.* [35]. The analysis of heavy metal in sediments enables the detection of pollution deteriorating water quality and provides information about the "critical sites" of water system [44].

In the present study the concentrations of heavy metals in marine sediments of Abu-Qir Bay were recorded in Table (5) and illustrated in Figure (3) to be as following:

**Zinc:** Zinc concentrations in the sediment of Abu-Qir Bay varied between 29.43-164.44 mg/kg at stations 2 and 5 during summer and 45.56 - 461.88mg/kg at stations 4 and 1 in winter, respectively. The seasonal average variations of zinc are ranged between 84.08±50.50mg/kg in summer and 164.01±151.40mg/kg during winter (Fig. 3b). The relatively high values may be attributed to precipitated metal content at higher pH values 7.98, 7.41 to be enriched with zinc and a high content of organic matter 3.62%, where various metals are mainly bound to humic substances in water and sediments. According to El-Gohary *et al.* [8] Abu- Qir Bay is subjected to severe pollutants of domestic sewage, agricultural and industrial pollutions. Positive correlation coefficient (r= 0.673, 0.480, 0.811 and 0.797) are deduced between zinc with Cr, Cd, TOM and TP respectively. These relations explain strong association of Zn on the complexion of Cr, Cd, TP and TOM, Table (6).

The sediments ability to accumulate heavy metals under oxygenated and anoxic conditions is evaluated using the distribution coefficient, $K_d$ of metal that defined as the ratio of metal concentration in sediment (mg/kg) to the dissolved metal concentration (µg/l).

Table 5: concentrations of Pb, Zn, Cr, Cu and Cd in marine sediment samples of Abu-Qir Bay during summer 2009 and winter 2010 (mg/Kg; dry wt.)

| Seasons | Stations | Pb | Zn | Cr | Cu | Cd |
|---|---|---|---|---|---|---|
| Summer 2009 | 1 | 159.64 | 35.12 | NM | 9.60 | ND |
| | 2 | 117.08 | 29.43 | NM | ND | 0.24 |
| | 3 | 53.20 | 77.84 | NM | ND | ND |
| | 4 | 56.76 | 113.56 | NM | ND | 3.48 |
| | 5 | 70.96 | 164.44 | NM | 117.32 | 4.68 |
| | Min. | 53.20 | 29.43 | ----- | =9.60 | =0.24 |
| | Max. | 159.64 | 164.44 | ----- | 117.32 | 4.68 |
| | Mean | 91.53 | 84.08 | ----- | 63.46 | 2.80 |
| | ±SD | 40.97 | 50.50 | ----- | 53.65 | 1.88 |
| Winter 2010 | 1 | 121.24 | 461.88 | 66.6 | 48.24 | 3.0 |
| | 2 | 107.76 | 108.24 | 44.68 | 20.12 | ND |
| | 3 | 115.84 | 125.60 | 274.2 | 166.32 | ND |
| | 4 | 86.20 | 45.56 | 95.40 | 18.40 | 2.04 |
| | 5 | 83.52 | 78.76 | 271.60 | 22.56 | ND |
| | Min. | 83.52 | 45.56 | 44.68 | 18.40 | =2.04 |
| | Max. | 121.24 | 461.88 | 274.2 | 166.32 | 3.0 |
| | Mean | 102.91 | 164.01 | 150.5 | 55.13 | 2.52 |
| | ± SD | 15.37 | 151.40 | 101.23 | 56.65 | 0.48 |
| | ERL | 46.7 | 150 | 81 | 34 | 1.2 |
| | ERM | 218 | 410 | 370 | 270 | 9.6 |
| | TLV | 100 | 200 | -- | 75 | 1 |

ERL: Effects Range Low, ERM: Effects Range Median, T LV: Threshold limit value (Long *et al*., 1995),
ND: not detected, NM: not measured.

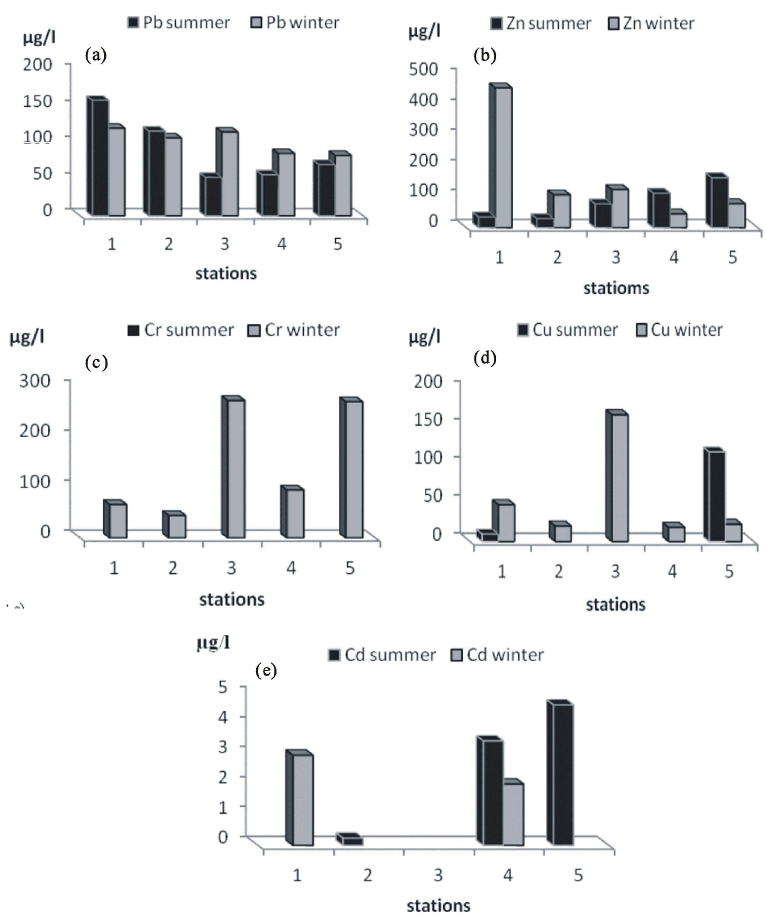


Fig. 3: Concentrations of heavy metals in sediments of Abu-Qir Bay

Table 6: Correlation matrix of various parameters of Abu-Qir Bay sediments (2009/2010), Level of significance (r = 0.707) at p = 0.05

| parameters | Pb | Zn | Cr | Cu | Cd | $CaCO_3$% | TOM% | Total P% |
|---|---|---|---|---|---|---|---|---|
| Pb | 1 | | | | | | | |
| Zn | 0.091063 | 1 | | | | | | |
| Cr | -0.6623 | 0.673967 | 1 | | | | | |
| Cu | 0.087173 | 0.274401 | 0.57415 | 1 | | | | |
| Cd | -0.38961 | 0.480891 | 0.34574 | 0.207265 | 1 | | | |
| CaCO3% | 0.490422 | -0.32301 | 0.185328 | 0.279283 | -0.44013 | 1 | | |
| TOM% | -0.27599 | 0.8117 | 0.605292 | 0.994645 | 0.766101 | 0.228363 | 1 | |
| Total P% | -0.25087 | 0.79709 | 0.596185 | 0.99682 | 0.753323 | 0.248872 | 0.99963 | 1 |

Table 7: Log values of the distribution coefficients $K_d$ of heavy metals in Abu-Qir Bay, Egypt. (Log $K_d$ L/kg), during summer 2009 / winter 2010

| seasons | stations | Pb | Zn | Cd | Cr | Cu |
|---|---|---|---|---|---|---|
| Summer 2009 | 1 | 4.0 | 4.08 | ------ | ------ | ---- |
| | 2 | 3.80 | 3.40 | 2.28 | ------- | ---- |
| | 3 | 3.55 | 4.80 | ------ | ------- | ---- |
| | 4 | 3.33 | 4.59 | 3.47 | ------- | ---- |
| | 5 | 3.40 | ----- | 3.54 | ------- | ---- |
| | Mean | 3.61 | 4.26 | 3.35 | ------- | ---- |
| Winter 2010 | 1 | 3.97 | 4.60 | 3.69 | 4.72 | 4.03 |
| | 2 | 3.73 | 3.73 | ----- | 3.10 | 3.52 |
| | 3 | 3.92 | 3.84 | ---- | 3.83 | 4.74 |
| | 4 | 3.75 | 2.69 | 3.69 | 4.10 | 3.55 |
| | 5 | 3.68 | 3.73 | ---- | 5.36 | 3.67 |
| | Mean | 3.81 | 3.72 | 3.65 | 3.94 | 4.07 |

$$K_d = \frac{\text{[Metal] sediment}}{\text{[Metal] water}}$$

$K_d$ depends on the nature of sediments, geochemical parameters of sediments and water, pH, salinity and specific characteristics of each element, Nguyen *et al.* [45]. The logarithmic values of $K_d$ are shown in Table (7). The minimum and maximum $K_d$ values of Zinc are $0.49x10^3$ and $63.8x10^3$ at stations 4, 3, during winter and summer respectively, Table (8). Generally, the higher $K_d$, the stronger the sorption of metal to the sediments. The logarithmic mean values of $K_d$ of zinc ranged from 3.72 to 4.26 L/kg, indicated that Zn exhibited higher values.

**Copper:** Copper is present in two forms; lithogenic and /or biogenic. The lithogenic copper is found incorporated in clay minerals, after decomposition of organic matter the free copper may adsorbed on the surface of clay minerals. Copper concentration values are ranged from a minimum of = 9.6mg/kg at station 1 to a maximum of 166.32mg/kg at station 3 during summer and winter, respectively. The seasonal average values of copper ranged between 55.13±56.65mg/kg in winter and 63.46± 53.65mg/kg in summer, Table (5) and Figure (3d). The distribution coefficient $K_d$ of Copper showed a minimum of $3.31x10^3$ at station 2 and a maximum of $54.71x10^3$ at station 3 during winter, Table (8) with log $K_d$ values ranged from 3.52 to 4.74 L/kg, Table (7). The higher $K_d$ values indicate stronger sorption of copper to the sediment where copper is strongly adsorbed to the surface of manganese oxide [19]. Positive correlations (r= 0.99 and 0.99) were observed between Cu, TOM and TP indicated that Cu is strongly associated with TOM and TP, Table (6).

**Lead:** Lead occurring in sediments persists in two mineral associations, one with clay minerals and the other with authigenic minerals and/or biogenous debris. Pb was mainly associated with Fe-Mn oxide fraction and had retention in sediments [46]. The Lead concentration values in sediments of Abu-Qir Bay are fluctuated between 53.20 and 159.64 mg/kg at stations 3 and 1 during summer. The seasonal average values are 91.53±40.97, 102.91±15.37 mg/kg in summer and winter respectively (Fig. 3a). High concentrations are recorded at stations 1, 2 during both seasons may be affected by the disposal and wastes of the ships beside the effect of El-Tabia Pumping station. Log $K_d$ values of lead ranged from 3.33 to 4.0 L/kg in summer and 3.38 to3.97 L/kg in winter.

Table 8: Distribution coefficient of some heavy metals in Abu-Qir Bay

| Season | station | Pb x10[3] | Zn x10[3] | Cd x10[3] | Crx10[3] | Cux10[3] |
|---|---|---|---|---|---|---|
| | 1 | 10.03 | 11.99 | ----- | ---- | --- |
| Sumer2009 | 2 | 6.267 | 2.53 | 0.19 | ----- | --- |
| | 3 | 2.22 | 63.80 | ----- | ---- | --- |
| | 4 | 2.16 | 39.02 | 2.95 | ---- | --- |
| | 5 | 2.50 | ----- | 3.44 | ---- | --- |
| | Mean | 4.04 | 18.00 | 2.20 | ---- | ---- |
| | 1 | 9.23 | 39.65 | 51.63 | 10.67 | 4.92 |
| Winter2010 | 2 | 5.33 | 5.33 | 1.26 | 3.31 | --- |
| | 3 | 8.39 | 6.87 | 6.76 | 54.71 | --- |
| | 4 | 5.69 | 0.49 | 12.69 | 3.56 | 4.86 |
| | 5 | 4.77 | 5.34 | 230.17 | 4.72 | ----- |
| | Mean | 6.51 | 5.21 | 8.76 | 11.70 | 4.42 |

Lead showed positive correlation with carbonate (r = 0.490) and negative correlations with each of Cr (r= -0.662), Cd (r= -0.389), TOM (r= -0.275) and TP (r= -0.250), Table (6).

**Cadmium:** The major specific sources of Cadmium are atmospheric deposition, smelting and refining of non ferrous metals, manufacturing processes related to chemicals and metals and domestic wastes water [47]. Cadmium concentrations in Abu-Qir Bay are ranged from a minimum value of =0.24mg/kg at station 2 to a maximum of 4.68mg/kg at station 5 during summer (Fig. 3e). The seasonal average variation of Cadmium in the Bay is fluctuated between 2.52±0.48 mg/kg and 2.80±1.88 mg/kg for winter and summer, respectively. Highly positive correlations are found between Cadmium and both of TOM (r=0.766) and TP (r=0.753) Table (6). The higher $K_d$ mean values for Cadmium were (2.20, 4.42) x$10^3$, with Log $K_d$ mean values of 3.35 and 3.65 L/kg, indicate strong sorption of Cadmium to the sediment, Tables (7, 8).

**Chromium:** The major sources of Chromium are domestic wastewater and manufacturing processes, atmospheric fallout from anthropogenic sources and wind borne soil particles. The concentrations of Chromium in Abu-Qir Bay sediments fluctuated between a minimum of 44.68mg/kg at station 2 and a maximum of 274.2mg/kg at station 3 during winter. The seasonal variation of chromium is 150.5±101.23mg/kg (Fig. 3c). The distribution coefficient $K_d$ of Chromium is found to be a minimum of 1.26x$10^3$ at station 2 and a maximum of 230.17x$10^3$ at station 5 with an average of 8.76x$10^3$. The logarithmic mean value of Cr was 3.94 L/kg, Tables (7, 8). Positive correlations are observed between Cr with Cu, TP and TOM (r=0.574, 0.596 and 0.605). The positive loadings on Cr indicate that; as concentrations of TP and TOM increase, Cr level increases.

Salomons and Forstener [48] showed that the distribution of heavy metals in marine deposits was influenced by sediment texture, clay content, organic carbon, iron hydrous oxides and carbonates. The concentration averages of the studied metals in sediments reveal decreasing in order: Zn>Cr> Pb> Cu> Cd. The present study showed that the most selected metals had concentration values during winter higher than those of summer. El Bouraie *et al.* [35] observed that the highest concentration values of most elements were during winter closure period of River Nile (low flow conditions). This phenomenon may be attributed to the increase in organic matter concentrations which facilitate settling of metals to the sediments during hot seasons [49]. Pb was mainly associated with Fe-Mn oxide fraction and had retention in sediments [46]. Domestic and industrial effluents are the major sources of the observed high levels of Zn, Cu, Pb and Cr. They are mainly precipitated as soluble oxide [50]. The positive correlations between Zn and each of Cu, TOM and TP and Zn with Cr, Cd, TOM and TP refer to heavy metals in Abu-Qir Bay originate from similar sources and have similar reactivates towards biological and non biological particles and /or forming complexes closely related to each other.

A Comparison between averages of metal concentrations in sediment and water lead to: the mean concentration values of sediments were higher than water samples. However, Pb and Cd were found at 4-7 fold and Zn, Cr and Cu at 5 -12 fold higher concentrations in sediments. This indicates metal mobilization from sediments to overlying water due to low pH and microbial activity [51]. The concentration values of metals were compared with other background concentrations of elements as shown in Table (9). Pb, Cr and Cu concentrations values were higher in most scales, while Zn and Cd were lower than other regions in the literature.

Table 9: Concentrations of some heavy metals (mg/kg dry weight) in Abu-Qir Bay sediments compared to other regions

| Location | Pb | Zn | Cr | Cu | Cd | Reference |
|---|---|---|---|---|---|---|
| Abu-Qir Bay | 91-103 | 84.1-164.0 | 150.5 | 55.1-63.5 | 2.5-2.80 | Present study |
| El Max fish farm | 27-46.5 | 86.6-331.0 | ----- | 38.5-48.8 | 1.3-3.33 | [32] |
| East Rosetta | 0.06-0.16 | 0.32-0.62 | 0.90-1.73 | ---- | ----- | [8] |
| Lake Edku | 1.58-1.98 | 59.3-63.9 | 45.4-66.5 | 2.10-2.18 | 0.89-1.26 | [19] |
| El- Max Bay | 8.8-88.6 | 51.4-448.0 | 12.2-103 | 3.3-47.4 | 2.54-7.54 | [31] |
| Nile Delta Egypt | 4.64-93 | 147-522.0 | 14.7-40.4 | 11.8-60.2 | 1.04 | [35] |
| Abu-Qir Bay | 50.11 | 100.02 | ----- | 57.73 | ---- | [10] |
| Eastern Harbor | 50.69 | 102.74 | ---- | 40.05 | ---- | [10] |

To evaluate the metal concentrations of present study comparing the metal concentrations by data-base of Toxicity guideline according to Long and Morgan [52] and Long *et al.* [53], Table 4. Most ranges of heavy metals in the investigated area are not exceeded the effect range low (ERL) and the effect range median (ERM), Table 5. This indicates that there is very small adverse effect on the benthic marine community and on the biota throughout the whole studied area, because ERLs were intended to represent concentrations below which effect was rarely observed. For all trace metals, the adverse effects were less than 10% when concentrations were below the ERLs (rarely), occasionally (between ERLs-ERMs,10% -15% occurrence) and frequently (> ERMs > 50% occurrence), Long and Morgan and Long *et al.* [52, 53].

## CONCLUSION

- Abu-Qir Bay is one of the most polluted areas due to the adverse effect of effluents from land-based sources. Domestic and industrial effluents are the major sources of the observed higher levels of Zn, Cu, Pb, Cr and Cd. Most of the higher values are recorded at the stations which receive drainage waters.
- The grain size data revealed that the sediments in Abu-Qir Bay are composed of different types of sand-sized sediments. The low percentages of TOM are due to the structure of sediments in the investigated area was mainly sand i.e. has low affinity to absorb contaminates.
- The mean concentration values of metals in marine sediments were higher than those in water samples due to their metal mobilization from sediments to overlying water by the action of pH and microbial activity.
- The concentration averages of the studied metals in marine sediments were ranged in the order: Zn>Cr>Pb>Cu>Cd, while in water was Pb>Zn>Cr>Cu>Cd.
- Heavy metals concentrations are not exceeded the effect range low (ERL) and the effect range median (ERM) except Zn and Pb in some stations. This indicates that there is very small adverse effect on the benthic marine community and on the biota throughout the whole studied area.
- The present study recommends a long-term follow-up for the physicochemical, geochemical and biological evolutions at monthly, seasonally and annual levels to identify changes occurring in a particular coastal area.

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