Evaluation of Heavy Metals Pollution in Seawater, Suspended Particulate Matter and Sediment from Abu-Qir Bay, Alexandria, Egypt

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INTRODUCTION

The contamination of coastal and marine environments by heavy metals is a worldwide problem not only in the developing countries, but also in the developed ones as well (Boran et al., 2010). Industrial and agricultural activities, vehicle emissions, domestic waste, and shipping traffic, especially in and close to harbors, are causes of heavy metal pollution (Masindi & Muedi, 2018). Heavy metals are toxic, long

ARTICLE INFO

Article History:
Received: April 16, 2021
Accepted: April 27, 2021
Online: April 30, 2021

Keywords:
Abu-Qir Bay;
Heavy metals;
Distribution coefficient;
Water Quality Index

ABSTRACT

The level of heavy metals (Mn, Fe, Co, Ni, Cu, Zn, Pb, and Cd) in seawater, suspended particulate matter (SPM) and sediment along Abu-Qir Bay coast, Alexandria, Egypt, were evaluated by selecting nine stations as hot spots during winter 2020. Results showed that, the average concentrations of the investigated heavy metals followed the following order: Fe > Zn > Mn > Ni > Pb > Co > Cu > Cd in seawater, Fe > Zn > Mn > Pb > Cu > Ni > Co > Cd in SPM, and Fe > Mn > Zn > Ni > Co > Cu > Pb > Cd in sediment. Moreover, the distribution coefficient (Kd) revealed that, Fe was highly stable in sediments, and the log (Kd) value was 6.521 in all water bodies. In addition, geo-accumulation index (Igeo), pollution load index (PLI), modified degree of contamination (mCd), potential ecological risk index (RI), as well as the mean effect range median quotient (MERM – Q) were calculated. Calculations recorded that, the values of Igeo for Cd in surface sediments ranged between 1 and 3 indicating that, the study sites were moderate to strongly contaminated with Cd. The mCd values of Ni, Cu, Zn, Pb, and Cd ranged between 1.32 and 4.24, reflecting a low to moderate degree of contamination. The studied metals presented a moderately toxic ecological risk (150 ≤ RI < 300) except for St 5 & St 8, that showed a considerable toxic ecological risk (RI > 300). Based on MERM – Q classification, all samples had medium-low toxicity; Ni, Cu, Zn, and Pb may be originated from anthropogenic sources, whereas Cd emerged from natural sources with some contribution of anthropogenic source. Redundancy analysis (RDA) revealed that the TOC % and fine sand % of the sediment had a certain influence on the Fe enrichment. The data of the water quality index (WQI) revealed that St 2, St 3, St 4, St 5 & St 6 were slightly polluted, and could be considered hot spots.

INDEXED IN

Scopus, Elsevier, DOAJ, IUCAT
persistent, not easily oxidized, degraded, taken away, or converted to less harmful components through biological or chemical processes, which severely damage marine environments (Sun et al., 2020).

Coastal systems like bays receive considerable quantities of heavy metals (Cao et al., 2018), among which is Abu-Qir Bay, a shallow semi-circular basin situated 35 km east of Alexandria city. It extends for about 50 km from Abu-Qir Head-Montazah in the west to Rosetta mouth of the Nile River in the east, and northwards to about 40 km in the Mediterranean Sea (Fig 1). The surface area of the Bay is about 360 km$^2$ and its water volume is 4.3 km$^3$, while the maximum depth reaches 22 m (Abdel Ghani et al., 2013). It is noteworthy that the Bay receives several discharges as; freshwater from Rosetta mouth of the Nile River loaded by nutrients, industrial and domestic wastes from El-Tabia pumping station (TPS), and the outlet of Lake Edku (Boughaz El-Maddya) carrying trace metals, pesticides, humic acids, and nutrients. In addition, it receives industrial wastewaters from 22 different factories of paper, fertilizer, food processing and canning, and textile manufacturing industries. The Bay is also exposed to pollution from the activities of gas production and Abu-Qir Electrical Power Station (EPS) as well as fishing boats.

Hence, sediment should be analyzed to assess levels of contamination by heavy metals in the aquatic environment because heavy metal concentrations in water are sometimes lower than the detection limits (Salati and Moore, 2010). Therefore, sediments are considered as sensitive indicators to monitor contaminants in the aquatic systems (Pekey et al., 2004). Furthermore, high concentrations of heavy metals in sediment can indicate anthropogenic sources (Tylmann, 2011).

The main objective of the current study was to assess the heavy metals contamination in Abu-Qir Bay sediment. That target was achieved by identifying the sources of pollution, evaluating the environmental impact of contaminated sediments, and setting an application of principal component analysis and RDA to investigate the distribution and source relationship of the heavy metals in seawater, particulate matter, and sediments. Moreover, the current study was conducted to evaluate the water quality index (WQI) of Abu-Qir Bay through measuring some physical and chemical parameters; the temperature of water, salinity, pH, dissolved oxygen (DO), oxidizable organic matter (OOM), and total alkalinity (T. Alk.) in the surface water as well as heavy metals, (Mn, Fe, Co, Ni, Cu, Zn, Pb, and Cd) in water and suspended particulate matter (SPM). This task was managed by studying nine stations (St 2 to St 10) in front of Abu-Qir city, Abu-Qir EPS, Boughaz El-Maddya, TPS, and the paper and fertilizer factories in Abu-Qir area.
MATERIALS AND METHODS

1. Sampling

Triplicate surface sediment (7 samples), and seawater (9 samples) were collected from nine stations during winter 2020, representing the hot spots influenced by human activities; industrial and agriculture discharge along Abu-Qir Bay, Alexandria (Figure 1). The Sediment samples were collected using Van-Veen grab sampler, packed in clean polyethylene bags, and preserved at 4°C in an ice box. Before analysis, the samples were dried at room temperature and grinded using an agate mortar. Seawater samples were collected using PVC Niskin’s bottle, packed in pre-washed plastic bottles, and stored at 4°C for preservation and laboratory analysis to evaluate physicochemical parameters and heavy metals.

2. Analytical methods

2.1. Physicochemical parameters of seawater

The water sample was sub-sampled and immediately the following parameters were measured in-situ i) water temperature, pH and salinity using calibrated CTD device, model, (YSI 6000). ii) Fixing of dissolved oxygen (DO). Then, at laboratory DO was determined by using Winkler’s method (Grasshoff et al., 1999), Oxidizable organic matter (OOM) was determined using the method depicted by FAO (1976), and total alkalinity (T. Alk.) was determined according to APHA (1995).
2.2. Dissolved and particulate heavy metals in seawater

The volume of water samples (3-4 L) was filtered using 0.45 µm membrane filter paper. The dissolved metal ions were determined after preconcentration using the cation exchange resin (chelex-100 in ammonia form) following the description of Gao et al. (2002). The membrane filters with their content of suspended particulate matter (SPM) were washed several times, and then dried at 65 °C for 48 hrs to a constant weight. Each dried membrane filter was placed in a Teflon cup, a mixture of HNO_3-HClO_4-HF (3:2:1) (6 ml) was added, and the Teflon cup was then heated. After complete digestion, the sample was evaporated until dryness, then 6N HNO_3 (1 ml) was added and the volume was completed with 0.1N HCl to the final volume of 25 ml (Abdullah & Royle, 1974). The concentrations of Mn, Fe, Co, Ni, Cu, Zn, Pb, and Cd were determined by ICP-OES (Agilent). The results were expressed in µg/L for both seawater and SPM.

2.3. Heavy metals in Sediments

The heavy metals in surface sediments were digested according to the method described by Oregioni and Astone (1984). Exact weight of each dried sediment sample (about 0.25-0.3 g) was placed in a Teflon beaker. Concentrated HNO_3 (3 ml) was added dropwise to the sample. The outcome was then heated at 80 °C until dryness, then a mixture of HNO_3/HClO_4/HF (3:2:1) (5 ml) was added to the sample. After complete digestion, temperature was increased gradually to 120 °C to evaporate the HClO_4 residue. Afterwards the sample was cooled at room temperature, and the residue was rinsed with 0.1N HCl (5 ml). The sample was filtered and washed several times with deionized water, and the final volume was adjusted to 25 ml. The concentrations of Mn, Fe, Co, Ni, Cu, Zn, Pb, and Cd were measured by ICP-OES (Agilent). The results were expressed in mg/kg dry weight.

2.4. Geochemical parameters of sediments

The grain size analysis was determined by the dry sieving method of Folk (1974), and the sediment texture was classified according to Folk (1980). The total organic carbon (TOC) was determined according to the method reported by Gaudette and Flight (1974). According to that method, the sediment sample was oxidized by K_2Cr_2O_7 and concentrated H_2SO_4, then the excess dichromate was titrated against (NH_4)_2Fe(SO_4)_2·6H_2O solution and diphenylamine was used as an indicator.

2.5. Quality control and quality assurance

The reagents used during the present study were of analytical grade (Merck), triplicate analysis for samples showed good accuracy. All glassware and plastic vessels were washed with solution of diluted HNO_3 and deionized water, then they were dried. To test the precision, blanks were treated using the same reagents as samples. IAEA certified reference material, for marine sediment (SD-M-2/TM), was employed for quality control. In this study the precision of measurements for all metals was within 10 % RSD. In terms of preparing the solution, seawater certified reference materials CASS-4
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from National Research Council (NRC) in Canada, were treated in a way similar to that used for the other samples. The recovery of the selected metals ranged from 92 to 110 % and the precision was within 10 % RSD.

2.6. Statistical analysis
Principal component analysis (PCA), as a varimax rotated was conducted with IBM-SPSS program (version 22) applying Kaiser normalization.

RESULTS AND DISCUSSION

1. Seawater physicochemical parameters
The horizontal distributions of physicochemical parameters of Abu-Qir Bay seawater are presented in Figure (2). Abu-Qir seawater temperature ranged from 16.10 to 17.16 °C, and the max value was found near Abu-Qir EPS (St 5). The recorded temperature values flowed the behavior of winter season (Radwan, 1996; Zakaria et al., 2019). The salinity ranged from 37.24 to 38.21, and the max value was observed at St 5. Changes in salinity may be attributed to fresh-marine water mixing. The salinity of Abu-Qir Bay coastal water was influenced by the discharge of wastewater from the surrounding urbanized area (Zakaria et al., 2019). The pH values of seawater ranged between 7.13 and 8.61, indicating that it was in the slightly alkaline side. This may be because of increasing phytoplankton and the photosynthesis processes that resulted in higher pH values as well as an increase in the dissolved oxygen concentrations (Das et al., 1997). Moreover, the values of DO ranged between 8.64 mg/L at Sts 2, 3, 4 & 5 and 10.24 mg/L at Sts 9 & 10. Based on temporal variations, the DO in surface water recorded the highest values that could be related to the entry of oxygen from the atmosphere into the surface water and then to the algal photosynthesis (Das et al., 1997). Whereas the low values of DO may be due to the decomposition of organic matter and respiration of marine organisms as well as the biochemical reactions (Das et al., 1997). It was noticed that, the average value of OOM was 2.92, with a maximum value of 10.24 mgO$_2$/L at St 2 and a minimum of 0.32 mgO$_2$/L at Sts 5, 7 & 8. The high value of OOM at St 2 could be attributed to the impact of huge organic pollutants flow from TPS and Rosetta mouth (Alam El-Din & Al-Hogaraty, 2001). The values of T. Alk. ranged between 3.00 mmol/L at St 8 and 4.80 mmol/L at St 6, with an average value of 3.29 mmol/L. The change in pH, salinity, DO, and alkalinity may be due to the water flow of TPS (Figure 2).

2. Heavy metals distribution in seawater
The fluctuations of heavy metals concentration in seawater of Abu-Qir Bay are presented in Table (1). The range and average concentrations (µg/L) were 1.467-12.738 (5.716) for Mn, 7.242-22.594 (14.502) for Fe, 0.508-3.119 (1.632) for Co, 1.808-9.398
(5.103) for Ni, 0.458-3.738 (1.432) for Cu, 4.600-18.333 (12.014) for Zn, 1.625-9.325 (4.733) for Pb, and 0.333-2.090 (0.874) for Cd. Though the highest concentrations of Mn, Co, Cu and Pb were detected at St 3, yet the highest levels of Zn and Cd were detected at St 10 & St 2, respectively. Remarkably, St 5 showed the highest concentrations of Fe and Ni. On the other side, St 8 presented the lowest levels of Mn, Co, Ni, Cu, Zn, Pb and Cd, whilst the lowest concentration of Fe was recorded at St 4.

![Figure 2. Horizontal distribution of some physicochemical parameters of Abu-Qir Bay seawater.](image)

High values of Ni (8.783 µg/L), Pb (7.079 µg/L) and Cd (1.421 µg/L) were detected at St 7, St 10 & St 3, respectively. Besides, high concentrations of Zn (18.111 & 16.159 µg/L) were measured at St 3 & 6, respectively. Low values of Mn (1.483 µg/L), Cu (0.542 µg/L) and Zn (4.658 µg/L) were recorded at St 4. Moreover, low concentrations of Cd (0.458 & 0.471 µg/L) were measured at St 4 & St 6, respectively. In Abu-Qir Bay seawater, Fe and Zn were the prevailing metals, whilst Cd was the least abundant (Table
1). The average concentrations of the studied heavy metals followed the successive sequence of Fe > Zn > Mn > Ni > Pb > Co > Cu > Cd.

3. Heavy metals distribution in SPM

The fluctuations of heavy metal concentrations in SPM of Abu-Qir Bay seawater were presented in Table 1. The range and average concentrations (µg/L) were 1.811-12.645 (5.502) for Mn, 118.243-414.754 (277.282) for Fe, 0.092-0.858 (0.440) for Co, 1.115-3.575 (1.733) for Ni, 0.542-4.833 (1.886) for Cu, 3.325-26.652 (10.377) for Zn, 0.542-4.659 (2.182) for Pb, and 0.008-0.292 (0.110) for Cd. The highest concentrations of Mn, Cu, Zn and Pb were detected at St 6, whereas the highest levels of Co and Ni were observed at St 4. Meanwhile, St 2 & St 7 showed the highest values of Fe and Cd, respectively. On the other side, St 7 presented the lowest concentrations of Co, Cu, Zn and Pb, while the lowest values of Mn and Fe were recorded at St 9. In addition, St 2 & St 5 presented the lowest values of Ni and Cd, respectively. Markedly, high values of Zn (19.000 µg/L) and Pb (4.413 µg/L) were detected at St 10. Besides, high concentrations of Fe (345.635, 394.167 & 338.281 µg/L) were recorded at St 3, St 4 & St 5, respectively. The average concentrations of the studied heavy metals in SPM followed the sequence of: Fe > Zn > Mn > Pb > Cu > Ni > Co > Cd.

Table 1. Heavy metals concentrations in seawater and SPM of Abu-Qir Bay.

<table>
<thead>
<tr>
<th>St No</th>
<th>Mn (µg/L)</th>
<th>P</th>
<th>D</th>
<th>Fe (µg/L)</th>
<th>P</th>
<th>D</th>
<th>Co (µg/L)</th>
<th>P</th>
<th>D</th>
<th>Ni (µg/L)</th>
<th>P</th>
<th>D</th>
<th>Cu (µg/L)</th>
<th>P</th>
<th>D</th>
<th>Zn (µg/L)</th>
<th>P</th>
<th>D</th>
<th>Pb (µg/L)</th>
<th>P</th>
<th>D</th>
<th>Cd (µg/L)</th>
<th>P</th>
<th>D</th>
</tr>
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<td>2</td>
<td>3.434</td>
<td>6.639</td>
<td>16.311</td>
<td>414.754</td>
<td>2.139</td>
<td>0.418</td>
<td>4.631</td>
<td>1.115</td>
<td>1.303</td>
<td>2.279</td>
<td>8.730</td>
<td>7.148</td>
<td>5.541</td>
<td>1.418</td>
<td>2.090</td>
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<td>3</td>
<td>12.738</td>
<td>4.413</td>
<td>16.960</td>
<td>345.635</td>
<td>3.119</td>
<td>0.262</td>
<td>5.802</td>
<td>1.349</td>
<td>3.738</td>
<td>2.611</td>
<td>18.111</td>
<td>12.937</td>
<td>9.325</td>
<td>3.135</td>
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<td>4</td>
<td>1.483</td>
<td>6.050</td>
<td>7.242</td>
<td>394.167</td>
<td>1.025</td>
<td>0.858</td>
<td>4.125</td>
<td>3.575</td>
<td>0.542</td>
<td>1.183</td>
<td>4.658</td>
<td>5.067</td>
<td>2.708</td>
<td>0.900</td>
<td>0.458</td>
<td>0.183</td>
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<tr>
<td>5</td>
<td>5.328</td>
<td>6.359</td>
<td>22.594</td>
<td>338.281</td>
<td>2.078</td>
<td>0.227</td>
<td>9.398</td>
<td>1.773</td>
<td>1.375</td>
<td>0.703</td>
<td>13.367</td>
<td>3.773</td>
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<td>299.638</td>
<td>0.993</td>
<td>0.659</td>
<td>4.536</td>
<td>2.181</td>
<td>1.261</td>
<td>4.833</td>
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<td>2.652</td>
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<td>3.792</td>
<td>2.658</td>
<td>16.925</td>
<td>220.417</td>
<td>1.533</td>
<td>0.092</td>
<td>8.783</td>
<td>1.317</td>
<td>1.083</td>
<td>0.542</td>
<td>11.558</td>
<td>3.325</td>
<td>3.975</td>
<td>0.542</td>
<td>0.667</td>
<td>0.292</td>
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<tr>
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<td>1.467</td>
<td>3.283</td>
<td>13.125</td>
<td>160.833</td>
<td>0.508</td>
<td>0.417</td>
<td>1.808</td>
<td>1.442</td>
<td>0.458</td>
<td>1.867</td>
<td>4.600</td>
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<td>2.508</td>
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<td>9.074</td>
<td>1.811</td>
<td>10.709</td>
<td>118.243</td>
<td>1.709</td>
<td>0.554</td>
<td>3.439</td>
<td>1.162</td>
<td>1.466</td>
<td>1.230</td>
<td>12.608</td>
<td>5.446</td>
<td>4.473</td>
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<td>6.548</td>
<td>5.659</td>
<td>14.135</td>
<td>203.571</td>
<td>1.579</td>
<td>0.476</td>
<td>3.405</td>
<td>1.683</td>
<td>1.659</td>
<td>1.722</td>
<td>18.333</td>
<td>19.000</td>
<td>7.079</td>
<td>4.413</td>
<td>0.968</td>
<td>0.103</td>
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</table>

The Criterion Continuous Concentration (***CCC)

| Marine Guideline | 1.0 | 70.0 | 1.3 | 15.0 | 4.4 | 5.5 |

**Minimal Risk Conc.**

| 20.0 | 50.0 | 2.0 | 10.0 | 20.0 | 10.0 |

D: Dissolved heavy metals, P: Heavy metals in SPM. * Australian water quality guideline values suitable for the protection of 95% of all species (ANZEC/ARMCANZ, 2000), ** National Recommended Water Quality Criteria (US EPA, 2006), *** World quality criteria (WQC, 1972).
4. Sediment characterization

The results of sediment grain size and total organic carbon (TOC %) of surface sediment of Abu-Qir Bay are listed in Table (2). The results of grain size showed a little variation and a uniform distribution from fine sand to silt sand. Finding the fine sediment can be due to human and terrestrial activities (El Nemr & El-Said, 2017). As shown in Table (2), sand content varied from 99.89 % at St 8 & St 9 to 23.74 % at St 2. Whereas silt content varied from 68.35 % at St 5 to 0.10 % at St 9. TOC % in Abu-Qir Bay sediment, recording range from 0.59 % at St 9 to 1.95 % at St 7, with an average value of 1.26 %. Except for St 5 & St 9, the TOC % recorded for all sediment samples was > 1, which is slightly higher than LEL and SEL (Persaud et al., 1992).

5. Heavy metals in sediments

The variations of heavy metal concentrations in the surface sediment of Abu-Qir Bay are given in Table (2). The range and average concentrations (mg/kg) were 416.477-1803.088 (862.857) for Mn, 29318.380-81203.242 (52549.293) for Fe, 29.642-68.579 (40.733) for Co, 47.341-112.765 (71.957) for Ni, 14.288-49.594 (30.021) for Cu, 63.975-204.539 (115.805) for Zn, 17.384-46.065 (28.186) for Pb, and 1.208-4.599 (2.570) for Cd. The highest concentrations of Zn, Pb, and Cd were detected at St 5, while St 8 revealed the highest contents of Fe, Co, and Ni. The highest levels of Mn and Cu were recorded at St 6 & St 10, respectively. On the other side, St 7 showed the lowest values of Mn, Co, Ni, Cu, Zn and Cd. The lowest concentrations of Fe and Pb were recorded at St 6 & St 10, respectively.

<table>
<thead>
<tr>
<th>Station number</th>
<th>Log Kd</th>
<th>ERL</th>
<th>ERM</th>
<th>TEL</th>
<th>PEL</th>
<th>SEL</th>
<th>Continental Crust Average</th>
<th>Shale Average</th>
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<tr>
<td>Min</td>
<td>416.477</td>
<td>29318.380</td>
<td>29.642</td>
<td>47.341</td>
<td>14.288</td>
<td>49.594</td>
<td>101.972</td>
<td>204.539</td>
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<tr>
<td>Max</td>
<td>1803.088</td>
<td>81203.242</td>
<td>17.384</td>
<td>46.065</td>
<td>17.913</td>
<td>46.975</td>
<td>17.384</td>
<td>1.268</td>
</tr>
<tr>
<td>Average</td>
<td>862.857</td>
<td>52549.293</td>
<td>35000.000</td>
<td>94.39</td>
<td>73.455</td>
<td>77.42</td>
<td>66.78</td>
<td>9.48</td>
</tr>
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</table>

Note: *LEL and **SEL refer to the lowest, and severe effect levels, respectively (Persaud et al., 1992).

Table 2. Heavy metal concentrations, textural parameters, and TOC in sediment of Abu-Qir Bay.
In addition to the highest levels of Fe, Co, and Ni, St 8 revealed high values of both Pb (38.809 mg/kg) and Cd (3.351 mg/kg) as well. Whereas low values of Zn (73.455 mg/kg) and Cd (1.268 mg/kg) were recorded at St 9. Moreover, low concentrations of Pb (17.512 & 17.913 mg/kg) were measured at St 9 & St 7, respectively. It was noticed that Mn and Fe were the most abundant heavy metals, while Cd was the least one (Table 2). The average concentrations of the investigated metals in sediments of Abu-Qir Bay followed the sequence presented as: Fe > Mn > Zn > Ni > Co > Cu > Pb > Cd.

Comparing heavy metal levels in sediments of Abu-Qir Bay with those of other studies is presented in Table 3. Results showed that, Mn and Fe metals recorded the highest levels in the present study compared to the mentioned values in Table 3. The exception was only for Mn values reported in Abu-Qir Bay (Faragallah et al., 2004) which were higher than those found in the current study. The observed concentrations of Cu were lower than those recorded in Abu Qir-Bay (Faragallah et al., 2004), the Egyptian coast along the Mediterranean Sea, the Eastern Harbour and the Western Harbour. On the other hand, they were higher than those recorded in Abu-Qir Bay (Abdel Ghani et al., 2013), eastern coast of Alexandria, eastern Mediterranean coast of Egypt, western part of the Egyptian Mediterranean Sea and El-Max Bay. The recorded concentrations of Zn were lower than those observed in Abu-Qir Bay (Faragallah et al., 2004), the Eastern Harbour, the Western Harbour and El-Max Bay, while they were higher than those observed in Abu-Qir Bay (Abdel Ghani et al., 2013), eastern coast of Alexandria, eastern Mediterranean coast of Egypt, western part of the Egyptian Mediterranean Sea and Egyptian coast along Mediterranean Sea. Additionally, the Pb gave concentrations lower than those mentioned in eastern coast of Alexandria, Egyptian coast along Mediterranean Sea, the Eastern Harbour, the Western Harbour and El-Max Bay. However, the upper-mentioned concentrations were higher than those mentioned in Abu-Qir Bay (Abdel Ghani et al., 2013), eastern Mediterranean coast of Egypt and western part of the Egyptian Mediterranean Sea. Markedly, the Cd levels in Abu-Qir exceeded those recorded in the eastern Mediterranean coast of Egypt, western part of the Egyptian Mediterranean Sea, the Eastern Harbour and the Western Harbour. The Cd concentrations were lower than those recorded in Abu-Qir Bay (Abdel Ghani et al., 2013), Egyptian coast along Mediterranean Sea and El-Max Bay.

6. Evaluation of the pollution environmental impact

6.1. Distribution coefficient (Kd)

The distribution coefficient is one of the important parameters for evaluating the potential migration of heavy metals in a sediment or the suspended matter that contacted with water column. Quantitatively, the distribution coefficient Kd is calculated as the ratio between concentrations of heavy metal in sediments and water according to following equation:

\[ Kd = \frac{[\text{Metal} (S)]}{[\text{Metal} (W)]} \]  (1)
Where, $K_d$ (L/kg) is the distribution coefficient, $Metal (S)$ is the concentration of the heavy metal in sediments (mg/kg) and $Metal (W)$ is the concentration of the heavy metal in water column (mg/L). Nabelkova and Kominkova (2012) mentioned that $K_d$ provides useful information about risk assessment. In case the $Log(K_d) > 5$, the probability that the metal has affinity to bind in sediments is indicated. While the values in the range $3 < Log(K_d) < 4$ would indicate that the metal is released from the sediment into the water body, and $Log(K_d) < 3$ indicates prevailing heavy metal in a water body.

Table 3. Comparing heavy metal values in sediment of Abu-Qir Bay with those of other studies in mg/kg.

<table>
<thead>
<tr>
<th>Location</th>
<th>Mn</th>
<th>Fe</th>
<th>Co</th>
<th>Ni</th>
<th>Cu</th>
<th>Zn</th>
<th>Pb</th>
<th>Cd</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Abu-Qir Bay</td>
<td>800-2520</td>
<td>12920-14480</td>
<td>-----</td>
<td>-----</td>
<td>38-561</td>
<td>118-179</td>
<td>-----</td>
<td>-----</td>
<td>Faragallah et al. (2004)</td>
</tr>
<tr>
<td>Eastern Mediterranean coast of Egypt</td>
<td>10.030-119.370</td>
<td>50.630-2182.100</td>
<td>-----</td>
<td>-----</td>
<td>0.550-17.990</td>
<td>1.860-14.030</td>
<td>8.540-19.250</td>
<td>0.100-0.310</td>
<td>Khaled et al. (2009)</td>
</tr>
<tr>
<td>The Eastern Harbour</td>
<td>7.800-188.970</td>
<td>10-30240</td>
<td>-----</td>
<td>-----</td>
<td>3.800-129.200</td>
<td>2.900-206.890</td>
<td>1.300-112.090</td>
<td>0.300-1.830</td>
<td>Abdel Ghani et al. (2013)</td>
</tr>
</tbody>
</table>

The overall mean of $Log(K_d)$ for each metal had been estimated considering the water bodies: Mn (5.213), Fe (6.521), Co (4.455), Ni (4.190), Cu (4.388), Zn (3.982), Pb (3.819) and Cd (3.503), Table 2. The following order: Fe > Mn > Zn > Co > Cu > Ni > Zn > Pb > Cd has been observed. Fe showed the highest $Log(K_d)$ values in all water bodies, indicating that Fe is highly stable in sediments. Whereas $Log(K_d)$ for the Cd
values indicated that the Cd is mainly contained in water body, suggesting that the studied water bodies can pose higher risk of Cd. To a certain degree of stability \((\log(Kd) > 4)\), metals can cause a threat to bottom organisms (Li et al., 2017). Generally, the metals may be released to water under certain conditions, and may endanger the entire aquatic ecosystem, given their toxicity profile (Li et al., 2017).

6.2. Geo-accumulation index \((I_{geo})\)

Geo-accumulation index \((I_{geo})\) was proposed by Müller (1981) to evaluate the degree of metals contamination in sediments by comparing the concentrations of metal with the pre-industrial levels and calculated using the successive equation (2):

\[
I_{geo} = \log_2 \left( \frac{C_n}{B_n} \right) \] (2)

Where, \(C_n\) is the metal \((n)\) concentration measured in sediment, \(B_n\) is the geochemical background value of the metal \((n)\), and factor 1.5 is a factor concerning the background level variations due to lithogenic impacts. In the present study, the average shale values stated by Turekian and Wedepohl (1961) were used as the background levels of heavy metals. Seven classes of \((I_{geo})\) index ranging from 0-6 were classified by Müller (1981), and organized from the uncontaminated to the highly contaminated sediments as described in Table (4).

It can be deduced from Tables (4 & 5) that, with reference to Müller scale, most of the \(I_{geo}\) values of Cd in surface sediments through all study areas were between 1 and 3 \((1 < I_{geo} < 3; \text{class } 3)\), indicating that those sites are moderately to strongly polluted with Cd. On the other hand, \(I_{geo}\) values of Ni, Cu, Zn, and Pb in surface sediments of most study areas were apparently lower than 0 \((I_{geo} < 0; \text{class } 0)\), indicating a practically unpolluted status.

Table 4. Classification of \(I_{geo}\) (Müller, 1981). The modified degree of contamination \((mC_d)\) (Abrahim & Parker, 2007), and potential ecological risk index, \(RI\) (Hakanson, 1980).

<table>
<thead>
<tr>
<th>(I_{geo}) class</th>
<th>Designation of sediment quality</th>
<th>(mC_d)</th>
<th>(mC_d) class</th>
<th>Contamination degree</th>
<th>(RI) values</th>
<th>Risk Intensity</th>
</tr>
</thead>
<tbody>
<tr>
<td>&lt; 0</td>
<td>Unpolluted</td>
<td>&lt; 1.5</td>
<td>0</td>
<td>Unpolluted</td>
<td>(RI &lt; 150)</td>
<td>Low ecological risk</td>
</tr>
<tr>
<td>0-1</td>
<td>Unpolloted to moderately polluted</td>
<td>1.5 (\leq mC_d &lt; 2)</td>
<td>1</td>
<td>Slightly polluted</td>
<td>(150 \leq RI &lt; 300)</td>
<td>Moderate ecological risk</td>
</tr>
<tr>
<td>1-2</td>
<td>Moderately polluted</td>
<td>2 (\leq mC_d &lt; 4)</td>
<td>2</td>
<td>Moderately polluted</td>
<td>(300 \leq RI &lt; 600)</td>
<td>Considerable ecological risk</td>
</tr>
<tr>
<td>2-3</td>
<td>Moderately to strongly polluted</td>
<td>4 (\leq mC_d &lt; 8)</td>
<td>3</td>
<td>Moderately to heavily polluted</td>
<td>(RI &gt; 600)</td>
<td>Very high ecological risk</td>
</tr>
<tr>
<td>3-4</td>
<td>Strongly polluted</td>
<td>8 (\leq mC_d &lt; 16)</td>
<td>4</td>
<td>Heavily polluted</td>
<td></td>
<td></td>
</tr>
<tr>
<td>4-5</td>
<td>Strongly to extremely polluted</td>
<td>16 (\leq mC_d &lt; 32)</td>
<td>5</td>
<td>Severely polluted</td>
<td></td>
<td></td>
</tr>
<tr>
<td>&gt; 5</td>
<td>Extremely polluted</td>
<td>(\geq 32)</td>
<td>6</td>
<td>Extremely polluted</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
6.3. Pollution Loading Index (PLI)

Pollution loading index (PLI) was proposed by Tomlinson et al. (1980) and Satyanarayana et al. (1994) to evaluate the integrated pollution status of synergetic groups for a particular station. If the PLI value > 1, a polluted condition is indicated, while PLI < 1 would signify no metal pollution. This parameter is expressed in the following equation:

\[
PLI = (CF_1 \times CF_2 \times CF_3 \times \ldots \times CF_n)^{1/n}
\]  (3)

Where, \( n \) is the number of selected metals, and \( CF \) is the contamination factor. \( CF \) can be calculated from the following equation (4):

\[
CF = \frac{\text{Metal concentration in the sediments}}{\text{Background value of the metal}}
\]  (4)

The contamination factor (CF) is used to evaluate the anthropogenic input of metals to sediment. The average shale value is the background concentration of the selected metal as given by Turekian and Wedepohl (1961).

The calculated PLI values for the studied metals are listed in Table (5) and represented in Figure (3). Most of PLI values of surface sediments fall above 1 (PLI > 1), indicating that they were polluted sites. On the other hand, St 7 was an unpolluted site (PLI < 1).

Table 5. Evaluation of heavy metals pollution in sediments from Abu-Qir Bay based on \( I_{geo} \), PLI, \( mc_d \), RI, and MERM-Q indices.

<table>
<thead>
<tr>
<th>Station number</th>
<th>( I_{geo} )</th>
<th>PLI</th>
<th>( mc_d )</th>
<th>RI</th>
<th>MERM-Q</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni</td>
<td>Cu</td>
<td>Zn</td>
<td>Pb</td>
<td>Cd</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>-0.54</td>
<td>-1.09</td>
<td>-0.54</td>
<td>-0.23</td>
<td>2.41</td>
</tr>
<tr>
<td>5</td>
<td>-0.87</td>
<td>-1.34</td>
<td>0.52</td>
<td>0.62</td>
<td>3.35</td>
</tr>
<tr>
<td>6</td>
<td>-0.25</td>
<td>-0.89</td>
<td>-0.03</td>
<td>0.18</td>
<td>2.73</td>
</tr>
<tr>
<td>7</td>
<td>-1.11</td>
<td>-2.24</td>
<td>-1.16</td>
<td>-0.74</td>
<td>1.43</td>
</tr>
<tr>
<td>8</td>
<td>0.14</td>
<td>-1.18</td>
<td>-0.14</td>
<td>0.37</td>
<td>2.90</td>
</tr>
<tr>
<td>9</td>
<td>-0.64</td>
<td>-1.64</td>
<td>-0.96</td>
<td>-0.78</td>
<td>1.49</td>
</tr>
<tr>
<td>10</td>
<td>-0.62</td>
<td>-0.44</td>
<td>-0.48</td>
<td>-0.79</td>
<td>2.28</td>
</tr>
<tr>
<td>Min</td>
<td>-1.11</td>
<td>-2.24</td>
<td>-1.16</td>
<td>-0.79</td>
<td>1.43</td>
</tr>
<tr>
<td>Max</td>
<td>0.14</td>
<td>-0.44</td>
<td>0.52</td>
<td>0.62</td>
<td>3.35</td>
</tr>
<tr>
<td>Average</td>
<td>-0.55</td>
<td>-1.26</td>
<td>-0.40</td>
<td>-0.19</td>
<td>2.37</td>
</tr>
</tbody>
</table>
6.4. Assessment according to modified degree of contamination (mC\textsubscript{d})

Abraham and Parker (2007) suggested a modified degree of contamination (mC\textsubscript{d}) to evaluate the overall contamination of sediment sample in the presence of multimetal rather than the contamination caused by one metal ion for one sample. According to equation (5) mC\textsubscript{d} can be calculated.

\[
mC_{d} = \frac{\sum_{i=1}^{n} C_{i}^{f}}{n}
\]  

(5)

Where, \( n \) is the number of selected metals and \( C_{i}^{f} \) refers to the contamination factors proposed by Hakanson (1980). Based on \( mC_{d} \) values, seven degrees of contamination were classified by Abraham and Parker (2007) as shown in Table (4). The \( mC_{d} \) values of the selected metals through all study areas are represented in Table (5) and Figure (4). The values of \( mC_{d} \) for Ni, Cu, Zn, Pb, and Cd ranged between 1.32 and 4.24, reflecting a low to moderate degree of contamination.

Figure 3. Pollution Loading Index (PLI) of surface sediments from Abu-Qir Bay.

Figure 4. Modified degree of contamination (mC\textsubscript{d}) index of surface sediments from Abu-Qir Bay.
6.5. Assessment according to ecological risk index ($RI$)

Hakanson (1980) proposed the ecological risk index ($RI$) to evaluate the ecological risks for aquatic organisms. According to the equations (6) and (7), the ecological risk index ($RI$) was calculated as a sum of five heavy metals (Ni, Cu, Zn, Pb, and Cd):

$$ E_r^i = T_r^i \times C_r^i $$

$$ RI = \sum E_r^i $$

Where $RI$ is the sum of the potential ecological risk factor ($E_r^i$), $T_r^i$ is the metal toxic response factor for a given metal, and $C_r^i$ refers to the contamination factor. The calculated $RI$ values for Ni, Cu, Zn, Pb and Cd in all study areas are listed in Table (5) and shown in Figure (5). Those metals presented moderate ecological risk (150 ≤ $RI$ < 300) for all studied sites, except for St 5 and St 8 that showed a considerable ecological risk ($RI$ > 300). The values for each investigated metal followed the sequence: Zn = Ni = 1 < Cr = 2 < Cu = Pb = 5.

6.6. Mean effect range median quotient ($MERM-Q$)

The mean ERM quotient ($MERM-Q$) is a method used to evaluate the possible biological effects of all the investigated metals and PAHs by comparing their observed concentrations with their limit concentrations and calculating the values using the equation (8) suggested by Long et al. (1998):

$$ MERM-Q = \frac{\sum (C_i / ERM_i)}{n} $$

Where, $C_i$ refers to sediment concentration of metal $i$, $ERM_i$ is the effect rang medium of metal $i$, and $n$ refers to number of metals. The $ERM_i$ values for each investigated metal were: Ni = 51.0, Cu = 270, Zn = 410, Pb = 218 and Cd = 9.60.
According to Long et al. (2000) and Gao and Chen (2012), MERM-Q can be classified into four categories: $MERM-Q < 0.1$ has 9% probability of being toxic (low), between 0.11-0.51 represents 21% probability of being toxic (low to medium), and between the range 0.51-1.5 indicates 49% probability of being toxic (high-medium). While $MERM-Q > 1.5$ indicates 74% of toxicity (high-priority sites). The calculated values for the sampling sites for Ni, Cu, Zn, Pb, and Cd varied from 0.27 to 0.63 and the average value was 0.44 (Figure 6 & Table 5). Based on this classification, all samples had low to medium toxicity (21% probability of being toxic).

Comparing the $MERM-Q$ calculated values with $ERM$ individual value, one can say that, the $MERM-Q$ is a more effective index for reducing the large data to a single number to assess the extent of each metal. In general, according to the results of $I_{geo}$, $PLI$, $mC_d$, $RI$ indices as well as $MERM-Q$, a considerable and intense heavy metals pollution of sediments through all study areas was detected. This may be due to human activities; industrial effluents of Petrojet company, paper and fertilizer factories, Abu-Qir EPS, and fishing boats, as well as the outlet of Lake Edku (Boughaz El-Maddya) which contains different types of pollutants as pesticides, humic acids, and trace metals.

7. Application of principal component analysis (PCA) and redundancy analysis (RDA)

Principal components analysis (PCA) is a useful tool used to understand the distribution and the sources of heavy metals and their relationship (Varol, 2011). In the present research, PCA was conducted on basis of the determined concentrations of heavy metals in seawater, SPM and sediments with varimax-rotation. The PCA results are represented in Table (6), the PC1 with a variance of 31.06% exhibited a significant positive correlation of the congeners Fe (0.92), Co (0.80), and Ni (0.81) of seawater,
indicating a common source that may be due to the exogenous discharge (Mao, 2013). The PC2 of the variance 23.70 % exhibited a correlation between Mn (0.94), Ni (0.83), and Cu (0.72) of SPM as well as Zn (0.72) of sediment samples, that indicated a common source as well as the sedimentation-re-suspension process. The mentioned metals either in particulate or sediments were strongly affected by the alkalinity of seawater (0.75). The PC3 results also indicated a good positive correlation between Mn (0.73), Cu (0.90), Zn (0.71), and Pb (0.72) of seawater samples. PC4 and PC5 of variance 12.69 % and 8.09 %, respectively showed a good correlation between Cd (0.74) of seawater samples and OOM (0.87) as well as between Cd (0.63) of particulate samples and TOC (0.74%). In the pollution assessment, Cd had higher $I_{geo}$ values (1 < $I_{geo}$ < 3; class 3), indicating that these sites were moderately to strongly contaminated with Cd. Therefore, Cd may be originated from natural sources with contributions from agricultural wastes (El-Nemr & El-Said, 2017).

Table 6. Rotated components matrix and water quality index for studied parameters of Abu-Qir Bay.

<table>
<thead>
<tr>
<th>Component</th>
<th>Total</th>
<th>Variance (%)</th>
<th>Cumulative (%)</th>
<th>Variables and loading values</th>
<th>Water Quality Index</th>
</tr>
</thead>
<tbody>
<tr>
<td>PCA1</td>
<td>10.87</td>
<td>31.06</td>
<td>31.06</td>
<td>Fe-w (0.92), Co-w (0.80), and Ni-w (0.81)</td>
<td>2 0.460161</td>
</tr>
<tr>
<td>PCA2</td>
<td>8.29</td>
<td>23.70</td>
<td>54.75</td>
<td>Mn-p (0.94), Ni-p (0.83), Cu-p (0.72), and Zn-s (0.72) &amp; alkalinity (0.75).</td>
<td>3 0.060052</td>
</tr>
<tr>
<td>PCA3</td>
<td>7.07</td>
<td>20.20</td>
<td>74.95</td>
<td>Mn-w (0.73), Cu-w (0.90), Zn-w (0.71), and Pb-w (0.72).</td>
<td>4 0.707431</td>
</tr>
<tr>
<td>PCA4</td>
<td>4.44</td>
<td>12.69</td>
<td>87.64</td>
<td>Cd-w (0.74) &amp; OOM (0.87)</td>
<td>5 0.160326</td>
</tr>
<tr>
<td>PCA5</td>
<td>2.83</td>
<td>8.09</td>
<td>95.73</td>
<td>Cd-p (0.63) &amp; TOC (0.74)</td>
<td>6 0.322984</td>
</tr>
<tr>
<td>PCA6</td>
<td>1.49</td>
<td>4.27</td>
<td>100.00</td>
<td>Cd-s (0.63)</td>
<td>7 -0.277910</td>
</tr>
</tbody>
</table>

To investigate the relationship between the environmental factors and the distribution of heavy metals in sediment, the RDA was used. The result of RDA for seawater and particulate matter as well as for sediment are represented in Fig. (7A & 7B). The angle between the heavy metal and environmental factors reflects their relationship. Metals in seawater such as Mn, Fe, Co, Ni, Cu, Zn, Pb, Cd and temperature, salinity, as well as TDS can be considered as significant parameters that reflect the water quality of Abu-Qir Bay coastal waters. Strong positive correlation of metals (Mn, Fe, Co, Ni, Cu, Zn, Pb, and Cd), pH, DO and T.alk. in particulate matter was also observed. The concentration of Fe in sediment was positively correlated to TOC and fine sand % (Fig. 7B) which accorded with the result of $K_d$, whereas the RDA analysis explained that Zn, Pb, and Cd contents in sediments are strongly related.
8. Water quality index (WQI)

In the current study, principle component analysis was employed to assess the water quality index (WQI) at each station and detect the hot spot stations. WQI can be calculated according to equation (9)

\[
WQI = \sum_{n=1}^{n} \left( \frac{\lambda_n}{\sum \lambda_n} \right) \times PC_n
\]

Where, \(n\) and \(\lambda_n\) refer to the number and the Eigenvalues of effective components, respectively. Whereas \(\sum \lambda\) is the sum of the Eigenvalues and \(PC_n\) that refers to the critical principal component scores (MacDonald et al., 2003). The data of water quality index (WQI) of Abu-Qir Bay are shown in Table (6). They depicted that, St 7 to St 10 were relatively good and varied between -0.23 at St 10 and -0.75 at St 8 meanwhile, water quality index of the other stations (St 2 to St 6) showed that they were slightly polluted to different degrees (0.060-0.707). Thus, they could be considered as hot spots. St 2 exists in front of Abu-Qir city and can be affected by human activities and domestic effluents. While St 3 to St 5 are exposed to pollution caused by the activities of gas production (Petrojet company) and Abu-Qir EPS. St 6 is located at the outlet of Lake Edku (Boughaz El-Maddya) which contains a different type of hazard materials as pesticides, humic acids, and trace metals as well as fishing boats.

CONCLUSION

The marine ecosystem is threatened by the discharge of industrial effluents which affects the sustainability of living organisms and hence public health. Identification of the sources of the heavy metals (Mn, Fe, Co, Ni, Cu, Zn, Pb, and Cd) as well as their distribution between water body and sediment of Abu-Qir Bay area were studied. The present study provided a detailed on heavy metal concentrations in seawater, SPM, and sediment. The level of contamination in Abu-Qir Bay and their ecological risks to aquatic
organisms showed that the anthropogenic activities are the fundamental source of heavy metals in Abu-Qir Bay. However, among the eight examined heavy metals in the surveyed area, the content of Cd was the highest in sediment and according to PCA, Cd may be originated from natural sources with some effects from agricultural wastes.

REFERENCES


