



Heavy Metals Distribution in Water, Particulate and Sediment of El-Mex Bay, Alexandria, Egypt

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Abstract: The aim of this study is to determine the distribution of the heavy metals (Fe, Cu, Pb, Mn, Zn and Cd) between dissolved and particulate form; as well as, in the sediment of El-Mex Bay. Surface and bottom water samples were collected seasonally during the period from September (summer) 2012 to April (spring) 2013. The sediment samples were collected once from all the selected stations in summer 2012. The metals content in the sediments decreased in the order of Fe > Mn > Zn > Pb > Cu > Cd. The measured heavy metal content varied greatly as follows: Fe, 1449-8625 $\mu\text{g g}^{-1}$ with an average of $4082 \pm 188 \mu\text{g g}^{-1}$; Mn, 165.08-865.92 $\mu\text{g g}^{-1}$ with an average of $315.6 \pm 178 \mu\text{g g}^{-1}$; Cu, 5.67- 48.17 $\mu\text{g g}^{-1}$ with an average of $26.04 \pm 19 \mu\text{g g}^{-1}$; Zn, 17.50- 138.75 $\mu\text{g g}^{-1}$ with an average of $57.07 \pm 130 \mu\text{g g}^{-1}$; Pb, 7.17- 87.50 $\mu\text{g g}^{-1}$ with an average of $26.81 \pm 54 \mu\text{g g}^{-1}$; Cd, 0.08-1.50 $\mu\text{g g}^{-1}$ with an average of $0.54 \pm 1.05 \mu\text{g g}^{-1}$. Metal Pollution Index ranged from 24.82 to 92.65 with an average 64. It can be indicated that stations II and VII suffered from metal pollutions with values of 92.56 and 87.23, The Enrichment Factor (EF) of heavy metals of El-Mex Bay sediments can be arranged as the following, $\text{EF}_{\text{Cd}} > \text{EF}_{\text{Pb}} > \text{EF}_{\text{Cu}} > \text{EF}_{\text{Mn}} > \text{EF}_{\text{Zn}}$. The difference in EF values due to the difference in the magnitude of input for each metal in the sediment. To evaluate water quality index, principal component analysis (PCA) was applied. According to PCA data, Station I and III could be considered as hot spots.

Keywords: Sediment, Heavy Metals, El-Mex Bay, Enrichment Factor, Wastewater

1. Introduction

Trace metals in seawater can exist in a variety of physical and chemical forms. The simplest physical distinction is particulate versus dissolved forms. This is somewhat of an operational definition with 0.4 mm or 0.2 mm pore size filters generally providing this separation. Particulate forms include those metals adsorbed onto particle surfaces, incorporated within particles of biogenic origin and incorporated in the matrix of aluminosilicate minerals or co-precipitated in other authigenic minerals. Dissolved metals include various soluble complexes of the trace metals and potential colloidal forms. The redox chemistry of the particular metal and its environment dictate the oxidation state and form of the parent species. For trace metals, the parent species can be the simple mono-, di-, or trivalent

cation such as Zn^{2+} , "or for metals existing in higher oxidation states [1]". Ecosystems are complex and dynamic. This makes linking any one effect to a specific cause very difficult and conditions cannot be controlled [2, 3, 4]. One of the major environmental problems in Alexandria city is seawater pollutions. Various pollutants are dumped daily by industrial, agricultural and domestic sources over Alexandria coasts through several outfalls, El-Mex Bay one of these disposal sites (El-Mex Pumping Station). It receives a heavy load of waste water ($2.6 \times 10^9 \text{ m}^3 \text{ y}^{-1}$) both directly from industrial out falls and indirectly from Lake Mariut via El-Mex pumping station. The main outfalls are; Misr Chemical Industries, Mex pumping station on El-Umum drian.combined wastewater from Tanneries and slaughterhouse, El-Noubaria Canal and Mahmoudeya Canal [5, 6]. El-Mex Bay is characterized by the presence of two water layers overlaying each other [7]. The Physico-

chemical characteristics of different water type in El-Mex Bay water showed an upper brackish layer characterized by higher temperature and low salinity, and a lower seawater layer which has properties similar to open Mediterranean with lower temperature and high salinity [8, 9].

El-Mex Bay is a part of Alexandria coast on the Mediterranean Sea. It is subjected to effluents contaminated with several anthropogenic materials including trace metals. One of these effluents is called Umum agricultural drain (rate $8 \times 10^6 \text{ m}^3/\text{d}$). The elevation in levels of trace metals concentrations in marine environment is a worldwide problem and the discharge of trace metal wastes has many obvious impacts on water, sediments, and biota, led to decrease in productivity, and increase in exposure of humans to harmful substances. The toxicity, bioavailability, bioaccumulation, biodegradability, persistence, mobility, solubility, extractability and many other critical properties is found to depend on the form and nature of the chemical species [10]. Metals exist in our natural waters in different labile and non-labile forms, but the labile ones are the most important in the environment. They are responsible for bioaccumulation of toxic metals in biota, animals and finally in humans. The aim of the present work is to determine the distribution of the trace metals (Fe, Cu, Pb, Mn, Zn and Cd) between dissolved and particulate form; as well as, in sediment of El-Mex Bay.

2. Material and Methods

2.1. Study Area and Sampling Sites

Eight stations were selected to cover the whole area of EL-Mex Bay. Surface and bottom water samples as well as sediments were collected seasonally during the period from September (summer) 2012 to April (spring) 2013. The sediment samples were collected once from all the selected stations in summer 2012. The positions of these stations are shown in Fig 1. El-Mex area lies at the western part of Alexandria city. it is one of the main fishing grounds of Alexandria located between longitude from $29^\circ 48' 20.44''$ to $29^\circ 51' 0.00''$ E and latitude from $31^\circ 8' 34.188''$ to $31^\circ 10' 29.85''$ N. EL-Mex Bay represent a shallow sheltered Estuary west of Alexandria, extends for about 15 km between EL-Agamy headland in the west to the Western harbor in the east and from the coast to a depth of about 30 m. The Bay has a mean depth of 10m. Its surface area is about 19.4 km^2 and its volume $190.3 \times 10^6 \text{ m}^3$ [11].

2.2. Analytical Methods

2.2.1. Dissolved and Particulate Heavy Metals

Filtrate water samples through the $0.45 \mu\text{m}$ membrane filter, then used chelating ion- exchange resin (Chelex-100 in ammonia form) to pre- concentration the dissolved heavy metals [12, 13]. Then, direct measurement using AAS. The membrane filter with its content of TSM was placed in a Teflon cup and 2 ml of concentrated nitric acid was evaporated to near dryness at 80°C [14]. After cooling 6 ml of mixed $\text{HNO}_3\text{-HClO}_4\text{-HF}$ (3:2:1) was added before heating

again. After complete digestion for 1 hour, the sample was evaporated to dryness and adding 1 ml 6N HNO_3 and complete to 25 ml with 0.1N of HCl in volumetric flask. The metals in this acid extracts were then determined by the AAS. All bottles filter membranes and lab wares that would be contact with samples were carefully pre-washed by 10% suprapure HNO_3 acid and Mili-Q water. Merck standard solutions diluted by Mili-Q water was use as standard.

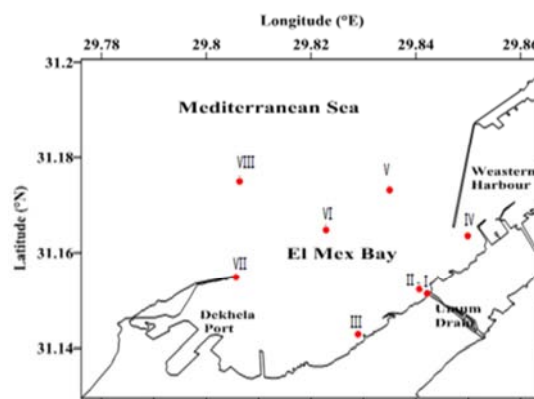


Fig. 1. Sampling Stations.

2.2.2. Sediments Analysis

The sampling has been carried out by means of plastic tube (PVC), digging gently into the uppermost layer of the sediment. Samples from each site were divided into two subsamples, then homogenized by mixing and kept in clean plastic containers. Samples were stored frozen until analysis. A sub-sample was taken to determine chemical and physical characteristics of the sediments such as grain size distribution, total organic matter and calcium carbonate contents.

i. Grain Size Analysis

About 25gm of dried samples was taken for mechanical analysis. The samples were subjected to the combined technique of dry sieving and pipette analysis [15].

ii. Total Organic Carbon (TOC)

Total organic carbon (TOC) was determined according to the method described by Gaudette and Flight [16]. This method utilizes exothermic heating and oxidation with potassium dichromate ($\text{K}_2\text{Cr}_2\text{O}_7$) and concentrated sulphuric acid (H_2SO_4) of powdered sediment sample and the titration of the excess dichromate with ferrous ammonium sulphate solution using diphenylamine as indicator. The organic carbon is converted to organic matter by multiplying the organic carbon values by the factor of 1.8.

iii. Total Calcium Carbonate (CaCO_3)

The total carbonate was determined by titration technique described by Molina [17]. About 1 g of each sample was treated with 50 ml standardized 0.5N HCl and then released amount of CO_2 was determined by back titration with previously standardized 0.25N NaOH solution using phenolphthalin indicator. The percentage of calcium carbonate ($\% \text{CaCO}_3$) was determined by the following equation:

$$\text{CaCO}_3\% = 100 \times 0.05 \times \{(\text{N}_{\text{HCl}} \times \text{V}_{\text{HCl}}) - (\text{N}_{\text{NaOH}} \times \text{V}_{\text{NaOH}})\}$$

N_{HCl} : Normality of standardized HCl, V_{HCl} : volume of standardized HCl

N_{NaOH} : Normality of standardized NaOH, V_{NaOH} : volume of standardized NaOH

iv. Heavy Metal Analysis

The total concentrations of heavy metals (Cu, Cd, Fe, Pb, Zn and Mn) were determined according to Oregioni and Aston [18]. Nought point five grammes of dried sample were digested using a mixture of nitric, perchloric and hydrofluoric acids in a previously cleaned and dried Teflon beaker, then evaporated to near dryness at 80°C. After complete digestion, the residue was transferred to a 25ml volumetric flask with 0.1 M HCl. The concentrations of different metals in the final extracts were measured using atomic absorption spectrophotometer in the flame mode (Shimadzu AA-6800).

2.3. Statistical Analysis and Quality Control

The accuracy of the analytical procedure used was reputedly checked by analyzing reference samples (IAEA-365 Monaco). Quality control samples represented 10% of the total analytical load. Duplicates, spikes and blanks were treated identically using the same reagents for testing the precision, respectively. Percentage recovery for spiked samples ranged from 93 to 105%, while precision agreed within 10%.

The analytical precision was tested by subjecting 10 times sediment samples to the previous procedure for the determination of total heavy metals. The results showed good reproducibility and a precision (expressed as the% Coefficient of Variation) of individual extractions varying from 1.08 to 6.76%. Thus, the CV% calculated for the total heavy metals (Fe, Mn, Cu, Zn, Ni and Cr) was within the range of precision. Where the maximum value was 6.76% for Zn and the minimum value was 1.08% for Pb.

The statistical analysis was performed which included correlation matrices between the different investigated variables and testing the significance of a relation between different variables. Different computer programs were used in this work: Excel 2007 and SPSS 18.

3. Results and Discussions

Physicochemical parameters; such as, Temperature, pH and Organic matter play an important role in distribution of trace metals in El-Mex Bay. The average values of water temperatures ranged from 17.30°C in winter 2013 to 27.25°C in summer 2012, and for pH value of seawater is around 8.2 (slightly basic); while, the average of OOM ranged between minimum 1.44 mgO₂l⁻¹ in winter and maximum 9.95 mgO₂l⁻¹ in spring. The concentrations of dissolved trace metals increase with temperature so that elevated temperatures tend to enhance toxic effects of metals on organisms.

3.1. Dissolved and Particulate Heavy Metals

Trace metals are natural components of the Earth's crust

and some of them (e.g., copper, selenium, and zinc) are essential as trace elements to maintain the metabolism of the human body even if, at higher concentrations, they may have toxic effects. Many other metals (e.g., mercury, cadmium, lead, etc.) have direct toxic effects on human health. Owing to their chemical characteristics, metals remain in the environment, in many cases only changing from one chemical state to another one and eventually accumulating in the food chain [19]. The regional and seasonal distribution of dissolved and particulate heavy metals in the present study area are shown in Tables 1-4.

3.1.1. Iron (Fe)

Iron considers one of the oldest metals known to man and largest uses in industry and human activities. Its concentration in dissolved form ranged from 4.73 to 51.72 µg l⁻¹ in summer 2012, from 9.96 to 25.32 µg l⁻¹ in autumn 2012, from 7.71 to 17.71 µg l⁻¹ in winter 2013 and from 5.42 to 24.30 in spring 2013, with an average concentration distributed between 10.04 and 30.47 µg l⁻¹ at surface water and from 7.53 to 22.81 µg l⁻¹ at bottom water. While in particulate form ranged from 1253.97 to 8564.71 µg g⁻¹ in summer, ranged from 6490.20 to 9953.94 µg g⁻¹ in autumn, ranged from 2341.64 to 9871.83 µg g⁻¹ in winter and ranged from 1524.53 to 9558.06 µg g⁻¹ in spring, with an average ranged from 2582.03 to 9292.33 µg g⁻¹ at surface water and from 4448.10 to 7996.61 µg g⁻¹ at bottom water.

3.1.2. Copper (Cu)

In case of dissolved copper, this also is essential element to biota. D-Cu concentration in summer ranged between 1.94 and 7.77 µg l⁻¹, in autumn, it ranged between 2.70 and 11.21 µg l⁻¹, in winter ranged between 1.45 and 2.84 µg l⁻¹ and in spring ranged from 1.61 to 3.17 µg l⁻¹ with an average value ranged from 1.45 to 11.21 µg l⁻¹. Low concentration of D-Cu is due to consumption by flora blooming, the highest level of copper concentration is related to the allochthonous input of industrial and agricultural wastes. High decomposition rate of organic matter and the release of copper from decay of organisms by the action of bacteria evolved in the increasing levels of copper at waste water and seawater [20]. But in P-Cu concentrations ranged from 90.48 to 489.41 µg g⁻¹ in summer, ranged from 93.77 to 773.33 µg g⁻¹ in autumn, ranged from 100.76 to 271.19 µg g⁻¹ in winter and ranged from 93.02 to 400.00 µg g⁻¹ in spring with an average values ranged from 115.93 to 294.54 µg g⁻¹ in surface water and ranged from 108.96 to 510.04 µg g⁻¹ in bottom water.

3.1.3. Manganese (Mn)

Mn is seasonally affected by high dust input in. Its concentration in El-Mex Bay ranged from 0.91 to 7.57 µg l⁻¹, ranged from 0.90 to 31.51 µg l⁻¹, ranged from 0.32 to 2.13 µg l⁻¹ and ranged from 1.14 to 169.43 µg l⁻¹ in summer, autumn, winter and spring, respectively. Mn in particulate form in El-Mex Bay water ranged from 224.56 to 996.92 µg g⁻¹ in summer, ranged from 107.14 to 947.13 µg g⁻¹ in autumn, ranged from 424.64 to 1200.00 µg g⁻¹ in winter and ranged from 116.46 to 1200.00 µg g⁻¹ in spring with an average values ranged from 390.71 to 829.42 µg g⁻¹ at surface water

and from 385.26 to 937.57 μgg^{-1} at bottom water. Manganese is an important micronutrient for marine organisms via its use in photosynthetic and radical scavenging enzymes [21, 22].

3.1.4. Zinc (Zn)

The concentrations of dissolved Zinc ranged from 3.01 to 21.72 μgl^{-1} in summer, ranged from 4.25 to 35.08 μgl^{-1} in autumn, ranged from 1.64 to 12.02 μgl^{-1} in winter and ranged from 3.63 to 16.6 μgl^{-1} in spring, with an average ranged from 5.23 to 16.45 μgl^{-1} at surface water and from 6.75 to 19.93 μgl^{-1} at bottom water, and it was higher in bottom water value than those found in surface water. The concentrations of D-Zn in most surface water was lower than in the bottom water at many stations where they are assimilated by phytoplankton or adsorbed by biogenic particles, and increased in the bottom water as sinking particles undergo decomposition or dissolution, followed by oxidation and remineralization in deeper water. P-Zn concentrations in El-Mex Bay water ranged from 109.73 to 896.47 μgg^{-1} in summer, ranged from 151.93 to 984.98 μgg^{-1} in autumn, ranged from 236.36 to 980.95 μgg^{-1} in winter and ranged from 198.00 to 705.26 μgg^{-1} in spring with an average value ranged from 252.94 to 616.94 μgg^{-1} at surface water and ranged from 452.75 to 654.08 μgg^{-1} at bottom water, P-Zn concentration at bottom water was higher than surface water.

3.1.5. Cadmium (Cd)

Cadmium is a non-essential, harmful trace heavy metal for marine organisms, and its polluting effects and toxicity to organisms on a global scale are serious problems [23, 24]. In the present study, the concentrations of D-Cd ranged from ND to 0.64 μgl^{-1} in summer season, from ND to 0.37 μgl^{-1} in autumn, ND in winter and from 0.02 μgl^{-1} to 0.44 μgl^{-1} in spring. The average D-Cd concentration in El-Mex Bay ranged from ND to 0.20 μgl^{-1} at surface water and from ND to 0.17 μgl^{-1} at bottom water. Agricultural activity is a possible source of Cd (from phosphate fertilizer used in agricultural fields) that enters the coastal marine ecosystem [24, 25]. P-Cd concentrations in El-Mex Bay water ranged from 11.76 to 59.81 μgg^{-1} in summer, ranged from 2.76 to 25.57 μgg^{-1} in autumn, ranged from 9.28 to 83.87 μgg^{-1} in winter and ranged from 16.00 to 67.20 μgg^{-1} in spring with an average value ranged from 10.56 to 50.99 μgg^{-1} at surface water and from 14.57 to 37.17 μgg^{-1} at bottom water.

3.1.6. Lead (Pb)

Dissolved Lead (D-Pb); also, consider nonessential element for biota. The concentrations of D-Pb in El-Mex Bay water ranged from 5.02 to 26.39 μgl^{-1} in summer, from ND to 13.65 μgl^{-1} in autumn, from ND to 4.03 μgl^{-1} in winter and ND in spring at surface and bottom. The average D-Pb concentrations in El-Mex Bay water ranged from ND to 8.41 μgl^{-1} at surface water and from ND to 10.19 μgl^{-1} at bottom water. The average concentration of D-Pb in surface and bottom water showed decrease in spring period. The results of P-Pb concentrations in El-Mex Bay water ranged from 106.06 to 3509.09 μgg^{-1} in summer, ranged from 3.65

to 1586.99 μgg^{-1} in autumn, ranged from 4.55 to 933.33 μgg^{-1} in winter and ranged from ND to 1148.39 μgg^{-1} in spring with an average value ranged from 318.52 to 996.12 μgg^{-1} at surface water and from 299.75 to 736.93 μgg^{-1} at bottom water.

3.1.7. Heavy Metals in the Sediments

The spatial distribution of heavy metals (Fe, Mn, Cu, Zn, Pb and Cd) in El-Mex Bay sediments are shown in Figure 2. The metals content in the sediments decreased in the order of Fe > Mn > Zn > Pb > Cu > Cd. The measured heavy metal content varied greatly as follows: Fe, 1449-8625 μgg^{-1} with an average of $4082 \pm 188 \mu\text{gg}^{-1}$; Mn, 165.08-865.92 μgg^{-1} with an average of $315.6 \pm 178 \mu\text{gg}^{-1}$; Cu, 5.67- 48.17 μgg^{-1} with an average of $26.04 \pm 19 \mu\text{gg}^{-1}$; Zn, 17.50- 138.75 μgg^{-1} with an average of $57.07 \pm 130 \mu\text{gg}^{-1}$; Pb, 7.17- 87.50 μgg^{-1} with an average of $26.81 \pm 54 \mu\text{gg}^{-1}$; Cd, 0.08-1.50 μgg^{-1} with an average of $0.54 \pm 1.05 \mu\text{gg}^{-1}$.

3.2. Heavy Metals Bioavailability

It is meant to donate heavy metals in a water-soluble form that plant and animal communities can readily uptake and assimilate [26, 27]. It can be calculated as follows:

$$\text{Bioavailability} = \frac{\text{concentration of D-metals } (\mu\text{gl}^{-1})}{\text{concentration of T-metals } (\mu\text{gl}^{-1})} * 100$$

Where, D-metals= Concentration of Dissolved metals in water samples, T-metals= Concentration of Total metals in water samples. Bioavailability studies indicate that aquatic organisms uptake free metal ions (metal hydroxides) from solution quite efficiently; similarly, terrestrial animals uptake metal from solutions more efficiently than via direct particulate matter ingestion [28]. Bioaccumulation of metals by biota in surface water and by plants and animals in terrestrial environments can adversely affect humans. Factors that affecting on bioavailability are: Total concentration and speciation (physical-chemical forms) of metals, pH, redox potential, Temperature, Total organic content (both particulate and dissolved fractions), and suspended particulate content. Many of these factors vary seasonally and temporally, and most factors are interrelated. Environmental conditions that enhance dissolved metal abundances (for example, lower pH) result in greater metal bioavailability. Indirect controls, such as larger particle or sediment size, also can result in greater bioavailability of metals by reducing adsorption and increasing dissolved metal contents. Metal assimilation from ingested particulate matter is also important, however, because metals are highly concentrated in this form [29]. Temperature can strongly influence the rate of biological processes; rates double for every 10°C -temperature increment. Bioavailability values of the six metals in the water of the study areas listed in Table 5. The values ranged from ND to 5.16, 0.29 to 41.77, 0.03 to 2.98, 0.01 to 59.26, ND to 8.78 and 0.35 to 10.79 for Cd, Cu, Fe, Mn, Pb and Zn, respectively.

3.3. Partition Coefficient (Kd)

The partition coefficients of metals, defined as the ratio of

the metal concentration in particulate (μgkg^{-1}) to content of the dissolved metal concentration in water (μg^{-1}). In natural media, metal contaminants undergo reactions with legends in water and with surface sites on the solid materials with which the water is in contact. The metal partition coefficient (K_d ; also known as the sorption distribution coefficient) is the ratio of sorbed metal concentration (expressed in μg metal per kg sorbing material) to the dissolved metal concentration (expressed in μg metal per L of solution) at equilibrium. K_d depends on the nature of the Particulate, pH, salinity, geochemical parameters of the water and specific characteristics of each element [30, 31]. The logarithmic values of K_d are shown in Table 6, The values ranged from ND to 6.02, 3.14 to 5.53, 4.53 to 6.51, 2.84 to 7.29, ND to 6.81 and 3.91 to 5.45 for Cd, Cu, Fe, Mn, Pb and Zn, respectively [32, 33, 34].

3.4. Metal Pollution Index (MPI)

The overall metal contents at the sites investigated in this study were compared, using the metal pollution index (MPI) calculated according to Usero et al. [35] with the formula:

$$\text{MPI} = (\text{MFe} \times \text{MMn} \times \text{MZn} \times \text{MPb} \times \text{MCd} \times \text{MCu})^{1/6}$$

It is used to estimate the degree of pollution. According to the calculated data of the metal pollution index (MPI), it ranged from 24.82 to 92.65 with an average 64. It can be indicated that stations II and VII suffered from metal pollutions with values of 92.56 and 87.23, this may be due to the industrial wastewater and disposal of chemical and industrial wastes from petrochemical outfalls.

3.5. Enrichment Factor

Enrichment Factor (EF) was initially developed to speculate on the origin of elements in the atmosphere, precipitation, or seawater, but it was progressively extended to the study of soils, lake sediments, peat, tailings, and other environmental materials [36]. The formula to calculate EF is:

$$\text{EF} = \frac{(C_i/C_{ie})_S}{(C_i/C_{ie})_{RS}}$$

Where C_i is the metal in the sample and C_{ie} is the content

of immobile metal in the sample, and $(C_i/C_{ie})_{RS}$ is the ratio of heavy metal to immobile metal in the selected reference sample [36]. The selected reference sample is usually an average crust or a local background sample, the values for the surficial earth crust of Mn, Zn, Pb, Cd, Cu and Fe were taken from Martin and Meybeck [37]. The immobile element is often taken to be Al, Li, Sc, Zr or Ti, and sometimes Fe has been used [38]. In this study Fe has also used as an immobile to differentiate natural from anthropogenic components. According to Ergin et al. [39], the metal enrichment factor (EF) is defined as follows:

$$\text{EF} = \frac{(M/Fe)_{\text{sample}}}{(M/Fe)_{\text{crust}}}$$

According to Sutherland [40], five contamination categories are generally recognized on the basis of the enrichment factor: $\text{EF} < 2$, depletion to mineral enrichment; $2 \leq \text{EF} < 5$, moderate enrichment; $5 \leq \text{EF} < 20$, significant enrichment; $20 \leq \text{EF} < 40$, very high enrichment; and $\text{EF} > 40$, extremely high enrichment.

The results of EF values of Mn, Zn, Pb, Cd and Cu in El-Mex Bay sediments and the background concentrations of these metals are shown in Table 7. The EF values < 2 indicate the metal is entirely from crustal materials or natural processes; whereas EF values 2 suggest that the sources are more likely to be anthropogenic. Cd has the highest average EF of 22.57. EFCd ranged from 2.99 at station V to 51.58 at station VIII. Lead has the second highest average EF of 20.97, ranged from 2.21 at station III to 108.33 at station VIII. Copper has the third highest average EF of 7.41, ranged from 4.00 at station III to 10.34 at station V. For El-Mex Bay EF mean values (Mn, Cu, Zn, Cd and Pb), the order as the following, $\text{EFCd} > \text{EFPb} > \text{EFCu} > \text{EFMn} > \text{EFZn}$. The difference in EF values may be due to the difference in the magnitude of input for each metal in the sediment and/or the difference in the removal rate of each metal from the sediments [41]. The results of the present study showed that El-Mex Bay sediments were highly enriched in Cd and significantly enriched in Pb. Enrichment factors for Mn, Cu, Zn, Pb and Cd in most stations showed anthropogenic impact.

Table 1. Distribution of dissolved and particulate heavy metals in surface and bottom in summer at El-Mex Bay.

Stations	Fe		Mn				Zn					
	D		P		D		P		D		P	
	S	B	S	B	S	B	S	B	S	B	S	B
I	28.95		7200.00		5.88		565.38		10.38		211.54	
II	51.72		2632.73		2.30		913.08		15.21		250.91	
III	17.32	19.80	1262.14	3680.00	1.00	2.66	800.00	996.92	4.55	12.86	109.73	418.46
IV	40.32	22.06	2204.76	4031.75	0.91	1.82	895.24	457.14	2.01	11.60	342.86	244.44
V	23.76	13.66	1253.97	3693.88	4.72	1.65	355.56	681.63	8.17	10.85	196.83	404.08
VI	23.22	67.30	1298.36	8564.71	3.27	7.57	790.91	411.76	7.42	21.72	127.27	896.47
VII	50.45	21.70	1712.73	4742.86	1.50	2.06	672.38	774.03	10.30	14.75	556.36	503.90
VIII	8.02	4.73	3091.59	1975.44	1.50	2.46	614.49	224.56	15.58	16.82	228.04	249.12
Ave.	30.47	24.88	2582.03	4448.10	2.64	3.04	700.88	591.01	9.20	14.77	252.94	452.75

Table 1. Continued.

Stations	Cu				Pb				Cd			
	D		P		D		P		D		P	
	S	B	S	B	S	B	S	B	S	B	S	B
I	2.32		100.00		8.49		526.92		0.04		42.31	
II	4.19		116.36		9.65		3509.09		0.19		14.55	
III	3.36	6.03	123.89	166.15	10.50	6.34	120.35	353.85	0.00	0.13	35.40	46.15
IV	6.54	3.07	90.48	107.94	5.15	5.02	580.95	1990.48	0.00	0.00	14.29	28.57
V	2.04	2.13	95.24	106.12	7.50	6.50	2380.95	453.06	0.00	0.10	41.27	20.41
VI	2.57	7.77	106.06	489.41	10.21	26.39	106.06	938.82	0.00	0.64	30.30	11.76
VII	3.92	3.51	130.91	244.16	8.06	9.21	109.09	246.75	0.27	0.16	32.73	33.77
VIII	4.48	2.21	164.49	101.75	7.70	7.71	635.51	438.60	0.07	0.00	59.81	14.04
Ave.	3.68	4.12	115.93	202.59	8.41	10.19	996.12	736.93	0.07	0.17	33.83	25.78

Table 2. Distribution of dissolved and particulate heavy metals in surface and bottom in autumn at El-Mex Bay.

Stations	Fe				Mn				Zn			
	D		P		D		P		D		P	
	S	B	S	B	S	B	S	B	S	B	S	B
I	16.89		9802.23		1.21		551.94		15.17		891.56	
II	13.40		9913.13		4.87		231.03		18.72		907.04	
III	14.18	15.38	8980.79	9009.89	0.90	23.50	947.13	327.23	4.25	35.08	405.73	805.10
IV	11.86	11.36	8169.81	7896.30	10.85	18.51	165.00	740.74	21.46	15.40	181.13	642.96
V	10.94	11.05	9910.48	8555.84	6.61	31.51	409.85	257.14	16.10	13.32	984.98	400.00
VI	17.83	25.32	8180.36	8927.90	8.47	9.52	107.14	365.64	19.48	24.40	187.50	403.26
VII	18.51	16.23	9427.89	7099.54	3.15	15.42	506.82	197.26	14.36	17.48	151.93	471.23
VIII	9.96	10.85	9953.94	6490.20	1.00	13.28	206.74	423.53	22.02	17.15	743.47	596.08
Ave.	14.20	15.03	9292.33	7996.61	4.63	18.62	390.71	385.26	16.45	20.47	556.67	553.11

Table 2. Continued.

Stations	Cu				Pb				Cd			
	D		P		D		P		D		P	
	S	B	S	B	S	B	S	B	S	B	S	B
I	4.63		372.87		0.00		506.20		0.00		3.88	
II	5.32		308.21		2.00		556.45		0.37		4.17	
III	3.36	9.88	189.78	768.19	0.58	2.87	35.99	1586.99	0.00	0.07	9.82	2.89
IV	4.21	3.41	358.49	773.33	1.03	1.35	139.62	557.04	0.00	0.00	22.64	17.78
V	5.19	4.66	509.36	418.18	13.65	1.50	786.21	376.62	0.02	0.07	17.73	20.78
VI	2.70	6.27	100.00	335.55	2.58	13.42	66.07	133.42	0.28	0.15	10.71	2.76
VII	3.07	###	93.77	396.35	3.61	2.59	34.42	3.65	0.00	0.11	9.50	25.57
VIII	3.79	3.35	423.97	368.63	0.00	1.70	848.69	613.73	0.00	0.00	5.99	17.65
Ave.	4.03	6.46	294.56	510.04	2.93	3.90	371.71	545.24	0.08	0.07	10.56	14.57

Table 3. Distribution of dissolved and particulate heavy metals in surface and bottom in winter at El-Mex Bay.

Stations	Fe				Mn				Zn			
	D		P		D		P		D		P	
	S	B	S	B	S	B	S	B	S	B	S	B
I	8.14		9844.03		1.81		961.47		8.323		752.5	
II	9.25		9628.11		0.45		873.04		3.222		725.7	
III	11.21	11.80	8965.52	7250.79	0.58	0.33	865.71	1200.00	9.644	11.11	951.7	981
IV	10.46	11.07	5963.64	8997.51	1.05	0.88	828.57	980.91	7.192	12.02	462.3	977.6
V	10.61	13.23	4820.45	2341.46	1.58	2.13	900.00	813.01	2.595	6.702	236.4	328.5
VI	7.71	8.12	8370.97	9790.14	0.46	0.89	908.64	965.02	2.738	1.637	774.2	278.3
VII	9.08	9.67	9871.83	7461.45	1.72	0.32	424.64	822.94	5.455	6.653	770	891.9
VIII	17.71	9.39	3154.20	2621.78	0.50	1.72	873.28	843.56	2.653	2.373	262.6	467.3
Ave.	10.52	10.54	7577.34	6410.52	1.02	1.05	829.42	937.57	5.228	6.749	616.9	654.1

Table 3. Continued.

Stations	Cu				Pb				Cd			
	D		P		D		P		D		P	
	S	B	S	B	S	B	S	B	S	B	S	B
I	1.9		271.2		0.45		732.2		0		81.4	
II	1.9		117.1		0		182.9		0		34.3	
III	1.9	2	110.3	139.7	1.59	2.14	124.1	714.3	0	0	73.6	54
IV	1.9	2.8	116.9	151	2.53	4.03	106.5	717	0	0	33.8	19.9
V	1.6	1.7	113.9	117.1	0	3.42	4.545	933.3	0	0	29.5	39
VI	2.2	1.4	103.2	148.4	0.38	0.31	896.8	662	0	0	83.9	9.28
VII	2.3	2.8	102.3	149.7	0	1.32	290.4	415.6	0	0	19.6	33.5
VIII	1.5	1.6	100.8	114.9	0.03	0.94	210.7	625.7	0	0	51.9	67.3
Ave.	1.9	2.1	129.5	136.8	0.62	2.02	318.5	678	0	0	51	37.2

Table 4. Distribution of dissolved and particulate heavy metals in surface and bottom in spring at El-Mex Bay.

Stations	Fe				Mn				Zn			
	D		P		D		P		D		P	
	S	B	S	B	S	B	S	B	S	B	S	B
I	9.20		2550.54		114.23		959.14		12.78		365.59	
II	24.30		9519.19		169.43		116.46		8.98		668.35	
III	5.82	7.05	4480.00	9174.57	2.52	2.51	956.80	975.38	3.63	4.90	336.00	463.72
IV	7.68	6.85	3050.00	9558.06	7.04	1.68	278.00	589.47	8.87	11.03	198.00	705.26
V	6.01	6.85	4461.54	5589.29	1.14	1.60	1147.25	1010.71	4.75	6.85	694.51	442.86
VI	9.36	12.86	1524.53	6660.47	10.28	4.09	1116.98	570.54	8.14	12.05	397.48	468.22
VII	11.43	6.16	5202.99	9480.00	50.26	7.45	1008.55	1200.00	11.93	4.64	397.01	571.43
VIII	6.52	5.42	6609.17	3608.79	1.82	2.18	967.60	298.90	16.60	14.65	583.49	232.97
Ave.	10.04	7.53	4674.74	7345.20	44.59	3.25	818.85	774.17	9.46	9.02	455.05	480.74

Table 4. Continued.

Stations	Cu				Pb				Cd			
	D		P		D		P		D		P	
	S	B	S	B	S	B	S	B	S	B	S	B
I	3.17		236.56		0.00		1148.39		0.25		51.6	
II	2.41		400.00		0.00		339.24		0.26		40.5	
III	1.61	2.42	108.80	99.12	0.00	0.00	364.80	0.00	0.12	0.09	67.2	17.7
IV	1.84	2.28	110.00	143.86	0.00	0.00	0.00	0.00	0.10	0.04	16	42.1
V	2.14	2.09	127.47	110.71	0.00	0.00	272.53	1121.43	0.44	0.05	61.5	32.1
VI	2.49	2.15	95.60	93.02	0.00	0.00	588.68	136.43	0.14	0.02	32.7	18.6
VII	2.43	1.71	95.52	97.14	0.00	0.00	405.97	0.00	0.18	0.12	56.7	62.9
VIII	1.83	2.05	106.42	109.89	0.00	0.00	0.00	540.66	0.10	0.05	47.7	44
Ave.	2.24	2.12	160.05	108.96	0.00	0.00	389.95	299.75	0.20	0.06	46.7	36.2

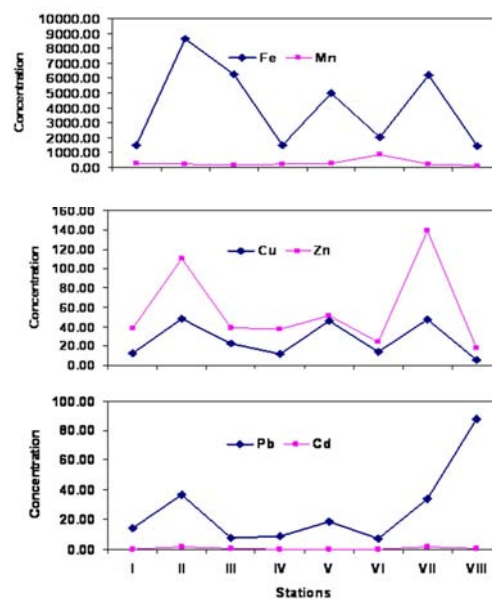
Fig. 2. Trace metals concentration (Fe, Mn, Cd, Cu, Pb and Zn) ($\mu\text{g/g}$) in El-Mex, Bay sediments during 2012.

Table 5. Bioavailability of trace metals in El-Mex Bay water during 2012-2013.

Metals	Seasons	Stations															
		I		II		III		IV		V		VI		VII		VIII	
		S	S	S	B	S	B	S	B	S	B	S	B	S	B		
Fe	S	0.40	1.93	1.35	0.54	1.80	0.54	1.86	0.37	1.76	0.78	2.86	0.46	0.26	0.24		
	A	0.21	0.14	0.08	0.08	0.09	0.09	0.09	0.16	0.10	0.30	2.89	0.21	0.08	0.17		
	W	0.03	0.04	0.12	0.16	0.18	0.10	0.22	0.56	0.07	0.07	0.08	0.13	0.56	0.51		
	Sp	0.36	0.25	0.13	0.08	0.25	0.07	0.13	0.12	0.61	0.19	0.22	0.06	0.10	0.15		
	Min.	0.03	0.04	0.08	0.08	0.09	0.07	0.09	0.12	0.07	0.07	0.08	0.06	0.08	0.15		
Max.	0.40	1.93	1.35	0.54	1.80	0.54	1.86	0.56	1.76	0.78	2.89	0.46	0.56	0.51			
Cu	S	2.27	3.48	2.64	3.50	6.74	2.77	2.10	1.97	2.37	1.56	2.91	1.42	2.65	2.13		
	A	13.95	18.31	1.74	1.27	1.12	0.98	1.66	1.33	0.53	1.48	0.85	1.43	0.89	0.90		
	W	0.69	2.06	2.82	1.40	4.31	1.85	41.77	0.36	2.08	0.97	2.58	1.86	0.36	0.29		
	Sp	1.94	2.47	1.49	5.65	6.25	2.38	1.63	3.11	3.06	5.38	1.76	1.59	2.10	2.28		
	Min.	0.69	2.06	1.49	1.27	1.12	0.98	1.63	0.36	0.53	0.97	0.85	1.42	0.36	0.29		
Max.	13.95	18.31	2.82	5.65	6.74	2.77	41.77	3.11	3.06	5.38	2.91	1.86	2.65	2.28			
Mn	S	1.03	0.25	0.12	0.27	0.10	0.40	1.31	0.24	0.41	1.81	0.22	0.27	0.24	1.08		
	A	1.11	0.95	0.05	6.70	1.93	3.30	2.78	7.78	2.02	3.57	6.50	2.04	0.48	3.04		
	W	0.05	0.01	0.02	0.03	0.13	0.09	0.08	0.26	0.01	0.03	0.11	0.02	0.06	0.20		
	Sp	10.64	59.26	0.26	0.26	2.47	0.28	0.10	0.16	0.91	0.71	4.74	0.62	0.19	0.72		
	Min.	0.05	0.01	0.02	0.03	0.10	0.09	0.08	0.16	0.01	0.03	0.11	0.02	0.06	0.20		
Max.	10.64	59.26	0.26	6.70	2.47	3.30	2.78	7.78	2.02	3.57	6.50	2.04	0.48	3.04			
Zn	S	4.68	5.72	3.98	2.98	0.58	4.53	3.99	2.61	5.51	2.37	1.82	2.84	6.40	6.33		
	A	7.48	10.97	1.04	2.33	1.98	2.54	1.03	2.79	1.56	5.75	7.35	2.65	1.06	2.80		
	W	1.09	0.44	1.00	1.12	1.53	0.56	1.09	2.00	0.35	0.58	0.70	0.63	1.00	0.51		
	Sp	3.38	1.33	1.07	1.05	4.29	1.54	0.68	1.52	2.01	2.51	2.92	0.81	2.77	5.92		
	Min.	1.09	0.44	1.00	1.05	0.58	0.56	0.68	1.52	0.35	0.58	0.70	0.63	1.00	0.51		
Max.	7.48	10.97	3.98	2.98	4.29	4.53	3.99	2.79	5.51	5.75	7.35	2.84	6.40	6.33			
Cd	S	0.09	1.29	0.00	0.28	0.00	0.00	0.00	0.47	0.00	5.16	0.82	0.47	0.12	0.00		
	A	0.00	3.73	0.00	2.27	0.00	0.00	0.44	0.21	1.57	0.73	0.00	0.60	0.00	0.00		
	W	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00		
	Sp	0.47	0.65	0.17	0.51	0.62	0.10	0.71	0.15	0.42	0.12	0.31	0.20	0.21	0.12		
	Min.	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00		
Max.	0.47	3.73	0.17	2.27	0.62	0.10	0.71	0.47	1.57	5.16	0.82	0.60	0.21	0.12			
Pb	S	1.59	0.27	8.02	1.76	0.88	0.25	0.31	1.41	8.78	2.73	6.88	3.60	1.20	1.73		
	A	0.00	5.49	1.58	0.18	0.20	0.25	2.39	0.42	0.33	3.44	2.52	0.46	0.00	0.28		
	W	0.06	0.00	1.26	0.30	2.32	0.56	0.00	0.36	0.04	0.05	0.00	0.32	0.02	0.15		
	Sp	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00		
	Min.	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00		
Max.	1.59	5.49	8.02	1.76	2.32	0.56	2.39	1.41	8.78	3.44	6.88	3.60	1.20	1.73			

Table 6. Log values of the partition coefficients (Kd) of trace metals in El-Max Bay water during 2012-2013.

Metals	Seasons	Stations															
		I		II		III		IV		V		VI		VII		VIII	
		S	S	S	B	S	B	S	B	S	B	S	B	S	B		
Fe	S	5.40	4.71	4.86	5.27	4.74	5.26	4.72	5.43	4.75	5.10	4.53	5.34	5.59	5.62		
	A	5.69	5.85	6.11	6.08	6.06	6.02	6.06	5.78	5.99	5.53	4.53	5.69	6.07	5.78		
	W	6.51	6.44	5.90	5.79	5.76	5.98	5.66	5.25	6.18	6.13	6.12	5.89	5.25	5.29		
	Sp	5.44	5.59	5.89	6.11	5.60	6.14	5.87	5.91	5.21	5.71	5.66	6.19	6.01	5.82		
	Min.	5.40	4.71	4.86	5.27	4.74	5.26	4.72	5.25	4.75	5.10	4.53	5.34	5.25	5.29		
Max.	6.51	6.44	6.11	6.11	6.06	6.14	6.06	5.91	6.18	6.13	6.12	6.19	6.07	5.82			
Cu	S	4.63	4.44	4.57	4.44	4.14	4.55	4.67	4.70	4.62	4.80	4.52	4.84	4.56	4.66		
	A	3.79	3.65	4.75	4.89	4.95	5.00	4.77	4.87	5.28	4.82	5.07	4.84	5.05	5.04		
	W	5.16	4.68	4.54	4.85	4.35	4.73	3.14	5.44	4.67	5.01	4.58	4.72	5.45	5.53		
	Sp	4.21	4.23	4.62	3.86	3.94	4.27	4.46	4.19	4.12	3.94	4.37	4.56	4.42	4.33		
	Min.	3.79	3.65	4.54	3.86	3.94	4.27	3.14	4.19	4.12	3.94	4.37	4.56	4.42	4.33		
Max.	5.16	4.68	4.75	4.89	4.95	5.00	4.77	5.44	5.28	5.01	5.07	4.84	5.45	5.53			
Mn	S	4.98	5.60	5.90	5.57	5.99	5.40	4.88	5.62	5.38	4.74	5.65	5.57	5.61	4.96		
	A	4.95	5.02	6.28	4.14	4.71	4.47	4.54	4.07	4.68	4.43	4.16	4.68	5.32	4.50		
	W	6.29	6.84	6.60	6.56	5.90	6.05	6.07	5.58	7.29	6.56	5.96	6.60	6.24	5.69		
	Sp	3.92	2.84	5.58	5.59	4.60	5.54	6.00	5.80	5.04	5.14	4.30	5.21	5.73	5.14		
	Min.	3.92	2.84	5.58	4.14	4.60	4.47	4.54	4.07	4.68	4.43	4.16	4.68	5.32	4.50		
Max.	6.29	6.84	6.60	6.56	5.99	6.05	6.07	5.80	7.29	6.56	5.96	6.60	6.24	5.69			
Zn	S	4.31	4.22	4.38	4.51	5.23	4.32	4.38	4.57	4.23	4.62	4.73	4.53	4.17	4.17		
	A	4.09	3.91	4.98	4.62	4.70	4.58	4.98	4.54	4.80	4.21	4.10	4.57	4.97	4.54		
	W	4.96	5.35	4.99	4.95	4.81	5.25	4.96	4.69	5.45	5.23	5.15	5.19	5.00	5.29		
	Sp	4.46	4.87	4.97	4.98	4.35	4.81	5.16	4.81	4.69	4.59	4.52	5.09	4.55	4.20		
	Min.	4.09	3.91	4.98	4.62	4.70	4.58	4.98	4.54	4.80	4.21	4.10	4.57	4.97	4.54		
Max.	4.96	5.35	4.99	4.95	4.81	5.25	4.96	4.69	5.45	5.23	5.15	5.19	5.00	5.29			

Metals	Seasons	Stations															
		I		II		III		IV		V		VI		VII		VIII	
		S	S	S	B	S	B	S	B	S	B	S	B	S	B		
Min.		4.09	3.91	4.38	4.51	4.35	4.32	4.38	4.54	4.23	4.21	4.10	4.53	4.17	4.17		
Max.		4.96	5.35	4.99	4.98	5.23	5.25	5.16	4.81	5.45	5.23	5.15	5.19	5.00	5.29		
	S	6.02	4.88	0.00	5.56	0.00	0.00	0.00	5.33	0.00	4.26	5.08	5.32	5.93	0.00		
	A	0.00	4.41	0.00	4.63	0.00	0.00	5.36	5.67	4.80	5.13	0.00	5.22	0.00	0.00		
	W	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00		
	Sp	5.32	5.19	5.76	5.29	5.20	6.00	5.14	5.83	5.38	5.92	5.51	5.71	5.67	5.91		
Min.		0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00		
Max.		6.02	5.19	5.76	5.56	5.20	6.00	5.36	5.83	5.38	5.92	5.51	5.71	5.93	5.91		
	S	4.79	5.56	4.06	4.75	5.05	5.60	5.50	4.84	4.02	4.55	4.13	4.43	4.92	4.76		
	A	0.00	4.24	4.80	5.74	5.69	5.60	4.61	5.37	5.48	4.45	4.59	5.33	0.00	5.56		
	W	6.21	0.00	4.89	5.52	4.62	5.25	0.00	5.44	6.38	6.32	0.00	5.50	6.81	5.82		
	Sp	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00		
Min.		0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00		
Max.		6.21	5.56	4.89	5.74	5.69	5.60	5.50	5.44	6.38	6.32	4.59	5.50	6.81	5.82		

Table 7. Enrichment factors of heavy metals in El-Mex Bay sediments of investigated area during September 2012.

St. No	EF _{Mn}	EF _{Pb}	EF _{Cu}	EF _{Cd}	EF _{Zn}
I	9.54	16.48	9.32	9.81	7.12
II	1.45	7.65	6.27	31.22	3.62
III	1.55	2.21	4.00	16.66	1.76
IV	8.63	10.29	8.76	20.17	7.13
V	2.76	6.75	10.34	2.99	2.89
VI	20.98	6.25	7.59	7.27	3.27
VII	1.78	9.80	8.61	40.85	6.30
VIII	5.68	108.33	4.38	51.58	3.41
Ave.	6.55	20.97	7.41	22.57	4.44
Background value*	720	20	32	0.2	127

*Martin and Meybeck

3.6. Statistical Analysis

i. Applications of Principal Component Analysis

Principle component analysis (PCA) has been effectively applied to the assessment of water quality during the period of study [42, 43].

Principal component analysis (PCA) is generally employed to reduce the dimensionality of the dataset while attempting to preserve the relationships present in the original data (SPSS version 18) [6, 41, 44]. It was applied for multivariate data derived from the water quality parameters analysis of seasonal average of surface and bottom water samples for four seasons at El-Mex Bay as shown in Table 8. The output data revealed that four factors (PC1, PC2, PC3 and PC4) affected water parameters with cumulative covariance of 93.13%. The covariances of four component factors are 29.33%, 26.57%, 21.92% and 15.32%, respectively for PC1, PC2, PC3 and PC4. PC1 represented positive loading to OOM (0.489). PC2 (26.57%) represented positive loading for temperature (0.969), D-Fe (0.967), D-Pb (0.876), P-Pb (0.843) associated with negative loading for pH (-0.858), P-Fe (-0.811) and P-Zn (-0.834). PC3 represented positive loading for D-Cu (0.912), D-Zn (0.977) and P-Cu (0.921) associated with negative loading for P-Mn (-0.966) and P-Cd (-0.922). PC4 represented positive loading for D-Mn (0.921) associated with negative loading for D-Cd (-0.786), while analysis of 8 sediment samples of El-Mex Bay

as represented in Table 9. The output data revealed that three factors PC1, PC2 and PC3 affected sediment parameters with cumulative covariance of 91.84%. The variances for PC1, PC2 and PC3 are 60.93%, 17.70% and 13.21%, respectively. PC1 represented positive loading for Cu 0.942, Zn 0.899, Cd 0.783, Fe 0.826, TOC 0.956 and TOM 0.956, while associated with negative loading for CaCO₃ -0.813. PC2 represented positive loading for Mn 0.896. PC3 represented positive loading for Pb 0.952.

ii. Water Quality Index (WQI)

Assessment of water quality can be a complex process undertaking multiple parameters capable of causing various stresses on overall water quality. To evaluate water quality from a large number of samples, each containing concentrations for many parameters is difficult but there is different approaches to calculate water quality like statistical analysis of individual parameter, multi-stressors water quality index, etc have been considered. Numerous water quality index has been formulated all over the world which can easily judge out the overall water quality within a particular area promptly and efficiently [45]. Water Quality Index (WQI) is calculated according to the following formula [41, 46, 47]

$$WQI = \sum_{n=1}^n (\lambda_n / \sum \lambda) \times PC_n \quad (1)$$

Where: n: The number of effective components, λ_n : are the Eigenvalue of the effective components, $\sum \lambda$: sum of the Eigenvalues and PC_n the principal component factor scores. High values of principal component factor scores mean that this station is considered as a hot spot. According to PCA data, Station I and III could be considered as hot spots. The PC1 and PC2 highly affected on pollution of station I and for station III the PC1 and PC3 are affected (Table 10).

iii. Sediment Quality Index (SQI)

Sediment Quality Index (SQI) is calculated by the same equation (1). High values of principal component factor scores mean that this station is from hot spots. According to PCA data, Stations II and VII could be considered as hot spots. The PC1 highly affected on pollution of stations II and VII, as shown in Table 10.

Table 8. Varimax rotated component loading matrix for seasonal average water analysis parameters of El-Mex Water.

Parameters	Component			
	PC1	PC2	PC3	PC4
pH	-0.380	-0.858	-0.297	0.089
T °C	-0.152	0.969	-0.028	0.025
OOM	0.489	-0.054	-0.300	0.797
D-Fe	0.021	0.967	0.189	-0.160
D-Mn	-0.031	-0.148	0.092	0.921
D-Cu	-0.092	0.251	0.912	-0.079
D-Pb	-0.159	0.876	0.291	-0.264
D-Cd	-0.195	0.367	0.195	0.786
D-Zn	-0.152	0.073	0.977	0.082
P-Fe	0.215	-0.811	0.428	-0.255
P-Mn	-0.130	-0.129	-0.966	0.012
P-Cu	-0.023	-0.184	0.921	-0.003
P-Pb	-0.262	0.843	-0.008	-0.262
P-Zn	0.052	-0.834	0.056	-0.339
P-Cd	0.158	-0.098	-0.922	0.189
Variance	29.33	26.57	21.92	15.32
CV (%)	29.33	55.89	77.81	93.13

CV: cumulative variance

Table 9. Varimax rotated component loading matrix for sediment analysis of El-Mex water.

Parameters	PC1	PC2	PC3
Pb	0.004	-0.212	0.952
Mn	-0.038	0.896	-0.266
Cu	0.942	-0.156	-0.129
Zn	0.899	-0.241	0.059
Cd	0.783	-0.411	0.229
Fe	0.826	-0.429	-0.209
TOC%	0.956	0.240	0.087
CaCO ₃ %	-0.813	0.442	0.281
Variance	60.93	17.7	13.21
CV (%)	60.93	78.63	91.84

Table 10. Principal component factor scores, water quality index (WQI) and sediment quality index (SQI) in El-Mex Bay.

St	Name	Latitude	Longitude	PC1	PC2	PC3	PC4	WQI	PC1	PC2	PC3	SQI
I	El-Umum Drain	31° 9' 4.86"	29° 50' 31.77"	0.367	1.954	-0.4	-0.18	0.588	-0.86	-0.04	-0.32	-0.64
II	In front of El-umum drain	31° 9' 8.28"	29° 50' 26.44"	-0.77	1.159	0.3	-0.26	0.093	1.413	-0.38	0.283	0.938
III	Petrochemical company	31° 8' 34.188"	29° 49' 44.36"	0.967	-0.34	1.269	-0.03	0.496	-0.49	-1.46	-1.33	-0.77
IV	The Western Harbor	31° 9' 48.92"	29° 50' 59.67"	-0.36	-0.48	1.719	-0.12	0.074	-0.87	-0.02	-0.32	-0.64
V	In front of western harbor	31° 10' 23.37"	29° 51' 0.00"	1.768	-0.63	-0.93	-0.74	0.127	0.523	0.353	-0.38	0.384
VI	Far 500 m from station 4	31° 9' 53.35"	29° 49' 22.33"	-1.03	-0.64	-0.82	-1	-0.87	-0.17	2.109	-0.45	0.235
VII	El-Dekhila port	31° 9' 17.38"	29° 48' 20.44"	0.062	-0.22	-0.54	2.311	0.194	1.421	-0.25	0.405	0.982
VIII	Far 1200 m from station 4	31° 10' 29.85"	29° 48' 22.93"	-1.01	-0.8	-0.59	0.011	-0.7	-0.97	-0.31	2.108	-0.48

4. Conclusion

El-Mex Bay is a part of Alexandria coast on the Mediterranean Sea. It is subjected to effluents contaminated with several anthropogenic materials including trace metals. One of these effluents is called Umum agricultural drain (rate

8x106 m3/d). The trace metals (Fe, Mn, Cu, and Cr) in their dissolved, particulate and sediments were determined seasonally in El-Mex Bay. The determination of the dissolved forms was made using chelating cation exchange resin (Chelex-100).

The results of the present study showed that El-Mex Bay sediments were highly enriched in Cd and significantly

enriched in Pb. Moreover, they were at contamination level overcome the background of Oceanic concentration (WQC) but were still lower than the hazardous one. principal component analysis (PCA) was applied, the results revealed the PC1 and PC2 highly affected on pollution of station I and for station III.

References

- [1] Bruland K. W. and Lohan M. C. (2003) Controls of Trace Metals in Seawater Volume 6; Published by Elsevier Ltd. (ISBN: 0-08-044341-9); pp. 23–47.
- [2] Tessier. A. and Campbell. P. (1988). Partitioning of trace metals in sediments. In: Kramer J. R., Allen H. E. (Eds.), Metal speciation: Theory, Analysis and application, Lewis publishers, Chelsea, MI, USA.
- [3] Buckley. D. E., Smith. J. N. and Winters. G. V. (1995). Accumulation of contaminant metals in marine sediments of Halifax Harbour. Nova Scotia: environmental factors and historical trends. *Applied Geochemistry*, 10: 175-195.
- [4] Islam. M. S. and Tanaka. M. (2004). Impacts of pollution on coastal and marine ecosystems including coastal and marine fisheries and approach for management: a review and synthesis. *Marine Pollution Bulletin* 48: 624-649.
- [5] Shaltout. N. A. (2008). Inorganic Carbon Cycle of Alexandria Coastal water. Ph. D. Thesis, Alexandria university, faculty of science.
- [6] Abdel-Rhman. M. Kh. (2013). Distribution of Nutrient Salts in hot spot areas at El-Mex Bay (Egyptian Mediterranean Sea) In relation to physicochemical parameters. Ms. c Thesis. Fac. Sc., Alex. Univ.
- [7] Mahamoud. Th. H., Masoud. M. S., Shaltout. N. A. (2008). Physico- chemical characteristics of different water type in El-Mex Bay, Alexandria, Egypt.
- [8] Said. M. A., El-Deek. M. S., Mahmoud. Th. H. and Shriadah. M. A. (1994). Effect of pollution on the hydrochemical characteristics of different water types in El-Max Bay area, west of Alexandria, Egypt. *Acta Adriatica*, 34 (1/2): 9-19.
- [9] Tayel. F. T., Fahmy. M. A. and shriadah. M. A. (1996). Studies of physicochemical characteristic of el-mex bay and new dekhela harbor of Alexandria. *bull. Nat. inst. Oceanogr&fish.*, A. R. E., 22: 1-18.
- [10] Lores E, Pennock J. 1998. The effect of salinity on binding of Cd, Cr, Cu and Zn to dissolved organic matter, *Chemosphere*, 37: 861-874.
- [11] Abd-Alla. A. M. (2007). Speciation of Trace Metals in Coastal Sediments of El-MexBay South Mediterranean Sea–West of Alexandria (Egypt). *Environ Monit Assess*, 132:111–123.
- [12] Riley, J. P. and Taylor, D. (1968). Chelating resins for the concentration of trace elements from sea water and their analytical use in conjunction with atomic absorption spectrophotometry. *Analy. Chem. Acta*, 40: 479–485.
- [13] Abdullah, M. I, and Royle L. G. (1974): A study of the dissolved and particulate trace elements in the Bristol Channel. *J. Mar. Biol. Ass. UK*. 54: 581-597.
- [14] UNEP/IAEA (1986): Reference methods for marine pollution studies, No. 39, 6.
- [15] Folk. R. L. (1974). Petrography of sedimentary rocks. Univ. Texas, Hemphill, Austin, Tex., 182.
- [16] Gaudette. H. E. and Flight. W. R. (1974). An inexpensive titration method for the determination of organic carbon in recent sediments. *Journal of sedimentary petrology*. 44 (1), 249-253.
- [17] Molina. B. F. (1974). A rapid and accurate method for the analysis of calcium carbonate in small samples. *J. Sed. Petrol.*, 44(2): 589-590.
- [18] Oregioni. B. and Aston. S. R. (1984). The determination of selected trace metals in marine sediments by flame atomic absorption spectrophotometry. IAEA Monaco Laboratory Internal Report. UNEP, reference methods for marine pollution studies, 38.
- [19] Tiemann. K. J., Gardea-Torresdey. J. L., Gamez. G., Dokken. K., Cano-Aguilera. I., Renner. M. W. and Furenlid. L. R. (2000). Effects of oxidation state on metal ion binding by *Medicago sativa* (alfalfa): Atomic and X-ray absorption spectroscopic studies with Fe(II) and Fe(III). *Environ. Sci. Technol.*, 34(4), 693–698.
- [20] Chester, R. (1990). *Marine geochemistry*. Academic Press, London, 346-42.
- [21] Horsburgh. M. J., Wharton. S. J., Karavolos. M., Foster. S. J. (2002). Manganese: elemental defense for a life with oxygen. *Trends in Microbiology* 10(11), 496–501.
- [22] Kernen. N., Kidd. M. J., Penner-Hahn. J. E., Pakrasi. H. B. (2002). A light dependent mechanism for massive accumulation of manganese in the photosynthetic bacterium *Synechocystis* sp. PCC 6803. *Biochemistry* 41 (50), 15085–15092.
- [23] Satarug. S., Baker. J. R., Urbenjapol. S., Haswell-Elkins. M., Reilly. P. E. B., Williams. D. J. and Moore. M. R. (2003). A global perspective on cadmium pollution and toxicity in non-occupationally exposed population. *Toxicol. Lett.*, 137, 65–83.
- [24] Kazuo. A. (2007). Concentration Level of Dissolved Cadmium and Its Variation in Surface Seawater of Urasoko Bay, Ishigaki Island. *journal of Oceanography*, 63: 341-347.
- [25] Bennet-Chambers. M., Davies. P and Knott. B. (1999). Cadmium in aquatic ecosystems in Western Australia: A legacy of nutrient-deficient soils. *J. Environ. Manage.* 57, 283.
- [26] Kavarsj. A. and Das. S., (1999). Effect of fertilization on the deposition, partitioning and bioavailability of copper, zinc and cadmium in four perennial ponds of an industrial town. *Ind. J. Environ. Health*, 41:6-15.
- [27] Nayak B. M., Ramakrishna. S., Jayaprakash, and Delvi M. R. (2009). Impact of heavy metals on water, fish (*Cyprinus carpio*) and sediments from a water tank at Tumkur, India, *International Journal of Oceanography and Hydrobiology*, 2:17-28.
- [28] Luoma. S. N. (1983). Bioavailability of trace metals to aquatic organisms—A review: *The Science of the Total Environment*, 28: 1-22.
- [29] Luoma. S. N. (1989). Can we determine the biological availability of sediment-bound trace elements?: *Hydrobiologia*. 176/177: 379-396.

- [30] Allen. H. E, Chen. Y, Y. Li, Huang. C. P and Sanders. P. F. (1995). Soil partition coefficients by column desorption and comparison to batch adsorption measurements. *Environmental Science and Technology*, 29(8): 1887-1891.
- [31] EPA. (2005). Partition coefficients for metals in surface water, soil and waste.
- [32] Abd-Alla. A. M. (2008). Trace Metal Behavior in Mediterranean-Climate Coastal Bay:El-Mex Bay, Egypt and its Coastal Environment. *Global Journal of Environmental Research*, 2(1): 23-29.
- [33] El Zokm. M. G, El-Gohary. S and Abd-El-Khalek. D. E. (2012). Studies of some heavy metals in water and sediment in El-Max fish farm, Egypt. *World Applied Sciences Journal* 18 (2): 171-180.
- [34] Bowen. H. J. M. (1979). *Environmental Chemistry of the Elements*. Academic Press, London.
- [35] Usero. J., Gonzales-Regalado. E. and Gracia. I. (1997). Trace metals in bivalve molluscs *Ruditapes' decussatus* and *Ruditapes philippinarum* from the Atlantic Coast of southern Spain *Environ, Int.*, 23: 291-298.
- [36] Gong. Q. and Deng. J. (2008). Calculating pollution indices by heavy metals in ecological geochemistry assessment and a case study in parks of Beijing. *Journal of China University of Geosciences*, 19(3):230–241.
- [37] Martin. J. M and Meybek M. (1979). Elemental mass balance of material carried by major world rivers. *Marine Chemistry* 7: 173-206.
- [38] Zhang. L., Ye. X., Feng. H., Jing. Y., Ouyang. T., Yu. X., Liang. R., Gao. C. and Chen. W. (2007). Heavy metal contamination in western Xiamen Bay sediments and its vicinity, China. *Marine Pollution Bulletin*, 54: 974–982.
- [39] Ergin. M., Saydam. C., Basturk. O., Erdem. E. and Yoruk. R. (1991). Heavy metal concentrations in surface sediments from the two coastal inlets (Golden Horn Estuary and Izmit Bay) of the Northeastern Sea of Marmara. *Chemical Geology* 91: 269–285.
- [40] Sutherland. R. A., (2000). Bed Sediment-Associated Trace Metals in an Urban Stream, Oahu, Hawaii. *Environmental Geology*, 39: 611–627.
- [41] El Zokm. M. G. (2010). Speciation of heavy metals along Egyptian red sea coastal. Ph. D. thesis. Chem. Dep. Fac. Sci., Alex. Univ.
- [42] Ouyang. Y., Nkedi-Kizza. P., Wu. Q. T., Shinde. D. and Huang. C. H. (2006). Assessment of seasonal variations in surface water quality. *Water Res.* 40, 3800-3810.
- [43] Zhou. F., Guo. H. C., Liu. Y. (2007b). Chemo metrics data analysis of marine water quality and source identification in southern Hong Kong. *Mar. Pollut. Bull.* 54, 745-756.
- [44] Mil-Homens. M., Branco. V., Lopes. C., Vale. C., Abrantes. F., Boer. W. and Vicente M. (2009). Using factor analysis to characterise historical trends of trace metal contamination in a sediment core from the tagus prodelta, water, air and soil pollution, 197: 277-287.
- [45] Bharti. N, Katyal. D. (2011). Water quality indices used for surface water vulnerability assessment. *International Journal of Environmental Sciences*.2(1).
- [46] Davis. J. C. (1986). *Statistics and Data Analysis in Geology*. John Wiley and Sons. Inc., New York.
- [47] El-Iskandarani. M., Nasr. S., Okabh. M. and Jensen. A. (2004). Principal component analysis for quality assessment of the Mediterranean costal water of Egypt. *Association for the advancement of modeling and simulation Techniques in Enterprises (AMSE)*, 65 (2): 69-83.
- [48] Saleh. Sh. M. K. (2006). Environmental assessment of heavy metals pollution in bottom sediments from the Gulf of Aden, Yamen. Ph. D. Thesis, Institute of Graduate Studies and Research, Alex. Univ, Egypt.1500.