

HEAVY METALS ACCUMULATION IN SEDIMENTS OF ALEXANDRIA COASTAL AREAS

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ABSTRACT: The concentrations of organic matter, carbonate, total phosphorus, major cations (calcium, magnesium, sodium and potassium) and some heavy metals (iron, manganese, zinc, copper, cadmium, cobalt, lead, nickel, chromium, aluminum and tin) were determined for sediment samples collected from near shore stations on Alexandria coast during summer 2004. The results showed that the concentrations of the major cations were in the order: Ca > Mg > Na > K. The high levels of heavy metals were recorded at regions which receive high effluents from brackish land based effluents.

Keywords: Sediment analysis, Alexandria coast.

Introduction

There is evidence that, in some coastal areas of the Mediterranean Sea the input of eutrophying substances, particularly phosphorus, nitrogen and organic matter, leads to significant alterations in the natural ecosystem. There is a shipyard which gives an additional source of trace elements to the coast. Alexandria coast is affected by brackish water especially at El-Mex region⁽¹⁾. Alexandria is the second largest city and one of the most important industrial centers in Egypt, where about 40% of the country's industries are localized⁽²⁾. The pollution quantity of the industrial waste effluents during the year 1994 at Alexandria was about 82800m³/day, however, the suspended matter was 244 ton/day⁽³⁾. Many chemical studies on Alexandria coast sediments have been reviewed by several authors⁽⁴⁻⁹⁾. The aim of the present study is to establish the levels of some heavy metals and major cations beside organic matter, carbonate and total phosphorus in sediment samples collected from Alexandria coast.

Material and Methods

Sampling

Five surface sediments were collected during August (2004) from (El-Montazah, Gleem, El-Shatbi, El-Mex and El-Agami) regions on Alexandria coast, Figure (1). The samples were kept in polyethylene bags, washed with distilled water and dried at 85°C in an oven, then grinded in an agate mortar.

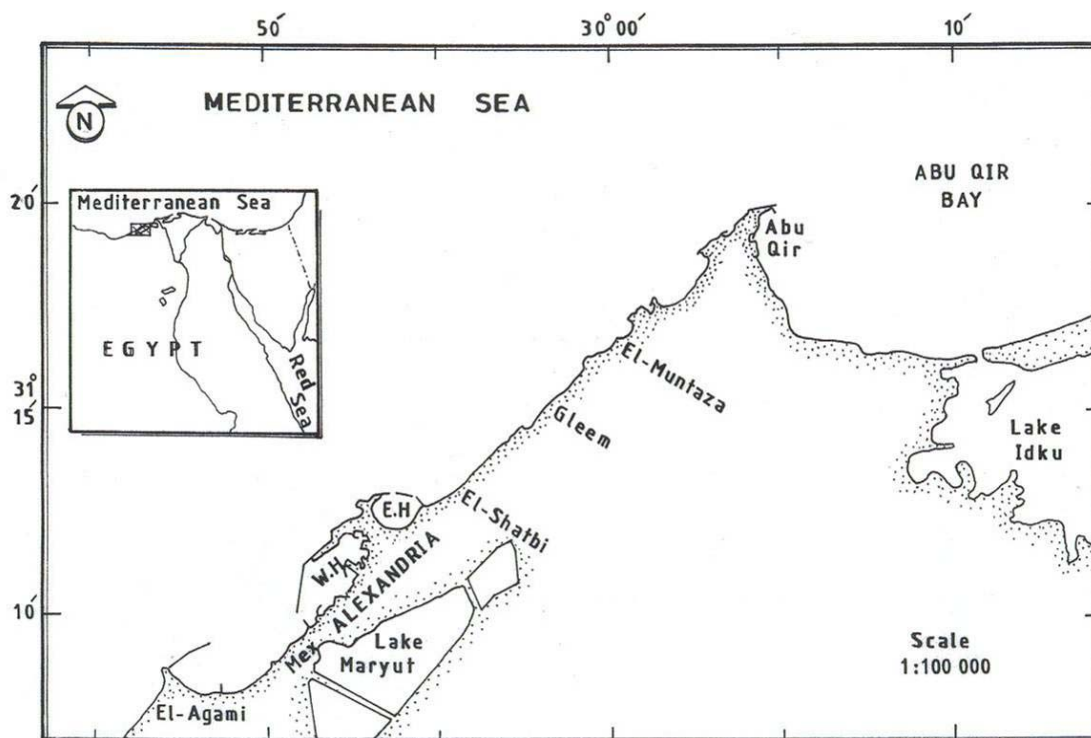


Figure (1). The area of study

Organic matter

The organic carbon in the sediment was determined by the following procedure⁽¹⁰⁾. Ten ml of chromic acid ($K_2Cr_2O_7 + H_2SO_4$) was added to 0.3 g of a finely powdered sample in a Pyrex tube and heated up to 85°C for approximately 15 minutes in an electric oven. The tube was removed from the heating advice and cooled by dipping in a cold water. The contents of the tube were rinsed into 250 ml beaker with distilled water to give a volume of an approximately 100 ml. using diphenylamine as indicator and then titrate against standardized 0.2 N ferrous ammonium sulphate solution. The percentage of the organic carbon is calculated as follows:

$$\%C = \frac{(B - U) \times D \times N \times A \times 100}{B \times W}$$

B= volume (ml) of ferrous ammonium sulphate required to blank (standard sea sand).

U= volume (ml) of ferrous ammonium sulphate required to titrate the sample.

D= 10 ml of chromic acid.

N= 0.4 N chromic acid.

A= meq. weight of C.

W= weight of sample.

The organic carbon is converted to organic matter with multiplying organic carbon values by the factor⁽¹⁰⁾ of 1.724.

Carbonate

It was determined by dissolving 0.5g of sample with an excess of 0.1 N HCl and back titration of the excess with 0.25 N NaOH using phenolphthalein as indicator⁽¹¹⁾.

Total phosphorus

500 mg of the dry sample was digested with a mixture of 2 ml concentrated nitric acid and 2 ml perchloric acid. The contents were left to evaporate on a hot plate and 1ml of HClO₄ was added before dryness and further heating was continued until the acid fumes ceased to evolve⁽¹²⁾ where phosphorus was determined according to molybdate method.

Calcium and magnesium

15 ml of acetic acid was added to 0.2g of the dry sample, in a clean dry conical flask (25 ml). The content was warmed on a water bath for 20 minutes, filtered through Whatman filter paper No. 2. The filtrate and washings were diluted to 250 ml volumetric flask. Calcium was determined by EDTA titrimetric method using murexide as indicator. Total calcium and magnesium concentrations were determined by titrating the sample against EDTA at pH= 10 using Eriochrome black-T as indicator. The difference between both titrations gives the magnesium content⁽¹³⁾.

Metals

10 ml of concentrated nitric acid and 10 ml of hydrofluoric acid were added to 0.5 g of the finely powdered sediment material into Teflon beaker and set a side for several hours. 5 ml conc. perchloric acid were added and evaporated to about 3 ml, cool and washed down the sides with a little distilled water, then add 5 ml of HClO₄ and evaporate just to dryness. 10 ml of concentrated pure HCl were added

and heat until the solution was clear and the fumes ceased. The digested material was filtrated and the residue was washed several times with deionized water. The filtrate was diluted with doubly distilled water to 100ml volumetric flask⁽¹⁴⁾. Analysis of Na and K were done using flame photometer model (Jenway, Falsted, G.T., Dumnaw, Essex UK serial No. 2907). The metals (Fe, Mn, Zn, Cu, Cd, Pb, Ni, Co, Cr, Al and Sn) were determined by atomic absorption spectrophotometer (AAS), Perkin – Elmer (Model 2380).

Results and Discussion

Organic Matter (OM)

The content of the organic matter in the sediment are varying due to its origin and geological history in the aquatic environment. Phytoplankton and zooplankton are the most abundant source of the organic material in the sediments⁽¹⁵⁾. The organic matter content of the sediment is a result of contribution of teragenous materials and the decomposition of plants and animals by the action of bacteria⁽¹⁶⁾. The high and low values of organic matter, Table (1), were 1.48% and 0.89% at El-Mex Bay and El-Agami, respectively. However, the OM values at El-Montazah, Gleem and El-Shattby were 0.96, 0.95 and 1.17%, respectively. The high OM content at El-Mex area is mainly attributed to discharging of sewage and domestic wastes from El-Umum drain.

Accumulation of organic matter in sediments is affected by the size of the basin, the width of the continental platform, the loptom relief, and other morphological features. Physical (temperature, light, oxygen,) and biological characteristics (competition among species, reproduction) are critical factors in the establishment and maintenance of the species inhabiting a sediment⁽¹⁶⁾. The quantitave distribution of organic matter content in the sediment depends principally on some factors:

- 1) The allocthonous organic load entering into the waters with sewage and industrial wastes.
- 2) The autochthonous organic production of the sediments.
- 3) The decomposition of organic matter.
- 4) Particle composition of the sediments.

The positive correlation between contents of OM and carbonate ($r= 0.364$) is mainly due to fermentation process, which may occur due to sinking dead materials yielding organic matter and releasing calcium carbonate to the surface sediment from dead calcareous shells. However, the positive correlations recorded between organic matter and most metals contents in the sediment, are probably due to the organic matter associated with sediment particles. This is largely responsible for the ability of sediment to adsorb the metals⁽¹⁷⁾.

Carbonate

The total carbonate content is certainly the most important environmental factor and one of the equilibria systems in the marine environment. It plays an important role in constructing the shells in all calcareous species⁽¹⁸⁾. CaCO_3 precipitation is controlled by photosynthesis. Although many calcite rich sediments may have largely alluvial source of carbonate, many other lacustrine carbonate sediments are truly endogenic. Their principal constituents have been precipitated directly from the water column. The concentrations of carbonate in the sediments, Table (1), ranged between 56.41% at El-Montazah area and 60.09% at El-Agami area. The higher value of carbonate is attributed to the aquatic plants and phytoplankton applied to extract CO_2 , and thus promote precipitation of carbonate with the increase of pH. A gradual increase in carbonate content from east to west side is recorded. The higher values are probably due to biogenic precipitation of carbonate by aquatic organisms building their calcareous shells⁽¹⁹⁾, and/or due to the calcium rich water where CaCO_3 is precipitated with increase of pH during photosynthesis. The distribution of carbonate is a function of the hydrodynamic regime and the magnitude of physical energy which might affect the degree of breakdown of skeletal materials and their subsequent redistribution⁽¹⁶⁾. Generally, the content of carbonate depends on the type of sediments. However, the sediments of studied area are mainly calcite and magnesium calcite, may explain the high carbonate content. The correlation coefficient matrix showed that carbonate is positively correlated with most heavy metals ($r=0.017, 0.075, 0.165, 0.512, 0.364, 0.834, 0.185$ and 0.486) with Mn, Zn, Cu, Co, Pb, Ni, Cr and Sn, respectively. The data suggested that, these metals may be present in the forms of carbonate in the contaminated sediment⁽²⁰⁾.

Total phosphorus

Marine sediments may contain phosphorus either incorporated in organic materials or as phosphate ions bound to various sediment components like aluminosilicate minerals and manganese oxides⁽²¹⁾. The phosphorus exists in water as dissolved or particulate, but in sediment as interstitial in pore water and as particulate phosphorus sorbed to particles. The sediment acts as reservoir of phosphorus in natural system. The phosphate concentration in water overlying sediment is buffered by sorption and adsorption immobilization and mobilization at the sediment-water interface. The total phosphorus contents in the sediments, Table (1), fluctuated between 45.32 mg/kg at El-Agami region and 276.90 mg/kg at the area of El-Mex. The high values are probably due to the great amounts of fertilizers including phosphate in the effluents of El-Umm drain, in addition to the domestic, sewage, agricultural and industrial effluents of this drain. For El-Montazah, Gleem and El-Shattbi regions, the total phosphorus contents were 107.60, 76.92 and 177.51 mg/kg, respectively. The phosphorus compounds are

mainly exist as dissolved substances. These are extracted from the solution and utilized for feeding by different organisms which on death, fall and accumulate on the bottom. These led to increase of the phosphorus content in sediment until released again into solution by the action of bacteria⁽²²⁾. The correlation coefficient matrix showed a strongly positive relation between TP and OM ($r=0.987$), indicating that the organic materials are the main sources of phosphorus in the study area. The significant positive correlation between phosphorus with iron, manganese and zinc ($r=0.669$, 0.866 and 0.884) respectively, pointed to the possible formation of strong phosphate complexes in the bottom water leading to be desorbed ion to Fe and Mn oxides and hydroxides in the bottom sediments⁽²³⁾.

Major Cations

Calcium

It is an essential element for metabolic processes in all living organisms as structural or skeletal material in many living organisms. It affects on the pH of biological systems and on the depression of the entry of Na^+ and K^+ into fishes and plants living in the wile⁽²⁴⁾. The values of calcium concentrations in the area under study, Table (2), ranged between 36.20% (362.0 mg/g) at El-Montazah and 40.29% (402.9 mg/g) at El-Agami. The higher values may be due to the ability of phytoplankton to extract CO_2 from water to increase the pH and precipitation of CaCO_3 . The calcium contents at Gleem, El-Shattbi and El-Mex regions were 37.05, 37.70 and 38.00%, respectively. The high values may be due to biogenic origin, where living organisms in the water readily absorb calcium to form their skeletal framework. So, when these organisms died, their skeletons begin to decay⁽²⁴⁾. Generally, the change in calcium content may be attributed to several factors such as the biodetrial mixture of mollusks, coralline, algae, echinoids, formainiferal tests, carbonate petetiods and the precipitation of CaCO_3 from the water column⁽²⁵⁾. The correlation coefficient matrix indicates that, calcium is positively correlated with magnesium ($r=0.712$), leading to associated distribution of Ca^{++} and Mg^{++} .

Magnesium

During chemical weathering, magnesium is released mainly as the soluble MgCl_2 and MgSO_4 . It remains largely in the sea and is partly precipitated as carbonate⁽²⁶⁾. The values of magnesium concentrations in sediment in the studied area. Table (2), ranged between 3.84 mg/g at El-Montazah region and 6.35 mg/g at El-Agami, probably due to precipitation of Mg^{+2} as carbonate. The high content of Mg^{+2} during summer may be attributed to the biogenic precipitation of aragonite and calcite by aquatic organisms, which build their shells from calcium and magnesium carbonates at high temperature and pH values, however, magnesium

contents in sediment depend on the nature and the type of sediment. Generally, calcium and magnesium may inhibit sorption of other cations especially trace metals, such as Mn, Zn, Cu, Pb and Cd on metallic oxide Al_2O_3 and $\text{FeO}(\text{OH})$.

Sodium

At deep seated condition and near-shore sediments have similar contents of alkali metals, and the bulk of these elements is associated with the type of clay fraction⁽²⁷⁾. The levels of sodium concentrations in the sediment of studied area, Table (2), ranged between 0.89 at El-Agami and 1.69 mg/g at Gleem. The slight variations in the concentrations of sodium can be attributed to minor changes in mineralogy or grain size of sediments⁽²⁷⁾. The high sodium contents in marine sediment may be attributed to the ability of certain organisms to concentrate sodium. The positive correlation coefficient of sodium with K^+ ($r= 0.516$), supposed that the distribution of both elements in the sediment may depend on each another. Also, weak positive correlations between Na^+ and organic matter ($r= 0.102$) and with phosphorus ($r= 0.239$) were deduced.

Potassium

It is considered as an active cation in aquatic environment⁽²⁸⁾. The K^+ concentrations, Table (2), assigned ranges between 0.39 and 0.68 mg/g at El-Mex and El-Montazah respectively. The changes in the K^+ contents at different samples stations of sediments depend mainly on the nature of the sediments⁽²⁷⁾. In the geochemical cycle, Na^+ and K^+ tend become separated during weathering and deposition processes⁽²⁹⁾, whereas igneous rocks contain roughly comparable amounts of Na^+ and K^+ . At deep seated condition where Na^+ and K^+ are mainly located in clay, but may also present in other mineral phases, such as alkali-feldspars⁽²⁷⁾. Because of the almost complete absence of such minerals in the sediment of the area, it is likely that Na^+ and K^+ are present as separate mineral phases or may be associated with the major mineral components (i.e. carbonate minerals). In general, the order of major cations concentrations in the sediments of the studied area is given in the following order: **Ca** (range 36.20 – 40.29%) >> **Mg** (0.38 – 0.64%) > **Na** (0.089 – 0.169%) > **K** (0.039 – 0.068%)

Heavy Metals

The distribution of metals in the sediment-water system is of complex pattern. The adsorption of metals to suspended matter and subsequent sedimentation removes pollutants from the water column. Most trace metals have a tendency to precipitate at pH values near neutrality⁽³⁰⁾. The pollutants are not only accumulated, but under different environmental conditions they can also become

mobile again and brought into the food chain⁽³¹⁾ The metal transportation into an estuary or marginal sea by precipitation of wind-blown materials can influence the heavy metal contents in sediments.

Iron

Due to the multivalency of iron (II, III) and its abundance in the earth's crust, it occurs in sediments in different forms⁽³²⁾. The total iron concentrations in the studied area fluctuated between minimum of 659.56 µg/g at El-Agami and a maximum of 2387µg/g at El-Mex, Table (3). At El-Mex and El-Umum drain the sulphate reducing bacteria producing H₂S to precipitate iron as FeS. The great amount of organic matter in the effluents of the drain may be associated with iron and deposited to bottom sediments. These processes could explain the high iron contents in the sediments of El-Mex region. Generally, the course of oxidation of iron is affected by many factors, (e.g. pH, temperature,.....). The slight the increase in iron content at El-Shattbi (2171.09 µg/g) and Gleem (2143.59µg/g) are attributed to the human activities and the high erosion rate⁽³³⁾. The sediments act as a major sink for pollutants in the aquatic environment where the suspended sediment particles settle the adsorbed pollutants to be removed from the water column⁽³³⁾. The iron content is positively correlated with manganese (r= 0.770). Both elements are closely associated in a geochemical cycle. The positive correlation between iron and organic matter (r= 0.591) may be attributed to the adsorption of iron on the complexing organic compounds, such as humic and fluvic acids.

Manganese

It is concentrated in minerals mostly as carbonates, oxides, silicates and sulphides. It may occur as particulate manganese or precipitating coating on mineral species, organic matter, and iron-manganese hydroxides⁽²³⁾. The manganese contents in the sediments of the studied area fluctuated between a minimum of 71.86 µg/g at El-Agami and a maximum of 164.60 µg/g at El-Mex, Table (3). The behavior of the Mn distribution in the sediment follows that of Fe. However, the high content of Mn at El-Mex may be attributed to the presence of different effluents from El-Umum drain. The different Mn content in the different regions of Alexandria coast related to the nature of sediments, mainly grain size⁽³²⁾, where the clay sediments are enriched with manganese. Generally, manganese is easily associated with carbonates in the form of Mn (II) and its relative stability depends on pH and dissolved oxygen in the particles at high contents of CaCO₃⁽³⁴⁾. The strong positive correlation of Mn with organic matter (r= 0.800) may be due to the high association of metal with organic matter of the sediments which probably bound to humic substances in water and sediment. Also, manganese in sediments is associated with phosphorus as indicated from the

correlation coefficient ($r= 0.866$), this is attributed to adsorption of phosphorus by Fe/Mn oxide in the sediments.

Zinc

It is essential and beneficial elements in human growth. Also, it is plant micronutrient, representing in an important constituent in the formation of enzymes and nucleic acid synthesis⁽³⁵⁾. Zinc may occur in sediments as carbonate, oxide and sulphate. Also, the organic matter enrichment in the sediment increases the deposition of sediments. The concentrations of zinc in the sediments of the area under study fluctuated between a minimum of 10.43 $\mu\text{g/g}$ at Gleem and a maximum of 75.48 $\mu\text{g/g}$ at El-Mex, Table (3). The highest zinc concentration at El-Mex is due to the continuous discharges through El-Mex pumping station. The low dissolved oxygen at El-Mex may also contribute to the increase rate of zinc sedimentation, which is favored only under anaerobic conditions where zinc is precipitated as ZnS ⁽³⁶⁾. The relative increase at El-Montazah (46.07 $\mu\text{g/g}$) and El-Shattbi (35.59 $\mu\text{g/g}$), could be related high rate of erosion in these regions. The strong association of zinc with the anthropogenic organic matter showed that zinc is enriched in sediment due the inputs of organic sewage. Zinc is positively correlated with organic matter ($r= 0.852$), due to the adsorption of zinc onto iron oxy-hydroxide which associated with organic matter in sediments⁽³⁷⁾. Also, positive correlation coefficients ($r= 0.884, 0.511$ and 0.656) are deduced between zinc and those of phosphorus, iron and manganese, respectively. These relations are attributed to adsorption of zinc by hydrous iron and manganese oxides. The magnitude of adsorption increases with pH.⁽³⁷⁾

Copper

It is a trace element in the earth's crust or seawater which exists naturally in marine ecosystem as a result of erosion of mineralized rocks and also from anthropogenic sources in the coastal area subjected to industrial and sewage effluents. The copper contents in the sediments of the studied area fluctuated between a minimum of 10.16 $\mu\text{g/g}$ at El-Agami and a maximum of 18.74 $\mu\text{g/g}$ at El-Mex region, Table (3). The high concentration at El-Mex is mainly due to the discharge from El-Umum pumping station. Generally, the high erosion rate is regarded as one of the most important sources, which increased the level of copper in El-Shattbi sediment (13.15 $\mu\text{g/g}$). In general, the increase in copper content in the sediment of different stations may be attributed to the removal of copper from the water column mediated by the decay of the plankton or due to adsorption on the suspended matter or the complexation with organic matter leaving the water body to the sediment⁽³⁸⁾. Positive correlations with total phosphorus ($r= 0.957$), Fe (0.654), Zn (0.842), Mn (0.947) and carbonate (0.165) are observed. The data

indicated that, association of metals with clay minerals or the adsorption of copper on iron oxides occurred in addition to precipitation of copper. Also, the positive correlation with OM ($r= 0.912$) explained by the immobilization of Cu by surface adsorption and complexation by organic matter⁽³⁹⁾.

Cadmium

The primary uses of cadmium are in electroplating other metals or alloys for protection against corrosion and in the manufacture of storage batteries and some biocides⁽⁴⁰⁾. The major specific sources on the worldwide basis are atmospheric deposition, smelting and refining of nonferrous metals, manufacturing processes related to chemicals and metals and domestic waste water. Cadmium is precipitated as CaCO_3 and is mobilized to the water phase by acidification. So, Cd is sorbed to sedimentary organic matter and the binding intensity is very sensitive to pH variation. The concentrations of cadmium in the sediment of the area under study fluctuated between a minimum of $1.73 \mu\text{g/g}$ at El-Agami and a maximum of $10.56 \mu\text{g/g}$ at El-Mex, Table (3). The high content at El-Mex is mainly attributed to the discharge waste waters from El-Umum drain which directly discharged to this region. There is a relative increase in Cd concentration in the sediment at El-Shattbi ($6.94 \mu\text{g/g}$) and El-Montazah ($8.24 \mu\text{g/g}$), probably due to the high erosion rate. The association of Cd with carbonate is reported⁽⁴¹⁾. Cd in sediments is less mobile than other metals due to the formation of CdCO_3 phases in alkaline media⁽⁴¹⁾. The positive correlation between Cd and organic matter ($r= 0.799$) is attributed to the formation of stable natural humic substances depending on the abundance of organic matter. However, the deduced positive correlation between Cd and Fe ($r= 0.771$) may be due to adsorption of Cd on $\text{Fe}(\text{OH})_3$ and Fe_2O_3 ⁽³³⁾.

Cobalt

It occurs in the earth's crust with concentration of about 25 mg/kg . High cobalt concentrations are found in coal and uranium ores, some crude oils, and other sulphides. In the present study, cobalt concentrations, Table (4), fluctuated between a minimum of $15.65 \mu\text{g/g}$ at Gleem and a maximum of $24.14 \mu\text{g/g}$ at El-Mex. The high value is due to the effect of El-Umum drain. In general, the distribution of cobalt depends on the sewage effluents and the structure of sediments and clays⁽⁴²⁾. Cobalt is positively correlated with carbonate ($r= 0.512$) supporting precipitation of CoCO_3 ⁽⁴³⁾. However, the correlations between Co and Fe, Mn and Zn are ($r= 0.315, 0.818$ and 0.712) respectively, indicated the association of the metals with clay minerals or the adsorption of both Co and Zn on the Fe_2O_3 and MnO_2 ⁽³³⁾.

Lead

The primary sources of Pb include manufacturing processes (particularly metals), atmospheric deposition, and domestic wastewater. Approximately 96% of all lead emission originates from anthropogenic sources⁽³³⁾, particularly combustion of leaded fuels, pyrometallurgical nonferrous metal production and coal combustion. Lead in sediments is chemically precipitated from surface water solution and the remainder has been transported in detrital particles⁽⁴²⁾. However, lead occurring in sediments has two distinct mineral associations, i) with the clay minerals and ii) with antigenic minerals and/or bigamous debris. The lead concentrations in sediments of the study area were fluctuated between a minimum of 2.08 µg/g at Gleem and a maximum of 26.45µg/g at El-Mex, Table (4). The high value is due to the effect of different wastes via El-Umum drain. It was reported that⁽⁴³⁾ agricultural wastes enriched the sediment with suspended organic matter, humic acids acquire a large fraction of Pb burden from the overlying water through suspended particles. Additional amounts deposited after the humic acids are buried in the sediments. We supposed that the concentration of Pb decreased at Gleem (2.08 µg/g), due to the remoteness from the source of pollution. In contrast with Zn, Cu and Cd, a slight increase in Pb content was recorded at El-Agami region, probably due to its high carbonate content, which increases the rate of precipitation of lead as lead carbonate. The positive correlation coefficient between Pb and organic matter ($r=0.737$) may be attributed to the formation of stable complexes. Also, the positive correlation between Pb and Fe concentrations ($r=0.147$) depicted that Pb is effectively adsorbed from the sea water by hydrous ferric oxide. The data suggested that the precipitation of lead in the sediment is minimum.

Nickel

Nickel ranks as the 23rd most abundant element in the earth's crust with an average concentration of 75 mg/kg. The major source of discharge is municipal wastewater followed by smelting and refining of nonferrous metal⁽³³⁾. The concentrations of nickel, Table (4) fluctuated between 3.36 µg/g at El-Montazah region and 17.39 µg/g at El-Mex. The higher value is associated with Fe and Mn, where Ni has been scavenged directly from water by hydrous MnO₂. Also, nickel is contained in ferromanganese minerals and some of nickel is likely to be contained in the clay minerals⁽⁴²⁾. The nickel element has tendency to form organic complexes that are more stable. This is supported by the positive correlation coefficients between Ni and both Fe and Mn, ($r=0.032, 0.510$) which are attributed to Co-precipitation from the water by Fe₂O₃.xH₂O. The high positive correlation between Ni and Mn may be due to scavenging of the former from surface water by MnO₂.xH₂O. The obtained positive correlation between Ni and the organic matter

($r= 0.793$) in the absorbent sediment of the area under study points to the relatively high concentrations of nickel exists in organic rich sediments⁽⁴²⁾.

Chromium

Chromium occurs in the earth's crust at an average concentration of 100 mg/kg. Atmospheric fallout is important source of chromium in surface water, from anthropogenic sources and windburn soil particles⁽⁴⁴⁾. The concentrations of chromium in the sediments, Table (4), fluctuated between 7.36 $\mu\text{g/g}$ at Gleem at 19.36 $\mu\text{g/g}$ at El-Mex. There is a slight increase in chromium content at El-Shattbi (13.81 $\mu\text{g/g}$). The high concentrations of chromium recorded at E-Mex reflect the direct effect of effluents. Meanwhile, the relative decrease of chromium content at El-Agami was attributed to other facts rather than pollution. Atmospheric chromium concentration closely parallels geographic areas of high population and industrial activity. Chromium is effectively adsorbed from seawater by hydrous oxides of manganese, nickel and cobalt⁽⁴²⁾. Under oxidizing conditions, chromium transformed to chromium (VI) oxidation state, and resulted in partial loss from the sediments.

Aluminum

It occupies the second position in order of abundance of the elements in the earth's crust. The aluminum contents in the sediments, Table (4), fluctuated between a minimum of 5.04 mg/g at Gleem and a maximum of 8.36 mg/g at El-Shattbi. The high aluminum content indicates terrigenous source by aluminosilicates such as clay minerals and feldspars⁽²⁷⁾. Such variations in the concentrations of aluminum can be attributed also to a minor change in mineralogy or grain size of sediments⁽²⁷⁾.

Tin

Tin was one of the first metals used in antiquity, known as early as 3000 B.C. and preceded only by Cu, Au and Ag. Tin have numerous applications, such as a protective coating, in solders, bearings and other alloys⁽⁴⁵⁾. The worldwide production of organo-tin compounds has risen as a consequence of their use as stabilizers in polyvinylchloride, homogeneous catalysts for vulcanization and as biogenic agents. The biocidal preparations include agrochemicals fungicide, preservatives and antifouling agents in marine paints⁽⁴⁵⁾. The total contents of tin in the sediments of the studied area, Table (4) were fluctuated between 0.73 $\mu\text{g/g}$ at El-Agami and 2.85 $\mu\text{g/g}$ at El-Montazah. At other regions, the tin contents were 0.92, 1.65 and 1.83 $\mu\text{g/g}$. The highest concentrations of tin at El-Montazah may be attributed to the industrial installations, since tributyl tin (TBT) is used as biocide for cooling waters or of Abu Qir fertilizers company.

A slight increase of tin content at El-Mex region (1.83 $\mu\text{g/g}$) is probably due to the effect of different sewages effluent from El-Umum drain. While, El-Agami region showed the lowest tin content (0.73 $\mu\text{g/g}$), which is located far way from the activity of ships. The increased use of organo-tin compounds as biocides and antifouling agents is reflected by increasing concentrations of such species and tin contents in the environment. However, the present work values are relatively lower than that reported 5.6 $\mu\text{g/g}$ for the Eastern Harbour and 2.9 $\mu\text{g/g}$ for the entrance of Eastern port Harbour. The trend, however, seems to be quite similar.

Table (1): Concentrations of carbonate (%), organic matter (%) and total phosphorus (mg/kg) in the sediment during summer (2004).

| Station | Organic matter % | Carbonate % | Total phosphorus mg/kg |
|-------------|------------------|-------------|------------------------|
| El-Montazah | 0.96 | 56.41 | 107.60 |
| Gleem | 0.95 | 58.10 | 76.92 |
| El-Shattbi | 1.17 | 59.75 | 177.51 |
| El-Mex | 1.48 | 60.00 | 276.90 |
| El-Agami | 0.89 | 60.09 | 45.32 |

Table (2): Concentrations of major cations Ca% (Mg, Na and K) (mg/g) in the sediment during summer (2004).

| Station | Ca % | Mg (mg/g) | Na (mg/g) | K (mg/g) |
|-------------|-------|-----------|-----------|----------|
| El-Montazah | 36.20 | 3.84 | 1.62 | 0.68 |
| Gleem | 37.05 | 4.92 | 1.69 | 0.51 |
| El-Shattbi | 37.70 | 4.52 | 1.37 | 0.41 |
| El-Mex | 38.00 | 5.54 | 0.95 | 0.39 |
| El-Agami | 40.29 | 6.35 | 0.89 | 0.40 |

Table (3): Concentrations of heavy metals (Fe, Mn, Zn, Cu and Cd) ($\mu\text{g/g}$) in the sediment during summer (2004).

| Station | Fe | Mn | Zn | Cu | Cd |
|-------------|---------|--------|-------|-------|-------|
| El-Montazah | 2096.48 | 113.97 | 46.07 | 11.55 | 8.24 |
| Gleem | 2143.59 | 100.39 | 10.43 | 10.36 | 3.61 |
| El-Shattbi | 2171.09 | 152.94 | 35.59 | 13.15 | 6.94 |
| El-Mex | 2387.00 | 164.60 | 75.48 | 18.74 | 10.56 |
| El-Agami | 659.56 | 71.86 | 18.71 | 10.16 | 1.73 |

Table (4): Concentrations of heavy metals (Co, pb, Ni, Cr and Sn) ($\mu\text{g/g}$), Al(mg/g) in the sediment during summer (2004).

| Station | Co | Pb | Ni | Cr | Al | Sn |
|-------------|-------|-------|-------|-------|------|------|
| El-Montazah | 17.67 | 16.71 | 3.36 | 12.21 | 6.73 | 2.85 |
| Gleem | 15.65 | 2.08 | 5.61 | 7.36 | 5.04 | 0.92 |
| El-Shattbi | 23.71 | 19.49 | 12.90 | 13.81 | 8.36 | 1.65 |
| El-Mex | 24.14 | 26.45 | 17.39 | 19.36 | 5.91 | 1.83 |
| El-Agami | 18.53 | 15.31 | 1.22 | 10.58 | 7.24 | 0.73 |

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