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The concentrations of some heavy metals of Al-Gabal Al-Akhdar Coast Sediment

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ABSTRACT

The concentrations of organic matter, carbonate, total phosphorous, and some heavy metals (iron, manganese, zinc, copper, cadmium, cobalt, lead, nickel and chromium) were determined for sediment samples collected from near shore stations on Al-Gabal Al- Akhder coast during summer 2008. The results showed that, the high levels of heavy metals were recorded at regions which receive high effluents from brackish water.

Keywords: Sediment analysis, Heavy metals , AL-Gabal AL-Akhdar coast.

INTRODUCTION

Heavy metals are among the normal constituents of the marine environmental but anthropogenic activities have contributed to the increase in metal contamination into marine environment and have directly influenced the coastal ecosystems (1). Metal pollution of the marine environment is less visible and direct than other types of marine pollution, but its effect on marine ecosystem and human are intensive and very extensive (2). Sediment contamination poses one of the worst environmental problems in marine ecosystem acting as sinks and sources contaminations in aquatic systems (3).There is an 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 metals to the coast (4).

The aim of the present study was to establish the levels of some heavy metals beside organic matter, carbonate and total phosphorus in sediment samples collected from AL-Gabal AL-Akhdar coast.

MATERIALS AND METHODS

Sampling

Three surface sediments were collected during Summer (2008) from (Al-Haniea, Al-Hamama, and Susa) regions on AL-Gabal AL-Akhdar coast, Figure (1). The samples were kept in polyethylene bags, and washed with distilled water and dried at 85^{o}C in an oven, then grinded in an agate mortar.

Organic matter

The organic carbon in the sediment was determined by the following procedure (5). 10 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^{o}C for approximately 15 minutes in an electric oven. The tube was removed from the heating device 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 chormic 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 of 1.724.

Figure 1. The area of study

Carbonate

It was determined by dissolving of 0.5g sample with an excess of 0.1 N HCl and back titration of the excess with 0.25 N NaOH using phenolphthalein as indicator (6).

Total phosphorus

0.5 g 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 further 1ml $HClO_4$ was added before dryness and further heating was continued until the acid fumes ceased to evolve. Cool, then warm to 100^oC for 10 minutes to decompose any phosphate. After filtration from the siliceous residue, the filtrate was diluted to 250 ml volumetric flask (7) where phosphorus was determined.

Metals

10 ml concentrated nitric acid and 10 ml hydrofluoric acid were added to 0.5 g of the finely powdered sediment material into teflon beaker and keep as it for several hours. Then 5 ml conc. perchloric acid was added and evaporated to about 3 ml, cool and washed with a little distilled water, then add 5 ml of $HClO_4$ and evaporate just to dryness. 10 ml of concentrated pure HCl was 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 100 ml volumetric flask (8).

The metals (Fe, Mn, Zn, Cu, Cd, Pb, Ni, Co and Cr) were determined by atomic absorption spectrophotometer (AAS), Perkin – Elmer (Model 2380).

RESULTS AND DISCUSSION

Organic Matter

The compositions and structures of the organic matter in the sediment are varying due to its origin and geological history in the marine and aquatic environment. Phytoplankton and zooplankton are the most abundant source of the organic material in the sediments (9). 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 (10).

The values of organic matter, Table (1), were 0.09% 0.08 and 0.4 % at Al-Hamama , Al- Haniea and Susa, respectively.The high organic matter content at Susa area is mainly attributed to discharging of sewage and domestic wastes from out lets .Accumulation of organic matter in sediments is affected by the size of the basin, the wide of the continental platform, the lootom 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.

The quantitative 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 organic matter and carbonate (r= 0.69), is mainly due to fermentation process, which may occur to sinking dead materials yielding organic matter and releasing of calcium carbonate to the surface sediment from death calcareous shells. However, the positive correlations recorded between organic matter and most metals in the sediment, is probably due to the organic matter associated with sediment particles. This is largely responsible for the ability of sediment to adsorb the metals (11).

Carbonate

The total carbonate content is certainly the most important environmental factor and one of the equilibiria systems in the marine environment. It plays an important role in constructing the shells in all species. $CaCO_3$ precipitation is controlled by photosynthesis. Although many calcite rich sediments may have largely allergenic source of carbonate, many other lacustrine carbonate sediments are truly androgenic. Their principal constituents have been precipitated directly from the water column (12).

The concentrations of carbonate in the sediments, Table (1), were 73 , 72.4 and 76.9 % at Al- Hamama , Al- Haniea and Susa, respectively. 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 organize by aquatic organisms building their calcareous shells (13)., 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 (14).Generally, the content of carbonate depends on the type of sediments. However, the sediments of investigated area are mainly calcite and magnesium calcite, to explain the high carbonate content (15).

The correlation coefficient matrix showed that carbonate is positively correlated with most heavy metals (r= 0.54 ,0.67 ,0.32 ,0.65 , 0.45 and 0.87) with Mn, Zn, Cu, Co, Pb, and Cr respectively, The data suggested that these metals may be present in the forms of carbonate in the contaminated sediment(16).

Total phosphorus

Marine sediments may contain phosphorus either incorporated in organic materials or as phosphate ions bound to various sediment components like alumino silicate minerals and manganese oxides. The phosphorus exists in water as dissolved or particulate and as particulate phosphorous sorbet to particles. The sediment acts as reservoir of phosphorous 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 phosphorous contents in the sediments, Table (1), were 8 , 9.20 and 33.4 mg/kg at Al- Hamama, Al- Haniea and Susa , respectively. The high values are probably due to the great amounts of fertilizers including phosphate in the effluents of out lets , in addition to the domestic, sewage, agricultural and industrial effluents.

The phosphorous compounds are mainly exist as dissolved substances. These are extracted from the solution and utilized for feeding by different organisms which up on death, fall and accumulate on the bottom. These lead to an increase the phosphorous content in sediment until released again into solution by the action of bacteria.

The correlation coefficient matrix, showed a strongly positive relation between total phosphorous and organic matter (r= 0.88), to assign that the organic materials is the main sources of phosphorous produced from the untreated domestic sewage into some the studied regions Al-Gabal Al- Akhdar coast e.g. Susa. The positive correlation between phosphorus with iron, manganese and zinc (r= 0.74, 0.75 and 0.81) respectively, pointed to the possible formation of strong phosphate complexes in the bottom water leading to a desorbed onto Fe and Mn oxides and hydroxides in the bottom sediments

Heavy metals

The distribution of metals in the sediment-water system is of a complex structure. The adsorption of metals to suspended matter and subsequent sedimentation removes pollutants from the water column. Enrichment of the sediment with metals may cause their transportation to the ground water, release of accumulated metals to the water column and consequent accumulation by aquatic organisms. Most trace metals have a tendency to precipitate at pH values near neutrality. The pollutants are not only accumulated, but under different environmental conditions they can also become mobile again and brought into the food chain. Thus, the sediment itself develop more and into a source of pollutants (17).The metal transport into an estuary or marginal sea by precipitation of wind-blown materials can influence the heavy metal contents in sediment.

Iron

Due to the multiagency of iron (II, III) and it's abundance in the earth's crust, it occurs in sediments of different forms (18).The total iron concentrations in the studied area were 335.16, 420 and 745.2 µg/g at Al-Hamama, Al- Haniea and Susa, respectively. Table (2). The great amount of organic matter in the effluents of the drain may be associated with iron and deposited to bottom sediments. These two factors could explain the high iron contents in the sediments of Susa region. Generally, the course of oxidation for iron is affected by many factors, (e.g. pH, temperature). Also the high contents are attributed to the human activities accompanied with increase of the amount domestic discharge from boats. The sediment acts 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. The iron content is positively correlated with manganese (r= 0.82). Both elements are closely associated in a geochemical cycle. The positive correlation between iron and organic matter (r= 0.78) may be related to the adsorption of iron on the complexing organic compounds, such as humic and fluvic acids.

Manganese

It is found in minerals mostly as carbonates, oxides, silicates and sulphides. It may occur as a particulate manganese or precipitating coating on mineral species, organic matter, and iron-manganese hydroxides. The manganese contents in the sediment of the area under study were 24.33, 28.90 and 40.88 aµg/g at Al-Hamama, Al- Haniea and Susa , respectively. The behavior of the Mn distribution in the sediment follows the same trend of Fe. However, the high content of Mn at Susa may be attributed to the presence of different effluents of variable sources e.g. sewage and domestic, agricultural and industrial wastes produced from out lets. The variable Mn content are different where the clay sediments are enriched in manganese. Generally, manganese is easy associated with carbonates in the form of Mn (II) and its relative stability depending on pH and dissolved oxygen in the particles at high contents of $CaCO_3$

The strong positive correlation of Mn with organic matter (r= 0.73), 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 where positive correlation coefficient (r= 0.94) is detected and is attributed to adsorption of phosphorus by Fe/Mn oxide in the sediment and phosphate is often present in domestic or industrial wastes (12).

Zinc

It is essential and beneficial elements in human growth. Also, it is plant micronutrient, being an important constituent in the formation of enzymes and nucleic acid synthesis (19). Zinc may occur in sediments as carbonate, oxide and sulphate. Also, the organic matter enrichment in the sediment increases the deposition of sediment. The concentrations of zinc in the sediments of the area under study were 6.61,8.16 and 20.67 µg/g at Al-Hamama, Al-Haneia and Susa regions, respectively, Table (2).The highest zinc concentration at Susa is due to the continuous discharges from out let. Since, sedimentation of zinc in favored only under anaerobic condition where zinc is precipitated as ZnS (20).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= 0.97), due to the adsorption of zinc onto iron oxy-hydroxide which associated with organic matter in sediments (21). Also, positive correlation coefficients (r= 0.80) are deduced between zinc and manganese. This relation is attributed to adsorption of zinc by hydrous iron and manganese oxides. The magnitude of adsorption increases with pH .

Copper

It is a trace element in the earth's crust or seawater and 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 area under study were 4.11, 2.21 and 7.4 µg/g) , Table (2). The high concentration at Susa is mainly due to the discharge from outlet pumping .Generally, the antifouling paints used for ships and boats are regarded as one of the most important sources. 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 (22).

Also, the major contributions of element to air-bone particulate matter are: (i) crust materials, such as argillaceous sediments, which are often enriched with metal copper, and (ii) man made sources, such as fossil fuel combustion, metallurgical industries and agricultural processes through the use of some copper compounds as inorganic pesticides. Positive correlations with total phosphorus (r= 0.957), Fe (0.75), Zn (0.72) and Mn (0.69) 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= 0.85) explained by the immobilization of Cu by surface adsorption and complexation by organic matter (23).

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 (24).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 it is mobilized to the water phase by acidification. So, Cd is sorbet 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 were 0,81, 0.79 and 1.40 µg/g at Al-Haniea, Al- Hamama and Susa regions, respectively, Table (2).

The high content is mainly attributed to the brackish effluents. The association of Cd with carbonate is reported (12). Cd in sediments is less mobile than other metals due to the formation of $CdCO_3$ phases in alkaline media.The positive correlation between Cd and organic matter (r=

0.82) 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=.0.84) may be due to adsorption of Cd on $Fe(OH)_3$ and Fe_2O_3 .

Cobalt

It occurs in the earth's crust of nearly 25 mg/kg. Large residues are found in coal and uranium ones, some crude oils, and other sulphides. The cobalt concentrations, were 2.11 , 5.04 , 8.90 µg/g at Al-Haniea, Al- Hamama and Susa regions, respectively , Table (3). In general, the distribution of cobalt depends on the sewage effluents and the structure of sediments and clays (25). Cobalt is positively correlated with carbonate (r= 0.88) to assign precipitation of $CoCO_3$[(43)]. However, the correlations between Co and Fe, Mn and Zn are (r= 0.65, 0.43and 0.83) 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 (14).

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 (18), particularly combustion of leaded fuels, hydrometallurgical 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 (25). However, lead occurring in sediments how two distinct mineral associations, (i) with the clay minerals and (ii) with antigenic minerals and/or bigamous debris.

The lead concentrations in sediments of area under study were of 1.40 , 2.70 and 7.53 µg/g at Al-Haniea, Al- Hamama and Susa regions, respectively , Table (3). The high value is due to the effect of different wastes of out let. It was reported that 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. The positive correlation coefficient between Pb and organic matter (r= 0.56) may be attributed to the formation of stable complexes. Also, the positive correlation between Pb and Fe concentrations (r= 0.86) depicted that Pb is effectively adsorbed from the sea water by hydrous ferric oxide. The data suggested that the precipitation of lead to 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 (18).The concentrations of nickel were 0.65 , 0.80 and 1.23 µg/g at El-Haniea, El- Hamama and Susa regions, respectively, Table (3). higher value is associated with Fe and Mn, where Ni has been scavenged directly from water by hydrous MnO_2. Also, nickel is contained in ferromanganese minerals and some of nickel is likely to be contained in the clay minerals (25).The nickel element is obviously clear from its strong correlation with other metals due to its tendency to form organic complexes that are more stable.

The positive correlation coefficients (r= 0.45 and 0.76) between Ni and both Fe and Mn, respectively, are attributed to Co- precipitation from the water by $Fe_2O_3.xH_2O$. The high positive correlation between Ni and Mn may be due to scavenging of the former from surface water by MnO_2 xH_2O. Positive correlation between Ni and the organic matter (r= 0.0.87) in the absorbent sediment of the area under investigation is deduced, to point the relatively high concentrations of nickel exists in organic rich sediments (25).

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 (12).The concentrations of chromium in the sediments, Table (3), were 4.11 , 2.80 , 9.40 g/g. µg/g at Al-Haniea, Al- Hamama and Susa regions, respectively , Table (3).. The high concentrations of chromium attributed ugully to the direct effect of effluents. Meanwhile, the relative decrease of chromium content at Al- Hamama region is attributed to such sector is far from the pollution sources. 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 (25).Under oxidizing conditions, chromium transformed to chromium (VI) oxidation state, and resulted in partial loss from the sediment.

Table (1): The concentrations of organic matter and total phosphorus in the studied area.

Region	Oraganic matter	Carbonate	Total phosphorus
El-Hamama	0.09	73	8
El-Haniea	0.08	72.4	9.20
Susa	0.40	76.9	33.40

Table (2): The concentrations of (Fe , Mn , Zn , Cu and Cd) in the studied area.

Region	Fe	Mn	Zn	Cu	Cd
El-Hamam	335.16	24.33	6.61	4.11	0.81
El-Haniea	420	28.90	8.16	2.16	0.79
Susa	745.2	40.88	20.67	7.44	1.40

Table (3): The concentrations of (Co ,Ni ,Pb and Cr) in the studied area.

Region	Co	Ni	pb	Cr
El-Hamama	2.11	9.11	1.40	4.11
El-Haniea	5.04	0.80	2.70	2.80
Susa	8.90	1.23	7.53	9.40

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