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COPPER SPECIATION IN THE SEDIMENTS OF THE POLLUTED EASTERN HARBOR OF ALEXANDRIA, EGYPT

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Abstract

The Eastern Harbor (EH)), a small shallow semicircular basin, is influenced by sewage disposal from Alexandria City. This study deals with regional distribution of total copper (TCu) and it species in the sediments of this polluted harbor. The high TCu content adjacent to the harbor's opening reflects the effect of untreated sewage discharges and that of the boatyard area resulted from antifouling paints. The TCu data indicate the increase in metal concentrations by a factor of~10 during the last decades, confirming the effect of increased sewage discharges into this area, causing health problems. A five step sequential extraction technique was used to describe the chemical association of copper with major sedimentary phases; exchangeable (F_1), carbonates (F_2), Fe/Mn oxides (F_3), organic/sulfides (F_4), and residual associations (F_5). The Cu fractions in the EH's sediments decreased in the following order: $F_5 > F_4 > F_3 > F_2 > F_1$. The distribution pattern of these fractions is mostly controlled by the mineral composition of sediments and the anthropogenic wastes introduced to the study area. The low association of copper with F_1 confirms that metal was low in the soluble form. The higher value of F_2 at the center of the EH coincided with abundance of the biogenic clastics as major source of carbonates in the sediments of this area. The high concentrations of F_3 in the suspended matter and sediments at the boatyard area and the EH's opening indicate the interaction between both phases. The high level of F_4 is not surprising, due to continuous accumulation of organic matter from large amounts of domestic sewage discharging. A significant positive correlation (r=0.971, n=4, p>0.02) between F_5 in suspended matter and sediments was detected, indicating interaction between both phases.

Introduction

The study of marine sediments represents a useful tool for determining the actual state of environmental pollution and for understanding the origin and mechanism of the phenomena. Sediments could be regarded as a historical reflection to changes occurring in the overlying water system and can be used as good indicators for metals in any study area. Meanwhile, sediments are major repository of trace metals in the coastal marine environment (24) and some times become a major potential source of trace metals, which can be eventually returned to the biosphere. The present study, a part of this project, deals with the regional distribution of total copper and its species in the sediments of the EH.

For the Egyptian coast, several authors paid attention to study the distribution of trace metals in marine sediments (16, 13, 14, 3, 22, 1).

A research project was carried out on the geochemical behavior of copper in the Eastern Harbor (EH) of Alexandria to cover the distribution of dissolved and particulate copper species in the water column and bottom sediments. The present study, a part of this project, deals with the regional distribution of total copper and its species in the

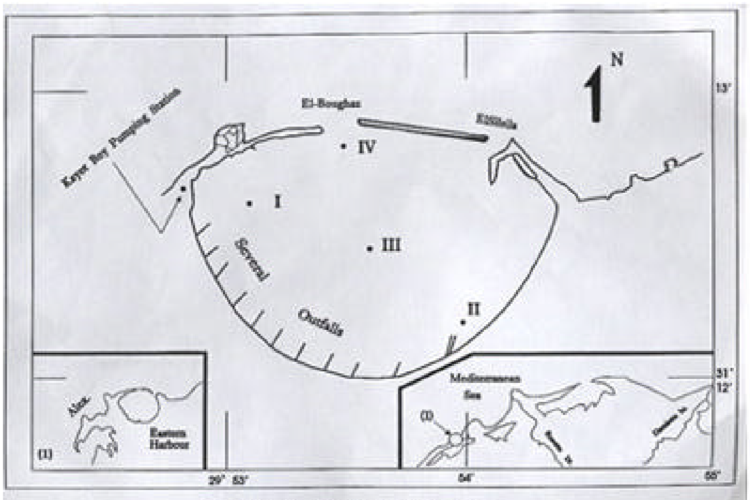

Fig. 1. Sampled stations in the Eastern Harbour

sediments of the EH.

Study Area

The EH, a relatively small, shallow and semicircular basin generally surrounded by Alexandria, lies between longitudes $29° \; 53'$ and $29° \; 54.4'$ E and Latitudes $31° \; 12'$ and $31° \; 13'$ N. Its area is about 2.53 x 10^6 m^2, with an average depth of 6.5 m and water volume of 16.44 x 10^6 m^3. This harbor is sheltered from the Mediterranean Sea by an artificial water break, about 750 m in length, leaving two openings through which the harbor's water is freely connected with the open sea water; El Boughaz and El-Silsila (Fig. 1).

The EH is mainly influenced by sewage disposal of the central part of Alexandria City, which is pumped into the Mediterranean Sea. The main sewage tube begins at

Kayet Bay Pumping Station (Fig. 1), which is the main metropolitan sewage pumping station of the central part of Alexandria. It discharged to the sea about $96x10^6$ m^3/yr during 1985-1986 as reported by Abu-El Kassem (4). Besides, small 11 sewage openings discharged about 15,000 and 10,000 m^3/day of untreated sewage wastes directly to the harbor in winter and summer, respectively (26). Also, large quantities of different wastes of the fishing and sailing boats anchoring inside the harbor were dumped into its northwestern part

Material and methods

An Ekman grab sampler was used to collect surface sediment samples at four stations selected to cover different regions in the EH (Fig. 1). The samples were sliced from the grab center, using a plastic spoon to avoid contamination by the metallic part of the grab and placed in self-sealed polyethylene bags for copper determination, which were previously washed (1:1 HCl) and rinsed with metal free water. Other sediment sub samples were placed in clean glass tubes for organic carbon determination. The samples were spread in the laboratory on plastic sheets for a few days at room temperature inside a clean cabinet until dryness to constant weight. They were sieved through 2-mm sieve to get rid of gravel. The pipette analysis technique was used for separation of sand, silt and clay fractions to illustrate the sediment types. The dry samples were ground in an agate mortar, homogenized and kept in clean well-stoppered polyethylene containers until analysis. The organic carbon was determined by the modified Walkaley-Black method (29).

Copper associated with sediments was subjected to a chemical leaching technique described by Tessier et al., (27). The following five copper fractions were determined; exchangeable (F_1), bound to carbonate (F_2), bound to Fe-Mn oxides (F_3), bound to organic matter-sulfides (F_4) and residual (F_5). The concentrations of total copper and its species were measured, using a Perkin Elmer Atomic Absorption Spectrophotometer (AAS).

For testing the accuracy of the method, five replicates of Standard Reference Material (SRM 1645) River Sediments from the National Bureau of Standards have been used, giving a mean coefficient of variation of 3.25%. For testing the precision of the sequential procedure used in the analysis, comparison of the sum of copper concentrations in the individual fractions with total metal concentration (5:1 $HF/HClO_4$) showed a good agreement.

Results and discussion

Total copper (TCu)

The problem of sediment pollution in the EH generally reflects the effect of uncontrolled discharges of unprocessed sewage and partly due to dumping of paints from the local fishing shipyard. The harbor's sediment distribution is a function of the bottom configuration and the current regime. Artificial obstruction of the seaward side of the harbor has resulted in the continuous accumulation of sewage solids for approximately 30 years, with the resulting reduction of bottom sediment texture and increased concentrations of chemical pollutants in the sludge material covering the bottom. The type of the sediments in the EH is sandy in nature (Table 1), confirming the same results obtained by El-Sayed et al. (16) for the same area.

As shown from Table 2, the high TCu content of the sediments adjacent to the harbor's opening (358.45 $\mu g.g^{-1}$) reflects the effect of untreated sewage discharges from Kayet –Bay Pumping Station. Nasr et al. (22) stated that the main outfall at Kayet Bay caused the high copper content in the harbor's sediments. Also the sediments of the boatyard area at western side of the harbor showed a high TCu value of325.80 $\mu g.g^{-1}$ (Table 2), mainly from the antifouling paints used for ships and boats in these areas. EL-Sayed et al. (16) and Nasr et al. (22) observed the same phenomena. The possible interpretation of these high TCu anomalies in the sediments is that they possess the capacity of removing much of the man's input very rapidly near its source and thus decreasing the element distribution further away from the points of discharges. The relative influence of organic matter on retention and complexation of heavy metals was reported by battiston et al. (7).

EL-Rayis et al. (15) found that copper was concentrated in the sand fraction of the sediments covering the shallower sides of the EH. In the present results, however, no relation between TCu and sand fraction of the sediments ($r = 0.2446$, $n = 4$, $p > 0.1$) could be obtained to support their finding.

A comparison between the levels of TCu in the sediments in the EH and those recorded by EL- Sayed et al. (16) and EL- Nady (13) for the EH indicates that the metal concentrations have increased by a factor of ~ 10 or more during the last decades. This finding confirms the effect of increased sewage discharges into the area. The TCu concentration in the sediments of EL-Agami, (2), far away from any land runoff, could be considered as a background level for this metal in the near shore area (Table 3).

Table 1: **Texture and organic matter content of the sediments of the Eastern Harbor**

Stations	Station depth (m)	Sand %	Silt %	Clay %	Type	Organic carbon ($mg.g^{-1}$)	Organic matter ($mg.g^{-1}$)
I	3.7	94.65	0.4	4.95	Sandy	8.6	15.48
II	4.0	98.05	0.2	1.75	Sandy	3.12	5.61
III	7.0	78.65	17.6	3.75	Sandy	3.24	5.83

	10.5	87.45	2.4	10.15	Sandy	29.18	52.52
Means ±S.D.						11.03 ± 12.36	19.86 ± 22.25

Table 2: Local distribution of total copper and its species in the sediments of the Eastern Harbor

Stations	Station depth (m)	F_1	F_2	F_3 ($\mu g.g^{-1}$)	F_4	F_5	Total copper $HF/HClO_4$
I	3.7	4.57	2.65	9.21	51.43	257.94	325.80
II	4.0	1.27	1.78	4.13	11.75	170.63	189.56
III	7.0	1.52	2.78	3.17	25.71	126.98	160.16
IV	10.5	2.03	2.29	10.48	77.78	265.87	358.45
Means ± S.D.		2.34 ± 1.51	2.37 ±0.44	6.74 ± 3.63	41.66 ± 29.14	205.35 ± 67.76	258.49 ± 98.22

Table 3: Means of total copper concentrations ($\mu g.g^{-1}$) in the present study compared with those in the coastal Egyptian sediments

Locations	Means	References
Eastern Harbor	258.49	Present study
Maadia Sector	150.83	(6)
Tabia Sector	193.76	(6)
Agami (reference)	20.0	(2)
Eastern Harbor	27.2	(16)
Eastern Harbor	14.00	(13)
Abu-Kir Bay	12.0	(13)
Alexandria coast (Beach) " " (Bottom)	4.22	(22)

Rosetta mouth	9.69	(22)
Rosetta mouth (inshore)	44.0	(28)
Rosetta mouth (off shore)	89.0	(2)
Rosetta branch		(2)
Damietta branch	44.0	(12)
	64.1	(20)
	40.12	

Table 4: Comparison between the average values ($\mu g.g^{-1}$) of copper species in the present study and those in the sediments of other Egyptian aquatic areas

Areas	F_1	F_2	F_3	F_4	F_5	References
Eastern Harbor	2.34	2.37	6.74	41.66	205.35	Present study
Maadia Sector	1.43	3.49	2.62	21.58	121.69	(6)
Tabia Sector	1.86	2.11	3.22	14.60	171.95	(6) (1)
Lake Mariut	1.03	1.20	6.80	36.40	28.80	(1)
L. Burullus	0.34	3.10	5.26	7.50	12.80	(1) (1)
L. Manzalah	0.67	1.90	12.40	28.10	32.20	(19)
L. Edku	0.16	0.80	9.30	11.80	16.90	(23)
L. Edku	0.16	0.55	0.53	0.81	0.48	
Coastal belt off Alexandria	1.31	4.84	8.43	1.46	14.11	

Copper speciation

On the basis of solid state speciation, the sequential leaching technique was applied to the sediments of the EH; copper in exchangeable (F_1), carbonate (F_2), oxide (F_3), organic (F_4), and residual associations (F_5) and the values are listed in Table 2. TCu was partitioned in a sequence of; F_5 (205.35±67.76) > F_4 (41.66± 29.14) > F_3 (6.74± 3.63) > F_2 (2.37± 0.44) > F_1 (2.34 ± 1.51), depending on their mean concentration in $\mu g.g^{-1}$.

As shown in Table 2, the distribution of copper in F_1 was limited, ranging from 1.27 to 4.57 $\mu g.g^{-1}$ at stations II and I, respectively. The higher concentrations of F_2 were observed at stations III (2.78 $\mu g.g^{-1}$) and I (2.65 $\mu g.g^{-1}$). The minimum value of 1.78 $\mu g.g^{-1}$ was recorded at station II. The reducible fraction (copper bound to Fe/Mn oxides) was enriched at stations IV (10.48 $\mu g.g^{-1}$) and I (9.21 $\mu g.g^{-1}$), giving lowest concentration at station III (3.17) µg.g-1. The organic fraction (F_4) was relatively high, ranging from 11.75 to 77.78 µ g.g^{-1} at stations II and IV, respectively. This maximum was associated with the highest organic matter content of 52.52 mg.g^{-1} (Table 1). The residual copper (F_5) association was the predominant fraction, giving highest concentrations at stations IV and I, of 265.87 and 257.94 µ g.g^{-1} respectively. Its lowest value of 126.98 µ g.g^{-1} was detected at stations III (Table 2).

The total abundance of trace elements in the sediments partly measures their availability in the source materials and also their reactivity. The geochemical cycle of anthropogenic trace elements in the marine environment is determined to a large degree by the interaction of metals with sediments. Recently, environmental studies and water quality standards have been concerned not only with the total concentration but also with trace metals speciation in aquatic environments.

Significant fractions of trace metals in natural and polluted waters are inert complexes, which influence the availability of these metals to aquatic organisms (18). However, particles and sediments in the system play a major role in reducing the toxicity of metals to organisms and algae (25 and 5).

The distribution pattern of copper among different fractions in sediments is mostly controlled by the mineral composition of sediments and the anthropogenic wastes introduced to the study area via domestic discharges.

A low association of copper with stage I (loosely held) gave a considerable idea that copper was low in the soluble form and tended to form a complex (with organic matter), co precipitated (with hydrous Fe /Mn oxides) or uptake by organisms and finally incorporated into sediments. Chester et al. (10) revealed that, on the average, only ~ 2.5% of TCu in the sediments collected from Atlantic Ocean was present in loosely held form (F_1). Generally, exchanges across the water-sediments interface occur in all aquatic systems. The mechanisms responsible for these phase changes are: precipitation/dissolution; adsorption/desorption; biological uptake and excretion and scavenging/ remobilization. Such mechanisms are consequently a function of environmental parameters (pH, temperature, dissolved oxygen), as well as anthropogenic discharges. The relationship between F_1 of the sediments and these parameters in the bottom water layer in July (sampling period) gave the following correlation coefficients (r); -0.9720, -0.0314 and 0.0349 for pH, dissolved oxygen and temperature, respectively. A similar observation between pH and F_1 was found by Khadr (19) for Lake Edku sediments and he attributed this to the narrow range of pH values.

The relatively higher value of F_1 at station I might be related to the more or less stagnant conditions at this location accelerating the rate of metal adsorption. El-Wakeel and El-Sayed (17) found that biogenic clastics are by far the major source of carbonate in the EH's sediments, especially in the central part, as well as in the adjacent shelf. This may explain the higher value of F_2 detected at station III (Table 2). For the region of the Gulf of St. Lawrence, Beltagy and D'anglejan (8) reported that the variation of an element with respect to carbonate is considered to reflect its association with biologically derived skeletal materials. Reducible oxide associated copper made only a small fraction of the

TCu in the sediments of the study area. The EH, polluted by sewage, showed high a concentration of iron (16.24 mg.g^{-1}) in its sediments, which under oxic condition is present in the form of hydrous ferric oxide (6). This is usually considered as an efficient scavenger for copper. El-Nady (13) pointed out that iron and manganese showed good correlation coefficient with copper in the EH and ascribed this correlation to the efficiency of manganese oxide particles to attract electro-statically other ions from the medium during their transportation.

The high concentrations of F_3 in the suspended matter (6) and sediments at stations I and IV indicate the interaction between both phases. The higher concentrations of F_3 in suspended particulates compared with those in the sediments explain the role of suspended matter in enriching the copper oxide fraction in the sediments by precipitation process, especially in condition of high average pH values of 8.06 and 8.40 recorded at these stations, respectively (6).

The high levels of F_4 is not surprising, due to the continuous accumulation of organic matter from large amounts of domestic sewage discharging into the EH (16). Stations to station variations of F_4 were reflected on the elevated standard deviation from the mean of 41.66±29.14 μ g.g^{-1} (C.V. = 70 %).

Several factors control the organic content of any marine sediments; 1) the rate of supply of organic matter; 2) its transportation by currents; 3) its rate of sedimentation; 4) sea bottom topography and 5) texture of the sediments. The maximum concentration of F_4 (Table 2) was recorded at station IV, directly affected by sewage discharges from the main Kayet-Bay outfalls. However, F_4 fraction in the suspended matter at this station was not the maximum, indicating that organic matter associated with sewage outfalls has deposited on the sediments at the entrance of the harbor, due to changes in current velocity, resulting in the observed enrichment of sediments with organic matter (52.52 mg.g^{-1}) and consequently with F_4 fraction (Tables 1 and 2). Copper is relatively concentrated in the organic fraction, indicating the strong complexing affinity of organic matter with copper (21).

Fishing shipyard in the western part of the harbor added organic material to this area, leading to elevation of F_4 in both suspended matter (6) and bottom sediment samples. Although station II was directly affected by sewage outfalls (Champelion) has recorded the lowest F_4 value of 11.75 μ g.g^{-1} (Table 2). This might be related to microbial activity (associated with sewage outfall) at the sediment surface, affecting decomposition of organic matter in the sediments giving the lowest value of 5.61 mg.g^{-1} (Table 1). A strong positive correlation between organic matter and F_4 fraction in the EH was recorded ($r = 0.9518$, $n= 4$, $p < 0.05$). This suggests that copper in the sediments was originally associated with organic matter at the time of deposition. It was proposed that metals may be concentrated on organic matter by ion exchange, complexing and chelation (11). Calvert and Price (9) also found a high correlation between organic carbon and copper in the West African Shelf. They concluded that copper was associated with organic detritus, either as sorbed ions or as metallo-organic complexes. Zhang et al. (30) found that F_4 was <5 to 10% of metal concentrations for Cu, Ni and Pb, due to low organic matter content.

The detrital fraction of trace elements essentially reflects the chemical composition of various source materials contributing to the sediments. This fraction normally constitutes detrital silicate minerals and slightly soluble sulfides. However, silicon is a structural element in alumino-silicate minerals, a well as diatom frustules (biogenic silicon). The most striking feature in copper speciation investigations on sediments is the predominance of the crystalline phase (F_5) over the other chemical forms, giving a mean value of 205.35 ± 67.76 $\mu g.g^{-1}$ for the EH (Table 2). A significantly positive correlation ($r = 0.971$, $n = 4$, $p > 0.02$) between F_5 in suspended matter (6) and sediments was detected, indicating interaction between both phase

The average values of copper species in the sediments of the present study compared with those of the other Egyptian areas are shown in Table 4. The similarity of analytical technique used by other authors, i.e. Tessier et al. (27) renders the inter-comparison between results to be of such possibility. Copper was mostly partitioned in sediments among F_4 and F_5, with exception of those of coastal belt of Alexandria, where F_3 contributed an important fraction. The present results are comparatively higher than most of the corresponding results given by other authors for samples collected from other areas, indicating a potential Cu pollution problem in the study area.

Conclusions

Artificial obstruction of the seaward side of the harbor has resulted in the continuous accumulation of sewage solids in the last decades. The high TCu content in the sediments adjacent to the harbor's opening reflects the effect of untreated sewage discharges from Kayet –Bay Pumping Station. Also, the sediments of the boatyard area at the western side of the harbor showed a high TCu value, from the antifouling paints used for ships and boats. A comparison between the levels of TCu in the EH sediments and previous records indicates that the metal concentrations have increased by a factor of ~ 10 or more during the last decades

The sequential leaching technique was applied to the sediments of the EH; copper in exchangeable (F_1), carbonate (F_2), oxide (F_3), organic (F_4), and residual associations (F_5). TCu was partitioned in a sequence of; $F_5 > F_4 > F_3 > F_2 > F_1$, depending on their mean concentration. The higher value of F_1 in the west of EH coincided with the more or less stagnant conditions at this location accelerating the rate of metal adsorption. The higher value of F_2 in the center of the EH is related to the biogenic clastic as major source of carbonate in the harbor's sediments. The high concentrations of F_3 in suspended matter and sediments in the western side and opening of the EH indicate the interaction between both phases. The high levels of F_4 coincided with the continuous accumulation of organic matter from large amounts of domestic sewage discharging into the EH. The strong positive correlation between organic matter and F_4 suggests that copper in the sediments was originally associated with organic matter at the time of deposition. The most striking feature in copper speciation investigations on sediments is the predominance of the crystalline phase (F_5) over the other chemical forms. A significantly positive correlation between F_5 in suspended matter and sediments was detected, indicating interaction between both phase

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