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ROLE OF HUMIC ACIDS ON THE OCCURRENCE OF METALS IN ABU-QIR BAY NEARSHORE SEDIMENTS

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Key words: humic acids, Abu-Qir Bay, trace metals, occurrence.

ABSTRACT

Trace metals; Fe, Cu, Pb, Zn, Mn, Ni, Cd, Cr and Co were measured in sixteen surficial nearshore sediments from Abu-Qir Bay and in front of El-Maadiya channel. Concentrations in the analyzed sediment samples indicate a non-polluted environment. However, high trace metal concentrations were observed in front of El-Tabia Pumping Station (TPS), where untreated or partially treated industrial and domestic wastewaters are discharged directly or carried by streams into the Bay. Humic acids isolated from the sediments have been characterized by higher trace metal levels than the proper sediment samples. Iron was the dominant metal in all humic acids and sediments examined. The relative contribution of humic acids bound metal to the whole metal content in the bulk sediments varies in a very wide range, and is directly dependent on the element related to the humic acid contents in the sediment. Therefore, high participation of humic acids as trace metals holder in the sediments emphasizes the major role it actually plays in the geochemical cycling of the elements (Fe, Cu, Zn, Pb, Cr, Mn, Ni, Co and Cd) in the aquatic environment.

INTRODUCTION

Coastal water bodies are mainly considered as the areas of conflictual utilization by man since the beginning of the industrial revolution. Abu-Qir Bay, lies at the eastern extremity of Alexandria coast, is an ideal example of the exploitation of the coastal areas along the Mediterranean Sea. There exist some different factories representing four major industrial activities namely food processing and canning, paper industry, fertilizers industry and textile manufacturing. The industrial wastes are discharged into the bay through El-Tabia Pumping Station (TPS) at an average rate of 1.5 to 2.0 $x10^6$ m^3 of heavily polluted water per day coming from about 36 factories extending from Kafr El-Dawar to Alexandria in a cultivated area. In addition, about $3.3x10^6$ m^3 per day brackish water were discharged from Lake Edku through Bougaz El-Maadiya to the western extremity of the bay depending on the local prevailing wind. The wastes coming from the pumping station are directly discharged to and eventually mixed with the water in Abu-Qir Bay, thus affecting its physico-chemical and biochemical characteristics. Therefore, the most important sink for particulate material in Abu-Qir Bay and enrichment of trace metals in post-industrial sediments has been shown by a number of authors (Moussa, 1973; Abdelmoneim and Shata, 1993 and Hafez, 1999). On the other hand, organic matter has the prime importance in the aquatic environment. It consists of the remains of biologically produced compounds as well as synthetic organic substances.

The most important products formed during the composition of organic substances are the humic acids. The humic substances (humic and fulvic acids) could mostly come from the terrestrial source due to leaching of the soils by rain. These substances are said to be (allochthonous), while in lacustrine, coastal and marine water, humic substances are partly or wholly formed locally (autochthonous).

Humic substances as humic acids and fulvic acids are able to interact with metal ions, metal oxides, metal hydroxides and clay minerals to form associations of widely differing chemicals and biological stabilities. These interaction products affected partially every reaction that takes place in these systems. The complexing of metal ions by humic substances over many years studied by several scientists (Senesi ***et al***., 1977; Preston and Riley, 1982; Bourg, 1986; Aboul-Naga, 1990 and Aboul-Naga, 1994).

Humic substances in Egyptian water as well as humic-metal interaction are still in need to further studies despite several studies carried out only on Egyptian lakes (Aboul-Naga, 1990; Aboul-Naga, 1994 and El-Sayed *et al*., 1996).

The present investigation was undertaken to study the existence and role of some trace metals in humic acids which are the major component of organic matter in Abu-Qir Bay as well as in nearshore sediments from Abu-Qir Bay and in front of Lake Edku (off El-Maadiya channel) and the relative contribution of metals to the bulk sediments. The association of trace metals, especially with humic substances, has been demonstrated in many investigations (Baker, 1973; Rashid and Leonhard, 1973; Rashid, 1974; Nissenbaum and Swaine, 1976; Chesire ***et al.***, 1977; Kerndorff and Schnitez, 1980; Templeton and Casteen, 1980; Fengler ***et al***., 1994 and El-Sayed ***et al***., 1996).

Study Area

Abu-Qir Bay is a small part of the Mediterranean Egyptian coast and is considered as an estuary (El-Rayis ***et al.***, 1993). It is a semicircular, semi-closed basin, bordered from the west by Abu-Qir peninsula and from the east by Rosetta branch of river Nile, with a shore line of about 50 km long and an area of about 560 km^2 with an average depth of about 12 m (Nessim and El-Deek, 1993). Abu-Qir Bay lies between longitudes 30° 4` and 30° 21` East and latitudes 31° 16` and 31° 30` North (Fig.1). Several rocky ridges are found in the north-western part of the bay. Due to these rocky ridges, a limited exchange of water exists between the open sea and the north-western part of the bay. Lake Edku is directly connected to the western extremity of the bay with a short deep channel (Boughaz El-Maadiya) of about 100 meters in length, 15 meters in width and an average depth of 5 meters. The amount of brackish water discharged from the lake to the bay was at a rate of about 3.3 million m^3/day (Anon, 1984), depending on the local prevailing wind. A predominant lake bay flow all the year around with a maximum speed between 60 and 100 cm/s along the axis (Mohamed, 1981). Abu-Qir Bay receives water from three sources; Rosetta mouth of the river Nile, Lake Edku via Boughaz El-Maadiya and Tabia Pumping Station. TPS is located in the south-western part of Abu-Qir Bay, nearly in the midway between Abu-Qir town and Boughaz El-Maadiya.

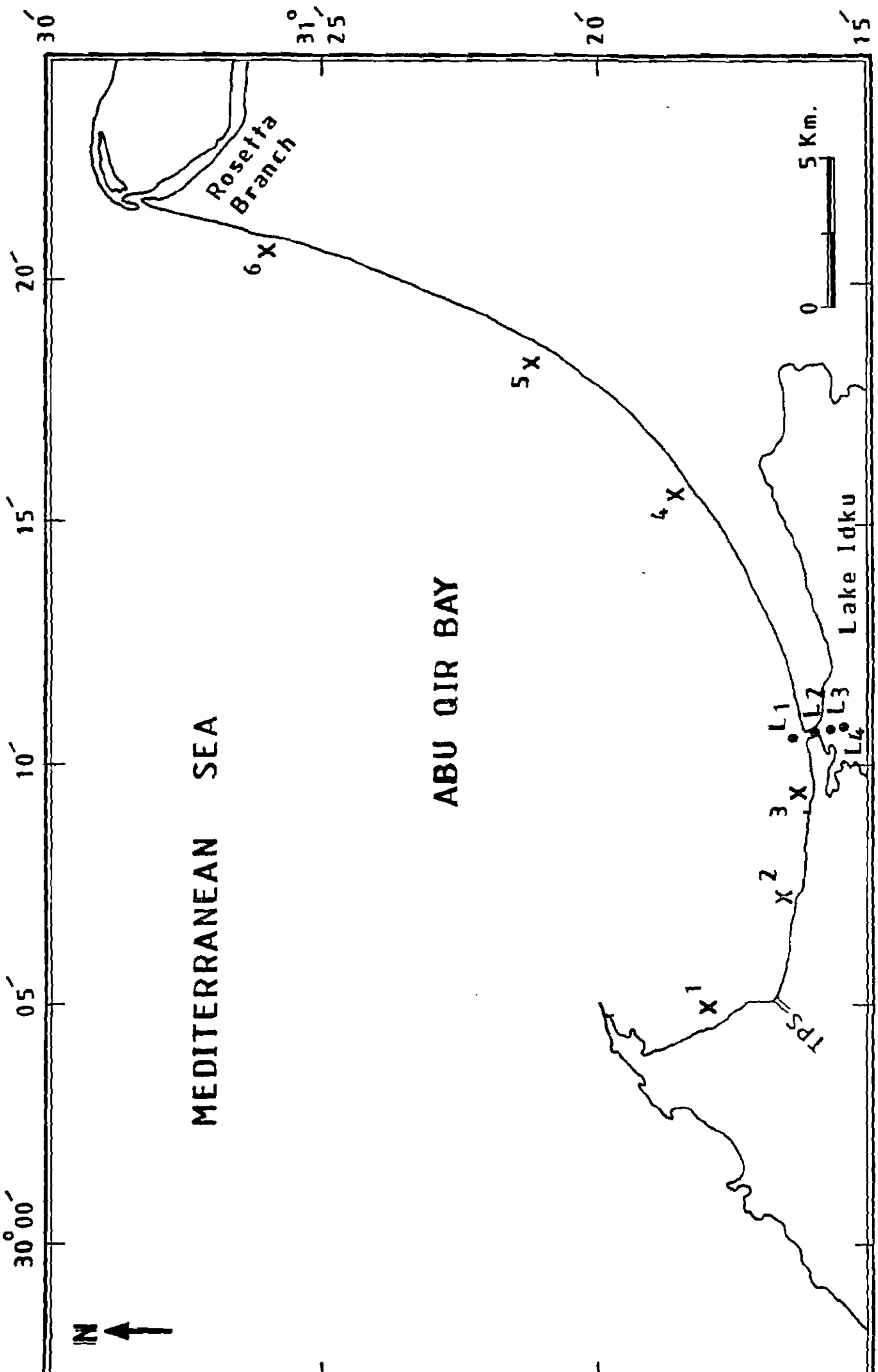

Fig. (1) Area of study and position of sampling stations.

MATERIALS AND METHODS

Twelve samples from surficial nearshore sediments (six samples at 2 m water depth and six samples at 3 m water depth) and four samples (L_1, L_2, L_3 and L_4) in front of El-Maadiya channel were collected during November, 1996 directly by diving. Sediments were dried at 40°C and subsamples were grinded in an agate mortar for trace metal analysis. The carbonate (CO_3^{--}) was determined from the weight loss (after excluded large shells) by treatment with 10% HCl. Heating with 50 ml HCl takes place to dissolve $MgCO_3$ in addition to $CaCO_3$. Organic carbon (OC) was determined by inexpensive titration method described by Gaudette and Flight (1974). The method utilizes exothermic heating and oxidation with potassium dichromate and concentrated H_2SO_4 of a portion of the sample, and the titration of excess dichromate with 0.5N ferrous ammonium sulfate solution to reach a sharp drop end point. Mud content was carried out under water current on 63 µm sieving size. Isolation of humic acids (HA) was carried out with 0.5N NaOH following published standard procedures (King, 1967 and Rashid and King, 1969). Trace metals in bulk sediments after sequential technique with concentrated acids HNO_3, HF and $HClO_4$, and extracted humic acids after sequential technique with concentrated HNO_3 and $HClO_4$ were determined by Flame Atomic Absorption Spectrophotometer (Varian 1250).

RESULTS AND DISCUSSION

Sediment Types

The basic information of the sediments in Abu-Qir Bay and off El-Maadiya region, illustrated in Table (1), shows the carbonate, organic carbon and mud content. The sediments consist largely of clay minerals with shell fragments, especially at stations 1, 2 and 3. The carbonate content was high (up to 44.4% and 40.9%) at station 2 at 2 m and 3 m depth, respectively. For El-Maadiya channel, the carbonate content was 20.5%, similar to the result obtained by El-Sayed (1993) who found 27% carbonate on the average of Lake Edku sediments. The sediments in the eastern part of the bay are mainly derived from

Table (1): The carbonate (CO_3^{--}%), organic carbon (OC%) and clay ≤63 μm%, humic acids in sediments (HA in sed. mg/g) and humic acids/organic carbon (HA/OC %) of the sediments in Abu-Qir Bay (1-6 / 2 m depth and 1-6 / 3 m depth) and off El-Maadiya region (L_1, L_2, L_3 and L_4).

Station	CO_3^{--} %	OC %	Clay %	HA in sed. mg/g	HA/OC %
1 / 2 m	29.9	2.06	98.0	3.82	18.5
2	44.4	3.76	87.3	30.98	82.1
3	13.6	0.41	24.5	0.75	18.3
4	16.4	0.84	54.9	0.29	3.5
5	6.7	0.31	18.0	0.09	2.9
6	4.6	0.21	7.2	0.06	2.9
Mean	19.3	1.26	48.3		
1 / 3 m	39.7	2.33	98.8	3.36	14.4
2	40.9	4.15	94.4	24.12	58.1
3	8.4	0.29	36.8	0.21	7.2
4	16.0	0.81	24.6	0.23	2.8
5	5.2	0.26	4.7	0.06	2.3
6	2.5	0.10	12.1	0.05	5.0
Mean	18.8	1.32	45.2		
L_1	17.7	0.68	39.8	0.37	5.4
L_2	16.8	1.69	99.6	6.13	36.3
L_3	28.0	1.79	49.6	5.31	29.7
L_4	19.5	1.08	35.0	6.35	58.8
Mean	20.5	1.31	55.9		

the discharge of soil wash through the drainage system. So, the Rosetta mouth affects the distribution of the sediment types in the bay. The sediment types varied from beach sand in the eastern part (≤63 μm ranged between 4% and 18%), to clayey silt and silty sand in the western side, the fine (≤63 μm) were at stations 1 and 2 contributes up to 98% of the sediments with an overlapping layer in between. In the south of the bay, close to the lake-sea connection (off El-Maadiya channel), the sediments contain on the average >55% of the fine fraction (≤63 μm). At stations 1, 2 and 3, to the west of El-Maadiya channel, the bottom was covered by a layer of sludgy material, originated from disposal of the industrial wastes through Tabia Pumping Station (TPS). The organic carbon values in Abu-Qir Bay sediments ranged between 0.1% and 4.15% with an average of 1.29% similar to the average of 1.31% off El-Maadiya channel (Table 1). The sediments of the bay showed the highest organic carbon concentrations at station 2; 3.76% and 4.15% at depths of 2 m and 3 m, respectively. These results are in agreement with those reported by Abdelmoneim and Shata (1993), who found that total organic matter is 14.04% in the zone in front of the paper factory and 1.71% off Boughaz El-Maadiya area. In addition, this result is rather similar to that of Hafez (1999), who found that organic carbon averaged 7.93 mg/g, 11.39 mg/g and 10.28 mg/g in El-Maadiya region, Tabia region and Abu-Qir Bay, respectively. The regional distribution of organic carbon relevant to carbonate (Fig.2) demonstrates a strong trend with higher concentrations at stations 2 at 2 and 3 m depths. Similarly, the classical trend of clay-organic matter association was found between clay and organic carbon content at all stations (Fig.3). Generally, the sediment at station 2 showed the highest clay and organic carbon concentrations and then decreased eastwardly, whereas the clay and organic carbon showed the lowest values at stations 5 and 6. Therefore, Abu-Qir sediments showed remarkable variations in the values of OC%, CO_3^{--}% and clay% due to the source of sediments derived from El-Tabia Pumping Station (TPS) and lake inflows which became environmental problems, caused by the introduction of wastes over many years. The general distribution pattern along the bay probably attributed to current regime in the bay.

Humic Acids

Values of humic acids (HA) in Abu-Qir Bay sediments at 2 m and 3 m depth ranged from 0.06 to 30.98 mg g^{-1} and 0.05 to 24.12 mg g^{-1}, respectively (Table 1). The concentrations were very high being 30.98 mg g^{-1} at 2 m depth and 24.12 mg g^{-1} at 3 m depth at station 2 in the bay, as compared with the other bay stations (Table 1 and Fig.4). Obviously, humic acid examined relative to the organic carbon percentage showed marked variations in their values, but revealed significant distribution pattern similar to the regional distribution of organic carbon content (Fig.4). There is a general similarity in the distribution of humic acids and organic carbon at 2 m and 3 m depths in Abu-Qir Bay sediments (Fig. 4).

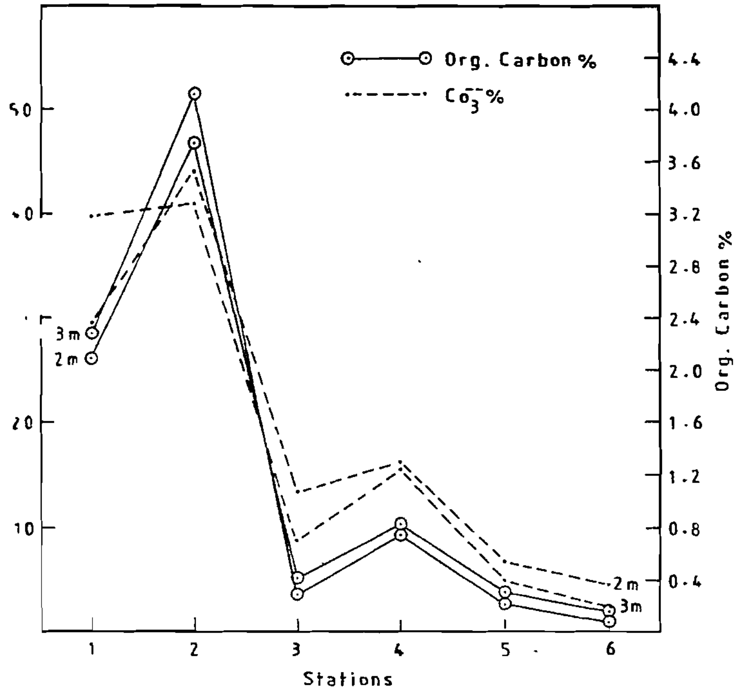

Fig.(2) The regional distribution of organic carbon % relevant to carbonate contents.

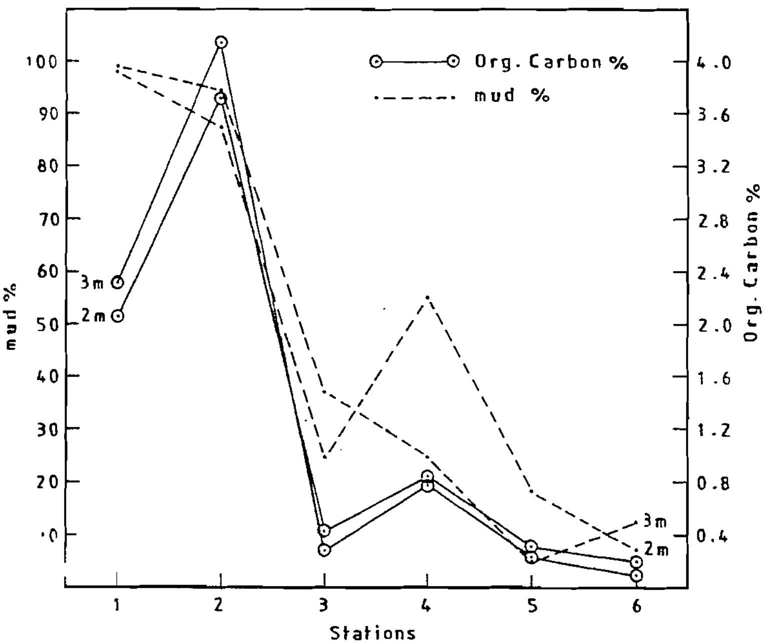

Fig. (3) The regional distribution of organic carbon % relevant to clay centents.

In the lake-sea connection, the humic acids/OC % showed high value up to 58.8% in Lake Edku (Fig.5). Despite the well defined sediment source, the origin of humic acid in Abu-Qir sediments may be resolved. According to Stevenson and Bulter (1970), humus synthesis in a two-stage process which involves decomposition of all plant components including lignin and the subsequent polymerization of products of microbial metabolism into high-molecular-weight polymers. The role of lignin is relegated to that of serving as a source of building blocks (polyphenols and quinones) for humus synthesis. Accordingly, fulvic acids represent initial products of "humification" and further condensation results in the formation of humic acids and ultimately coal. Several workers (Steinberg and Muenster, 1985) have shown that humic substances in sedimentary material constitute the major fraction (up to 80%) of the sedimentary organic matter.

Trace Metals in Sediments

Concentrations of trace metals (Fe, Cu, Zn, Pb, Mn, Cr, Co, Cd and Ni) in Abu-Qir sediment are listed in Table (2). Appreciable difference could be observed in the abundance of the elements in all stations with relatively high values for most metals at stations 1 and 2. The sediments consist largely of clay minerals being 98 and 98.8% at station 1 and 87.3 and 94.3% at station 2 at 2 m and 3 m depths, respectively, which have a relatively high natural metal content compared to sand and also a greater active surface area onto which metals may be adsorbed. Therefore, the relatively high values at stations 1 and 2 in the bay at most other stations and also off El-Maadiya channel result from a combination of different factors including industrial discharges to the bay in front of stations 1 and 2.

Table (3) shows that average concentrations of metals recorded their highest values at 3 m depth and attain their lowest average values off El-Maadiya region. Comparing the values of trace metals (Fe, Cu, Zn, Cd, Ni, Cr, Mn and Pb) with the values determined by Abdelmoneim and Shata (1993) for Cd, Pb, Ni and Fe in Abu-Qir Bay, it is obvious that the concentration of trace metals increased deducing that industrial wastes deposited from several factories are the main contributors of the heavy metals characterizing the investigated sediments. In addition, concentrations of most metals in the bay are nearly as high as in recent Skagerrak sediments in the North Sea (Fengler *et al.*, 1994). On the other hand, the mean concentration of trace metals demonstrated low values in the

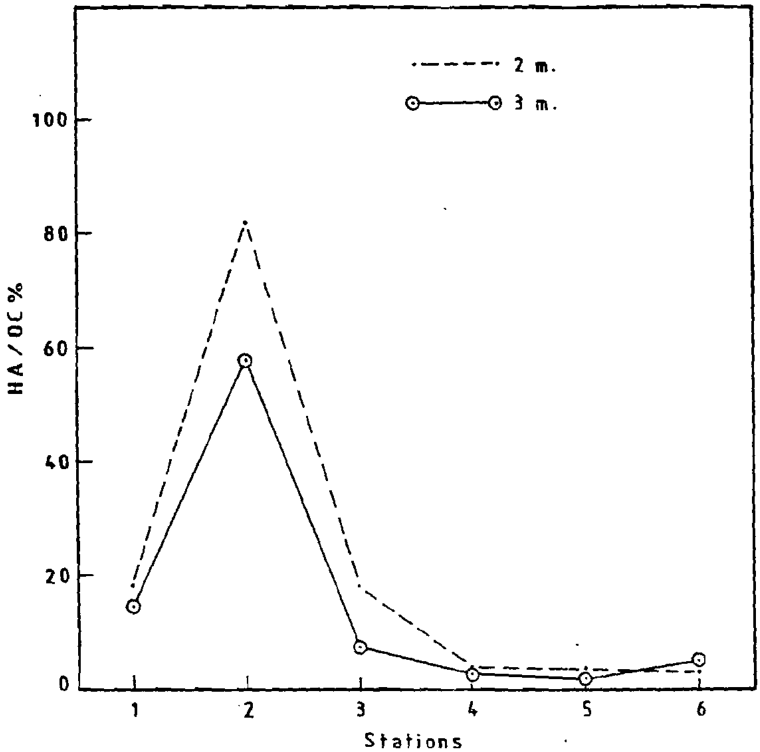

Fig.(4) The distribution of humic acids relative to organic carbon % at 2 m and 3 m depth in Abu - Qir Bay.

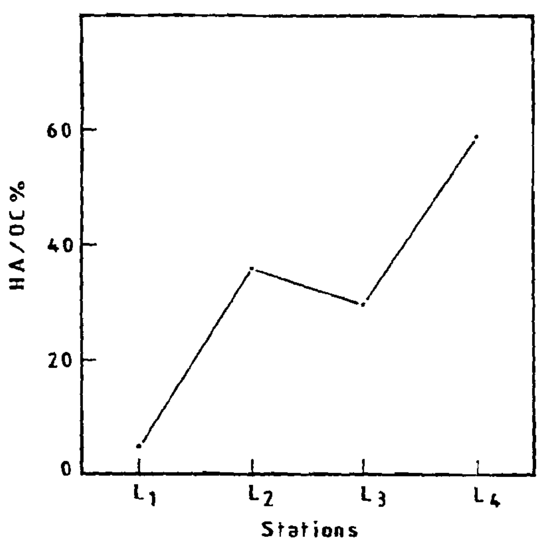

Fig. (5) The distribution of humic acids relative to organic carbon % off El-Maadiya region sediments of El-Maadiya channel, in agreement with El-Sayed data (1993), for studying the sediment characteristics and phase association and mobility of Fe, Mn, Zn, Cu, Pb and Cd in core sediments from Lake Edku.

Table (2): Trace metal contents in bulk sediments of Abu-Qir Bay (Fe in percent and other metals in ppm).

Station	Fe	Zn	Cu	Pb	Mn	Cr	Co	Cd	Ni
1 / 2 m	2.66	88	29	85	439	47	54	0.9	115
2	4.08	1140	39	80	315	449	78	4.4	173
3	2.77	126	12	37	554	274	36	3.3	40
4	3.12	99	18	44	407	117	50	5.1	86
5	3.87	97	17	77	617	384	60	3.1	78
6	2.27	56	7	87	362	176	31	4.0	59
1 / 3 m	3.34	110	24	56	554	61	29	3.0	65
2	4.85	484	59	87	249	256	66	1.4	196
3	4.13	132	16	48	779	201	50	4.4	79
4	3.12	119	16	64	562	91	57	3.7	86
5	2.23	68	6	84	363	87	25	5.1	47
6	4.31	170	15	93	137	419	82	6.1	106
L_1	2.04	88	9	33	342	60	22	3.0	44
L_2	4.67	57	22	30	198	52	35	4.1	82
L_3	3.33	120	28	44	357	53	27	4.8	48
L_4	3.41	79	15	40	468	67	27	4.2	57

Table (3): The average concentration of trace metals in Abu-Qir Bay at 2 and 3m depth and off El-Maadiya region (Fe in percent and other metals in ppm).

Location	Fe	Zn	Cu	Pb	Mn	Cr	Co	Cd	Ni
Abu-Qir at 2 m depth	3.13	97	20	68	449	200	51	3.5	91
Abu-Qir at 3 m depth	3.66	100	23	72	440	186	51	3.9	97
Off El-Maadiya region	3.36	86	24	37	341	58	28	4.0	58

Trace Metals in Humic Acid

Table (4) shows the results of trace metal contents (Fe, Cu, Zn, Pb, Mn, Cr, Co, Cd and Ni) in sedimentary humic acid. No sedimentary humic acid was available to determine trace metals in stations 5 and 6 (at 2 m depth) and stations 3, 4, 5 and 6 (at 3 m depth). The corresponding humic acids have higher trace metal levels than the sediment samples (Tables 2 and 4). This might be related, in part, to the change in sediments chemistry and the trace metals complexation by organic compounds. According to Kerndorff (1980), the concentration of trace metals given in humic acids should be regarded as minimum values as the extraction procedure used may cause hydrolysis, dissociation, metal precipitation and exchange of legends. Hirner *et al.* (1990) were also able to show significant enrichment of a number of trace metals with either dichloromethane extracts (Cr, Zn, Cd, Sb) or humic acids (Cu, Zn, As, Ag, Au). According to Nriago and Coker (1980), humic acids isolated from Lake Ontario sediments contain high concentrations of metals (Co, Cr, Cu, Ni, Zn, Fe and Mn). Therefore, a comparison of data for sediment and humic acid shows that all trace metals (Fe, Cu, Zn, Pb, Mn, Cr, Co, Cd and Ni) are enriched in the latter; i.e., in the humic acid fraction (Tables 2 and 4). In the sediments, iron is the most abundant element followed in a decreasing order by Mn, Cr, Zn, Ni, Pb, Co, Cu and Cd (Table 3). In humic acid, iron still keeps its superiority, the sequence is not the same since Cr and Pb are classed in the second and third positions after Fe, followed successively by Ni, Cu, Zn, Co, Mn and Cd (Table 4).

Table (4): Trace metal concentration in sedimentary humic acids of Abu-Qir Bay and off El-Maadiya region (in ppm).

Station	F	Zn	Cu	Pb	Mn	Cr	Co	Cd	Ni
1 / 2 m	4118	294	409	788	31	223	530	9	706
2	2571	246	100	205	13	468	105	2	361
3	7975	569	548	2670	-	2562	383	13	273
4	18013	357	922	2480	334	1179	318	32	1430
Mean	32677	1466	1976	6143	378	6432	1336	56	2770
1 / 3 m	5170	281	299	657	56	396	160	5	695
2	5522	199	120	236	30	447	150	2	344
L_1	38000	1200	870	2680	210	267	240	48	300
L_2	10148	110	183	322	31	132	89	22	266
L_3	7832	344	240	241	27	160	65	24	227
L_4	5721	233	140	265	30	201	51	21	306

The percentage of relative contribution of humic acid complexed trace metal, to the total metal load in the sediments is given in Table (5). The distribution of the metal between the bulk sediments and their humic acid depends on the abundance of the humic substances in the sediments. As shown in Table (5), humic acid complexed trace metals accounts for a major proportion of total pollution load of the sediments of Abu-Qir Bay and El-Maadiya region. The relative contribution of humic acids bound metal to the whole metal content in the bulk sediments (average percentage in stations 1, 2, 3 and 4 at 2 m depth) varies in a very wide range and is directly dependent on the element related to the humic acid contents of the sediments (Fig.6).

For manganese and iron, the contribution from humic acids is almost negligible since it does not exceed 1.17% and 5.9% with a mean of 0.6% and 2.1%, respectively, while in the sediment it was 449 ppm and 3.1%, respectively. The mean contribution from humic zinc to Abu-Qir Bay sediments at 2 m depth is about 6%, but may be as high as 12.7%. Humic acid constituted 18.5% of organic carbon of the sediment at station 1, but its cadmium and cobalt contents was about 37% of the total metals in the sediment. Chromium and nickel contributed from humic acids a mean of 23% and 24% of the total metal in the sediments, respectively. Humic acids constituted about 82% of organic carbon of the sediments at station 2 at 2 m depth and its lead and copper contents represented 79% of the total metal load in the sediment. These data agree with the results obtained by Aboul-Naga (1990) showing that the humic substances are a major reservoir of trace elements in recent marine sediment. Therefore, the high precipitation of humic substances as trace elements holder in the sediments added to its highly dynamic nature in the aquatic environment emphasizes the major role which it actually plays in the geochemical cycles of these elements (Fe, Cu, Zn, Cd, Cr, Ni, Pb, Mn and Co), which also have important environmental implications. Compared to the data of humic acids in lake Edku (Aboul-Naga, 1990) trace metals are enriched in Abu-Qir Bay in humic acid and relative sediments even at stations away from El-Tabia Pumping Station where a source of pollution might have left its imprint. Untreated or partially treated industrial and domestic wastewaters are discharged directly or carried by streams into the bay through El-Tabia Pumping Station. Comparing our data on humic bind metals (Table 6) with data obtained of organic bound elements for different types of sediments (Table 6). It seems that humic substances (humic acids and fulvic acids) in the major reservoir of some transition elements in the

Table (5): The percentage contribution of humic acid complexed trace metal to the total metal load in the sediments.

Station	Fe	Zn	Cu	Pb	Mn	Cr	Co	Cd	Ni
1 / 2 m	5.9	12.8	53.9	26.1	0.27	18.1	37.5	37.4	23.5
2	2.0	6.7	79.4	79.0	1.28	32.3	41.7	14.1	63.4
3	0.2	3.4	34.2	54.1	-	12.5	8.0	3.0	5.1
4	0.2	1.1	14.9	16.3	0.24	29.2	1.8	1.8	4.8
Mean	2.1	6.0	45.6	43.4	0.60	23.0	22.3	14.1	24.0
1 / 3 m	0.5	8.6	41.9	39.4	0.34	21.8	18.5	11.7	14.1
2	2.8	9.9	49.1	65.4	2.91	42.1	54.8	11.0	12.3
L_1	0.7	5.1	35.8	30.1	0.23	1.7	4.0	4.3	2.5
L_2	1.3	11.8	51.0	65.8	0.96	15.6	15.6	28.1	19.9
L_3	1.3	15.2	55.5	29.1	0.48	16.0	12.8	26.6	25.1
L_4	1.1	18.7	59.3	42.1	0.41	19.0	12.0	33.3	34.1

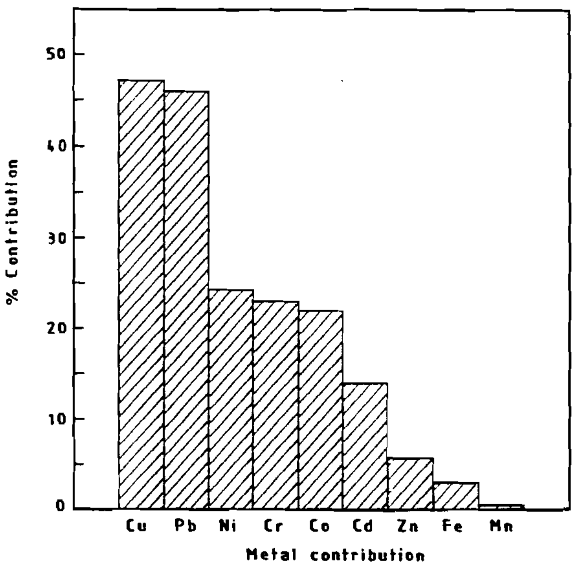

Fig. (6) The percent contribution of humic acid bound metals to whole metal content in the bulk sediments in samples at 2 m depth (in percent).

sedimentary organic matter (Table 6). In addition, humic substances react with metals, anions and organics and thus may present further threats to health and the environment by increasing the environmental distribution or inorganic and organic micropollutants.

Table (6): Percent contribution of organic-bound elements in sediments and suspended matter from different aquatic environments.

Locality and type of sediments	Fe	Mn	Zn	Cu	Ni	Co	References
Kara River estuary* sediments	-	1 - 11	9 – 15	4 – 29	13 – 31	21 – 34	Prohic, 1987
Yamaska and St. Francois Rivers Quebec Suspended matter	3.8 – 4.8	1.4 – 1.7	5 – 6	31 – 52	4.4 – 6.2	12 – 13	Tessier *et al.*, 1980
Lake Edku Sediments	0.03 – 0.79	1.1 - 13.0	0.9 – 60.9	2.1 – 43.0	1.6 – 24.9	1.1 - 16.0	Aboul-Naga, 1990
Recent Skagerrak sediments	-	0.6	5.7	21.1 – 30.5	-	-	Fengler *et al.*, 1994
Abu-Qir Bay Sediments	2.1	0.6	6.0	45.6	24.0	22.3	Present study

*** Organic matter and sulfides.**

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