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Enrichment of Fe, Mn, Cu, Zn, Pb and Cd in Humic Acid Sediment Cores, Lake Edku, Egypt

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ABSTRACT. The concentration of humic substances as humic and fulvic acids in Lake Edku sediment cores accounts for 54% of the total organic carbon in the three cores sediment samples. The total average trace metal concentrations of Fe, Mn, Zn, Cu, Pb and Cd are 55150, 1019, 79, 52, 42 and 3.5 ug g^{-1}, respectively in sediment core samples. The most abundant metals present in the humic acids were Fe, Zn, Cu, Pb, Mn and Cd. Significant portions of the total Pb, Cu and Zn found in the sediments were associated with humic acids. Smaller portions of Cd was found, whereas insignificant fractions of the total sedimentary Fe and Mn were recovered in association with humic acids. It is of interest to mention that while the total humic carbon represents only 29.5% of the total organic carbon, the humic acids contribute about 83% of lead and 75% of copper. These results reflect the importance of humic acids as a sink for these metals in lake sediment cores.

The organic matter of aquatic systems consists of the remains of biologically produced compounds as well as synthetic organic substances. Decomposition of higher molecular weight organic substances with high molecular mass is mostly due to microbiological action, this forming the smaller and more soluble fragments. The most important products formed during the composition of organic substances are the humic acids. These can be found in soils, in limnic and marine sediments, as well as in the corresponding aqueous solutions. Nissenbaum *et al.* (1972) show that humic substances are a major component of the organic matter contained in recent marine sediments. Values of 40% on an average and, in some cases, as much as 70% of the organic matter have been recorded (Nissenbaum and Swaine 1976). The attractive forces between metal ions with soluble, colloidal or particulate organic material range from weak, which leave the ions easily replaceable (physical adsorption), to strong, *i.e.*undistinguishable from chemical bonds as in metal chelation by organic material (Saxby 1969). Experimental studies showed that organic material can sorb between 1% and 10% dry weight of Co, Cu, Fe, Pb, Mn, Mo, Ni, Ag, V and Zn.

Rashid (1974) has shown that copper is preferentially sorbed on humic acids (53%), followed by zinc (21%), nickel (14%), cobalt (8%) and manganese (4%). Leaching experiments have demonstrated that copper is more firmly associated with organic material than other metals. Jonasson (1977) established the bonding strengths for Mo, Hg, Cu, Pb, Zn, Ni and Co onto humic or fulvic acids.

Finally, humic acids play an especially important role in trace element transport and retention by stream sediments because of the greater quantity present (Jenne 1976). Furthermore, the bonding ability of the corresponding humic acids is three to four times larger for divalent metal ions than for trivalent ions.

In recent years, a high degree of positive correlation has been often observed between the contents of organic materials and metal concentrations in aquatic sediments. This, however, does not necessarily involve preferential metal bonding by organic substances since a number of mechanisms (for instance, sorption by clay minerals and precipitation of Mn/Fe oxides) produce simultaneous accumulation of organic material and metals, especially in the fine-grained sediment fractions.

Extraction of metals from the organic fraction of sediment samples from Lake Malawi, containing 6.8% organic carbon-or approximately 12% organic substances, indicate that only zinc, copper and vanadium accumulate in association with organic materials, whereas iron, manganese, chromium, lead, cobalt and nickel are more or less diluted by these substances (Forstner 1977). On the other hand, the distribution of trace metals in humic substances in more heavily polluted sediments (Chen *et al.* 1976) proved to be 2 to 15 times higher than the total sediment on a weight basis.

Our knowledge of the concentration of humic acids in sediment cores in Lake Edku is still not adequate, although it is generally recognized that they comprise a large fraction of the total deposited organic matter. This paper deals with the distribution of humic substances isolated from three sediment cores and the concentrations of trace metals (Fe, Cu, Zn, Pb, Mn and Cd) in the humic acids. The total abundance of trace metals in the sediment, as well as in humic acids, was also determined.

Materials and Methods

Four lakes are found in the north of the Nile-Delta. These are Lake Manzalah, Lake Borullos, Lake Edku and Lake Mariut. The first three lakes receive drainage water from the main drains of the Delta irrigation system and are connected to the Mediterranean Sea, while the fourth lake, Lake Mariut is a closed one. Lake Edku is the smallest of the first three shallow lakes and the least anthropogenic pollution. It is directly connected with Mediterranean Sea at the western extremity through a narrow channel, Bougaz El-Maadia (Fig. 1). The lake-sea connection is located at the inner

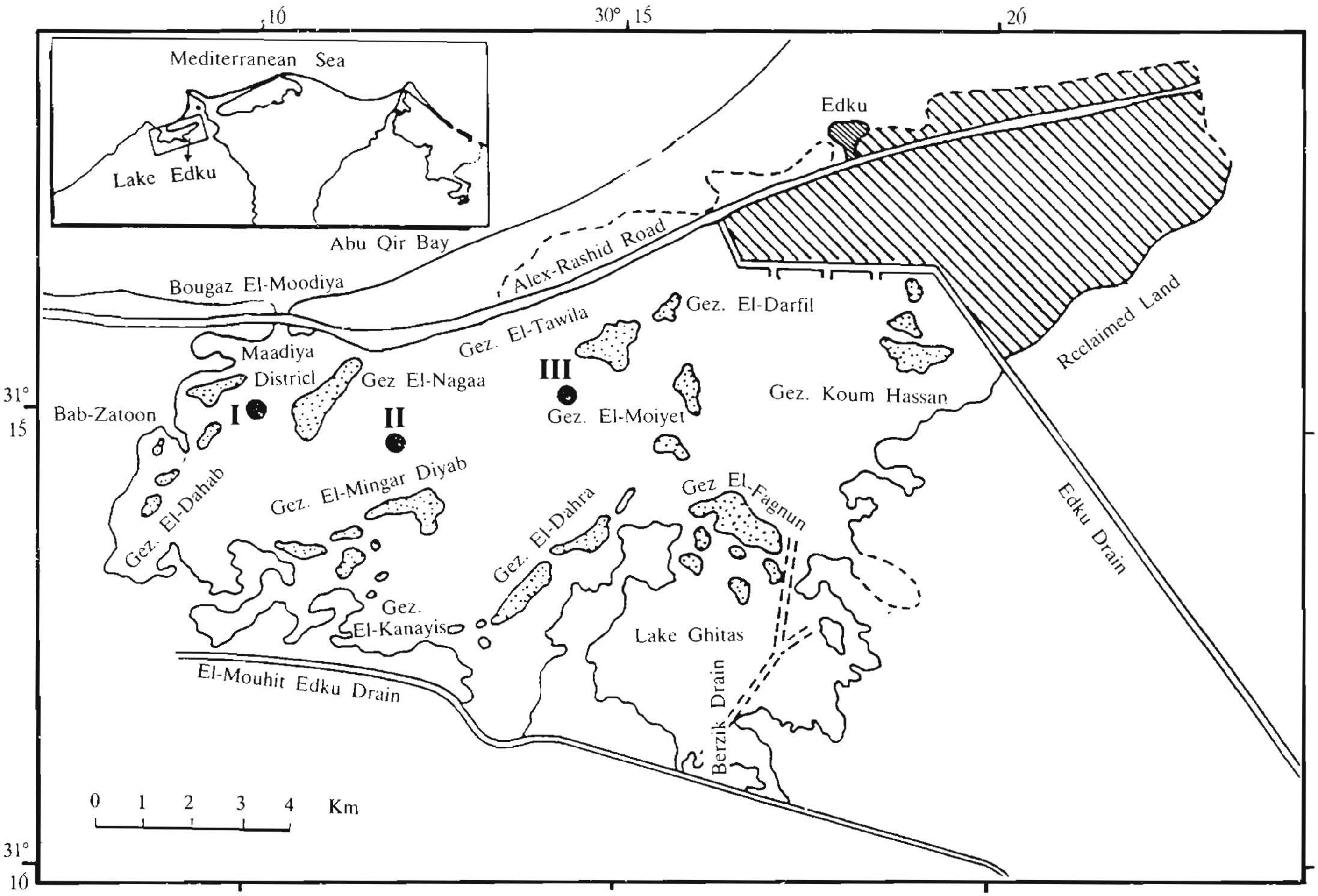

Fig. 1. Lake Edku and position of sampling station.

part of a partially sheltered bay known as Abu-Qir Bay. Lake Edku which lies west of Rossetta branch of the Nile, extends from east to west for a distance of about 19 km and has an average width of 6 km with an average depth of about one meter and the lake has an area of about 300,000 (Feddans). The lake bottom is characterized by sediment which are mainly silty-clay in the eastern basin or sand silt clay is mostly dominant in the western basin. This nature of the lake bottom, in addition to the fact that the whole lake is shallow favour the occurrence of rooted hydrophytes that spread all over the lake except for certain regions in the middle basin. However, the extremes southern part of the lake is very shallow and densely covered with plants such as *Potamogeton pectinatus* which hinder the fishing operations.

Humic acids described in this study were isolated from three sediment cores collected from a variety of locations in a shallow lake (Edku) to represent the three main sub-environments: The lake sea connection (core I), the central basin (core II) and the southern area affected directly by drains (core III) Fig. 1. Sediments of Lake Edku are derived principally from cultivated land in the drainage system. Drainage water flows into the lake through three main drains. The mean annual influx of drainage water is ($\simeq 1.0 \times 10^9$ m^3 yr^{-1}). This flow varies widely during the year with sudden increases during summer months (El-Sayed *et al.* 1993). Because of the shallowness of the lake, hydrophytes are flourishing all over the lake. In order to check for possible early diagenetic effects on the metal composition of humates, we analysed samples taken from 3 sediment cores (Table 1).

The extraction, isolation and purification of humic substances from different depth levels in cores employed in this study have been described by Nissenbaum and Kaplan (1972). Briefly, the procedure involves extraction (under nitrogen) with NaOH (0.2 N), repeated acid precipitation-base dissolution cycles, high-speed centrifugation and dialysis against deionized water (Milli-Q-Milli pure). Purification was achieved by the passage over the ion exchange resin Dowex 50×8 in the H^+ form and the extract was freeze dried. Fulvic acid was precipitated as barium salt at pH 4.5 - 4.8 (Majumdar and Rao 1978). After thoroughly washing with MQ water, the precipitate was freeze dried and weighed. Trace metals in humic acid samples were determined after complete acid dissolution using a 2:1 (v/v) mixture of HNO_3 and HCl, respectively.

Portions of sediment samples were dried at 70°C and carefully homogenized subsamples were powdered for determination of organic carbon and total trace metals concentration. Organic carbon content was determined by the method of Walkly and Black (1934). Total trace metals analysis was made using a 3:3:1 (v/v) mixture of HNO_3, HF and $HClO_4$, respectively. The relative standard deviation for ten and five replicates of a test sediment sample and humic acid sample, respectively, never exceeded 10% for the determination of total trace metals.

Total Fe, Mn, Zn, Cu, Pb and Cd concentrations in the sediment samples and the Fe, Zn, Cu, Pb, Mn and Cd concentrations in the humic acid samples were measured by Flame Atomic Absorption Spectrophotometer (Varian 1250).

Table 1. Distribution of humic substances as humic and fulvic acids (HA, FA), total humic substances (THS) and total organic carbon (TOC) in Lake Edku sediment cores

Core	Sample No	Depth (cm)	TOC (%)	HA (%)	FA (%)	THS (%)
I	1	0- 4	5.33	32.5	6.9	39.4
	2	4-10	6.51	21.8	14.4	36.2
	3	10-20	4.23	23.4	12.9	36.3
	4	20-38	1.73	23.4	10.1	33.5
Mean			4.45	25.3	11.1	36.4
II	1	0- 5	1.10	36.4	15.4	51.8
	2	5-10	1.37	41.1	37.7	78.8
	3	10-18	0.76	9.4	39.3	48.7
	4	18-41	0.40	9.4	30.4	39.8
Mean			0.91	24.1	30.7	54.8
III	1	0- 2	2.64	48.2	13.9	62.1
	2	2- 4	1.99	59.8	20.6	80.4
	3	4- 6	2.13	64.8	19.7	84.5
	4	6- 8	2.14	65.4	15.5	80.9
	5	8-10	2.52	17.1	47.6	64.7
	6	10-15	2.70	17.9	52.5	70.4
	7	15-20	2.23	22.9	44.7	67.6
	8	20-40	2.75	16.0	40.4	56.4
Mean			2.39	39.0	31.9	70.9
Mean			2.58	29.5	24.6	54.1

Results and Discussion

1. Occurrence of humic and fulvic acids in lake sediment cores.

The carbon content in Lake Edku sediment core samples averages 2.58% (Table 1). This value lies within, or near, the limit of other Egyptian Delta lakes. According to El-Wakeel and Wahby (1970), the organic carbon content in Lake Manzalah ranges between 0.19 and 4.05% with an average of 1.42%. Beltagy (1985) found that the organic matter content of sediments of Lake Borullus varies between 1.0 and 2.0%.

Lake Edku core sediment samples were generally well defined, but organic carbon showed wide variations with averages of 4.45%, 0.91% and 2.39% in cores I, II and III, respectively (Table 1). This most likely resulted from differences in local environmental conditions. The nature of the local environment may affect the generation of material through a combination of chemical, biological and physical processes. The TOC concentration is low in core II, with significant amounts being observed only in the surface (0-5 cm) and (5-10 cm) samples. On the other hand, the organic carbon content is high at all levels of core I (1.73 - 6.51%).

The fraction of organic matter in these sediments, present as humic substances (humic acids and fulvic acids), has been estimated in Table 1. Humic substances account for 36.4, 54.8 and 70.9% of the organic matter in sediment cores I, II and III, with a lake average of 54.1%. The highest value (70.9%) at core III is associated with relatively high humic acid contents ranging from 39.0% to 65.4%. A considerable proportion of the sedimentary humic acid was found in the upper parts of the cores (0-10 cm) while the highest fulvic acid (52.5%) contents were found in the deepest samples (>10 cm). Gershamovich *et al.* (1976) have also found extremely high contents of humic substances (60-90% total organic matter) in recent sediments. Comparing the results of the three sediments cores, it would appear that humic acids were 25.3% and 39.0% of the organic carbon in core I and III, respectively, while the core II contains relatively less humic acids (24.1%) and more fulvic acids (30.7%). This suggests that organic matter in core II is most probably composed of freshly accumulating material originating with low carbon concentration from a high carbon concentration form *in situ* production and a low degree of condensation.

2. Trace metal distribution in sediment cores.

Total trace metals concentrations in the sediment cores are given in Table 2. The results showed that the average total concentrations of Fe, Mn, Zn, Cu, Pb and Cd are 57787, 943, 81, 55, 42 and 3.4 ug g^{-1}, respectively. Recently, El-Mamoney *et al.* (1988), reported that the concentrations of Cd, Cu, Mn, Pb and Zn in sediments of Lake Burullus are 4.3, 66.8, 826, 110.2 and 129.7 ppm, respectively and 3.46% for iron. The concentrations of Zn, Cu, Pb and Cd demonstrate that the sediments of lake Edku are non-polluted while the concentrations of Fe and Mn indicate some enrichment with these two metals. As shown in Table 2, the core III sediments, derived from agricultural lands, are characterized by the highest Fe, Cu and Pb. These sediments have been enriched with Cu under the influence of high turbidity and water turbulence downstream from the drains (El-Sayed *et al.* 1993).

3. Trace metal abundance in sedimentary humic acids.

Of the elements usually regarded as major components of sediments and seawater, Fe, Mn, Cu and Cd are mostly found in high concentrations in the humic acids. Fe is almost always one of the predominant inorganic components of the humic acids. According to Sholkovitz *et al.* (1978), Fe (III) is the metal showing the highest

Table 2. Trace metal concentrations in sediment core samples (Fe in mg g^{-1} and all other trace metals in ug g^{-1})

Core	Sample No	Depth (cm)	Fe	Mn	Zn	Cu	Pb	Cd
I	1	0- 4	51.61	1780	97	43	44	3
	2	4-10	52.73	1219	98	47	34	3
	3	10-20	53.97	913	74	48	31	4
	4	20-38	76.48	1116	97	67	50	4
Mean			58.70	1257	92	51	40	3.5
II	1	0- 5	23.94	1194	48	29	42	3
	2	5-10	29.65	979	50	28	40	4
	3	10-18	30.76	680	46	26	39	4
	4	18-41	80.56	431	97	85	34	3
Mean			41.23	821	60	42	39	3.5
III	1	0- 2	43.82	1228	65	46	58	4
	2	2- 4	70.37	949	84	63	35	3
	3	4- 6	70.77	815	88	62	45	3
	4	6- 8	72.52	820	91	63	42	3
	5	8-10	67.95	737	81	58	43	4
	6	10-15	58.70	944	95	96	40	3
	7	15-20	83.72	1388	99	63	68	4
	8	20-40	56.38	951	70	55	51	4
Mean			65.53	979	84	63	48	3.5
Mean			55.15	1019	79	52	42	3.5

adsorption, has a very low solubility and is mainly found in a colloidal form in estuaries. On the other hand, cadmium, which shows the lowest concentrations in humic acids ($\simeq$ 1-2 ug g^{-1}), is the metal with the smallest surface-complex-formation constant and the greatest chloro-complex-fromation constant (Bourg 1983). As shown in Table 3, the concentrations of Fe, Cu, Pb, Zn, Mn and Cd were determined in ug g^{-1}, it is seen that humic acids in core II have the highest concentration of Fe. The next most abundant metal is Cu followed by Zn and Pb. Desai and Ganguly (1970) reported higher concentrations of Cu and Zn in humic acids from marine sediments on the coast of Bombay. On the other hand, Nriagu and Coker (1980) showed the humic acids isolated from lake Ontario sediments contain higher concentrations of Co, Cd, Cr, Cu, Ni, Zn, Fe and Mn. According to Raspor *et al.* (1984) trace metal content in ug g^{-1}, of humic acid from sediments of Mahakam Estuary, Borneo, were 3100, 118, 69.7, 7.9 and 0.6 for Al, Cu, Zn, Pb and Cd, respectively. It should be noted that in

Table 3. Trace metal concentrations in humic acid samples ug g^{-1})

Core	Sample	Fe	Mn	Zn	Cu	Pb	Cd
I	1	3223	4	120	229	144	<2
	2	3349	4	123	265	135	<2
	3	1548	3	168	148	128	<2
	4	1518	3	242	151	134	<2
Mean		2410	3.5	163	223	135	<2
II	1	9103	4	356	159	116	<1
	2	9020	4	363	115	119	<1
	3	10182	3	117	101	109	<1
	4	10453	4	101	153	123	<1
Mean		9690	3.8	234	132	117	<1
III	1	7209	5	163	112	60	<1
	2	7895	4	157	171	88	<1
	3	5673	3	199	161	135	<1
	4	4251	4	199	169	125	<1
	5	4323	4	182	105	94	<1
	6	6987	4	128	117	98	<1
	7	5649	4	107	149	101	<1
	8	4998	3	134	144	91	<1
Mean		5823	4	159	141	99	<1
Mean		5774	3.8	185	165	117	<1-2

the work reported by Raspor *et al.*, the humic acids were extracted under rather harsh pH conditions and we would expect that only the metals, or the portions of the metals, which are very strongly associated with or bound to the humates will remain. Hence, the values reported there are minimum values.

Based on the present results in Table(3)it can be concluded that the highest concentrations of Fe and Zn are contained in humic acids of core II, while the highest concentrations of Cu and Pb are present in humic acids of core I.

4. Relative contribution of trace metals from humic acids to bulk sediments.

The relative abundance of trace metals in humic acids and bulk sediments is listed in Table 4. It seems that the trace metal concentrations in the surface samples at depth from 0 to 10 cm were higher than in the deepest samples. On the other hand, appreciable decrease in the abundance of the measured metals in humic acids may be observed with depth. From the geopraphical distribution (Fig. 2), it is apparent that

Table 4. The occurrence of trace metals in humic acid samples relative to dry sediments ug g^{-1})

Core	Sample	Fe	Mn	Zn	Cu	Pb	Cd
I	1	1048	1	39	70	47	<0.5
	2	730	1	27	68	29	<0.5
	3	364	1	39	14	30	<0.5
	4	355	1	57	14	31	<0.5
Mean		624	1	41	41	34	<0.5
II	1	3314	2	130	58	424	<0.5
	2	3707	2	149	47	9	<0.5
	3	957	0.3	11	10	101	<0.5
	4	983	0.4	10	14	4	<0.5
Mean		2335	1.2	56	32	28	<0.5
III	1	3475	2.4	79	54	29	<1
	2	4721	2.4	94	70	53	<1
	3	3676	2.0	129	65	88	<1
	4	2780	2.6	130	71	82	<1
	5	739	0.7	31	18	16	<1
	6	1251	0.7	23	21	18	<1
	7	1294	0.9	25	30	23	<1
	8	800	0.5	21	17	15	<1
Mean		2342	1.5	72	43	41	<1
Mean		1767	1.2	56	39	35	<0.5

iron and zinc showed maximum binding capacity towards humic acids in core II. The order of abundance of trace metals in humic acids is Fe>> Zn> Cu> Pb>> Mn> Cd but in the sediments it is Fe>> Mn> Zn> Cu> Pb> Cd. So, the results indicate that Mn is depleted in the marine humates (<0.5 ug g^{-1}) while there are relatively large amounts of Zn and Cu in the fresh water humates (56, 39 ug g^{-1}). In addition, in the series of the elements studied, iron is the most abundant element in both sediments and still keeps its superiority in the humic acids. Manganese is second in abundance in the sediments while in humic acids it is the smallest one representing only 0.12%. According to Rashid (1972) marine humates solubililize Co, Cu, Ni and Zn but only small amounts of Mn. Sholkovitz (1978) demonstrated, both in the field and the laboratory, that dissolved iron and humic acids coagulated into particles during estuarine mixing of the Amazon River. On the other hand, the metals which form strong complexes with humic acids (*e.g.* Al, Cu, Ni, Cd and rare elements) were precipitated along with humic acids and iron hydrous oxides (Sholkovitz 1978, Sholkovitz and Copland 1981, Hoyle *et al.* 1984).

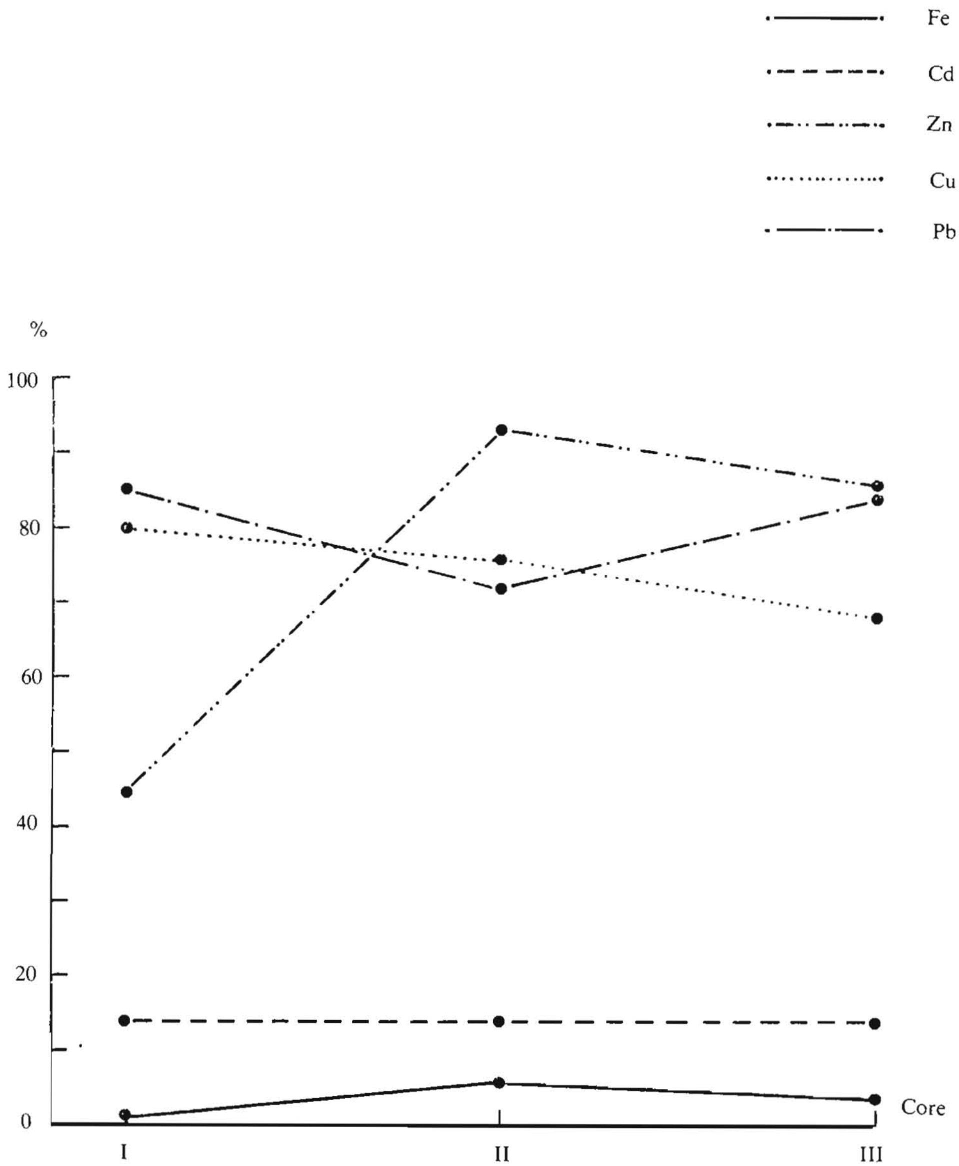

Fig. 2. The distribution of trace metal in humic substances relative to the bulk sediments.

The average concentration of trace metal pool in the lake sediments can be seen from Table (5) and the percentage contributions is shown in Table (6). The greatest contribution is Pb (83%) while the smallest one is that for Mn (<0.12%). Nissenbaum and Kaplan (1972) showed that humic substances are a major reservoir of trace elements in recent marine sediments. The order of contribution is Pb, Cu and Zn followed by Cd, Fe and Mn, respectively. Comparing the various metals, the percentage contribution may reach as high as 83, 75 and 70% for Pb, Cu and Zn, respectively. These results are relatively higher than the results reported by Aboul Naga (1990) for surface Lake Edku sediments, reflecting the importance of humic acids as a sink for these metals in sediment cores.

Table 5. Average conentration of trace metals in humic acid and bulk sediments ug g^{-1})

Core	Sample	Fe	Mn	Zn	Cu	Pb	Cd
I	HA	624	1	41	41	34	<0.5
	Sed.	58700	1257	92	51	40	3.5
II	HA	2335	1.2	56	32	28	<0.5
	Sed.	41230	821	60	42	39	3.5
III	HA	2342	1.5	72	43	41	<0.5
	Sed.	65530	979	84	63	48	3.5
Lake	HA	1767	1.2	56	39	35	<0.5
	Sed.	55150	1019	79	52	42	3.5

Table 6. Percentage contribution to the bulk sediments of trace metals from humic acids

Core	Sample	Fe	Mn	Zn	Cu	Pb	Cd
I	HA	1.06	0.08	44.57	80.39	85	<14.29
II	HA	5.66	0.15	93.33	76.19	71.80	<14.29
III	HA	3.57	0.15	85.71	68.25	85.42	<14.29
Lake	HA	3.20	0.12	70.89	75	83.33	<14.29

Conclusions

From the distribution of trace metals (Fe, Cu, Zn, Pb, Mn and Cd) in lake sediment cores and sedimentary humic acids, it is possible to draw the following conclusions. Humic substances can interact with inorganic materials in surface marine sediments by a variety of mechanisms. One mechanism is complexation of dissolved metal ions by electron-donor groups (ligands) within humic polymers. Nearly all metals are capable of forming such complexes and most of the N−, O− and S− containing functional groups in humic substances can serve as ligands. Iron is the most abundant metal in humic acids emphasizing that in humic acids contents of trivalent metal ions, like Fe and Al, are higher than those of divalent heavy metal ions. Desai and Ganguly (1970) and Raspor *et al.* (1984) also reported higher contents of trivalent (Al; Fe), rather than divalent cations, in humic acids isolated from shelf sediments of the Arabian Sea and from marine and estuarine sediments, respectively. The mean contribution of humic iron to lake sediments is 3.2%. Considering the trace metal contents of the humic acids investigated in sediments from three cores, in spite of the purification procedure applied, it follows that a significant amount of certain metals is still retained. Thus, a corresponding number of strong binding sites for heavy metals were retained in the humic substances. The complete removal of the heavy metal content would most probably be possible only after the breakdown of the molecular structure.

Humic acids may contribute as high as 80% of the trace metals in the bulk sediments. They are highly enriched in Pb, Cu and Zn (83, 75 and 70%, respectively) and to a moderate extent in Cd (<14%) when compared to the bulk sediments but depleted in the major elements like iron and manganese (3.2 and 0.12%, respectively). The relationship between lead and copper is established and gives (r) value of 0.5785 at 95% confidence level.

The relative contribution of trace metals in the humic acids to the bulk sediments showed wide variations between sampling stations depending on the concentration of the humic substances. It is of interest to mention that while the total humic carbon represents only 29.5% of the total organic carbon, the humic acids contribute about 83% of lead and 75% of copper. It is obvious that these metals are strongly bound to the humic acids (Raspor *et al.* 1984). These results are relatively higher than those reported on surface Lake Edku sediments (Aboul Naga 1990), reflecting the importance of humic acids as a sink for these metals in lake sediment cores.

Humic acids from the site that has some marine influence (core I) are characterized by a higher copper content than the humic acids from a proper lake sediments (core II) and sediments near a drain (core III). The presence of relatively higher concentration of some of the measured elements in core I may be attributed to mixing with organic material from the polluted Abu-Qir Bay. An appreciable decrease in the abundance of the measured metals in humic acids may be observed with depth.

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اثراء الحامض الهيومي بالحديد والنحاس والزنك والرصاص والمنجنيز والكادميوم في أعمدة الرواسب القاعية ببحيرة إدكو - مصر

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تكـون المواد الهيـومية كحـامض هيومي وحـامض فـولفي حـوالي ٥٤٪ من الكربون العضوي المتواجـد في عينات ٣ أعمـدة من الرواسب القـاعية. وكـان متوسط تركيـزات العناصر الشحيحـة مثل الحـديد والمنجنيـز والزنـك والنحاس والـرصـاص والكـادميــوم هي: ٥٥١٥٠، ١٠١٩، ٧٩، ٥٢، ٤٢، ٣,٥ ميكروجرام في الجرام على التوالي في عينات عواميد الرواسب القاعية.

وكانت أكثر العناصر تواجـداً في الحامض الهيـومي المستخلص هي الحديـد والزنك والنحاس والرصاص والمنجنيز والكادميوم.

وكـان النحاس والـرصـاص يمثـلان أكبر نسبـة أما الكـادميوم فيمثـل نسبـة متـوسطة وعـلى العكس فإن المنجنيـز والحديـد همـا العنصـرين الأقـل نسبـة في الحامض الهيومي.

ومما يثير الدهشة أن نذكر أنه بالرغم من ان الكربون الهيومي يمثل ٢٩,٥٪ فقط من الكربون العضوي فإنـه يحتوي عـلى حوالي ٨٣٪ من الـرصاص و٧٥٪ من النحاس. وهذه النتائج تعكس أهمية الحامض الهيومي كحوض لتجميع هذه العناصر في أعمدة الرواسب القاعية للبحيرة.