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## ASSESSMENT OF TRACE METALS IN THE SEDIMENTS FROM THE COASTAL ZONE OF ALEXANDRIA, EGYPT

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Freshly deposited surface sediments from the Alexandria coastal zone were collected and analysed in 1995 for their trace metal concentrations. Metal concentrations in the sediments vary between sites within a wide range for copper, zinc, iron, lead, chromium and cadmium. The statistical analysis between the metal concentrations and the different constituents (organic carbon, total nitrogen, silt, clay and total iron) showed significant correlations. The enrichment factors for the sediments ranged between 3 and 4-fold for copper, chromium and zinc and reached up to 9-fold for lead and 113-fold for cadmium. The highest index for cadmium and lead may be attributed to the anthropogenic inputs from the surrounding area, where they are highest in lower discharge areas.

*Keywords:* Surface sediments; trace metals; Mediterranean coast; Alexandria; pollution index

### INTRODUCTION

Many studies were performed to examine the main pollutants along the Mediterranean coast. Alexandrian coastal waters receive many pollutant substances from various sources such as domestic, industrial and drainage waters from the surrounding area. The area of the present study (Fig. 1), is limited by the longitudes 29°47' and 30°0' E and latitudes 31°8' and 31°17' N. The waste-water influence on the contamination of the coastal zone comes from Alexandria City. This occurs extensively at the Eastern, Western and New El-Dikheila

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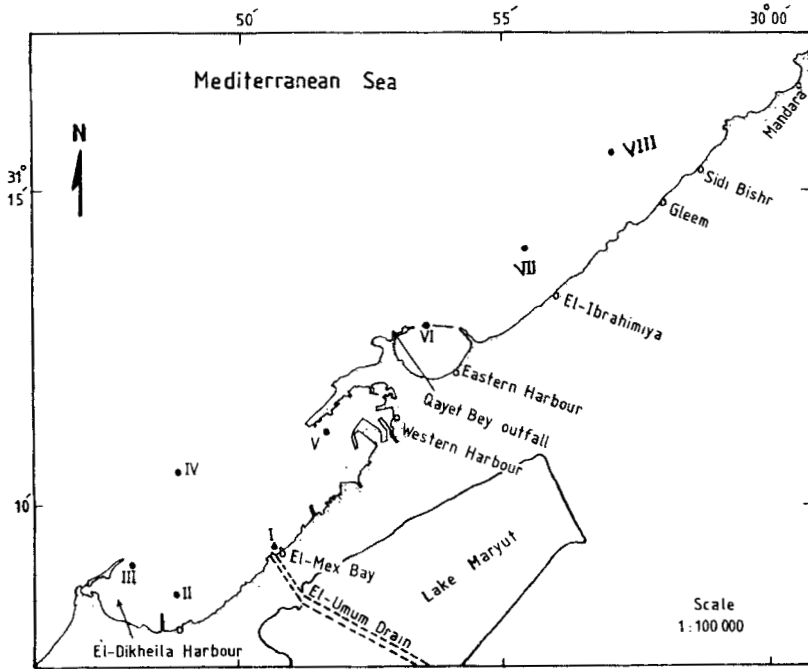


FIGURE 1 Position of sampling stations in the area investigated.

Harbours as well as El-Mex Bay and Abu Qir Bay borders of the city. The hydrography and chemistry of the Eastern and Western Harbours have been studied by many investigators. The Western Harbour receives about  $33 \times 10^6 \text{ m}^3$  a year of water from El-Nobarria Canal in addition to some sewage waters (Hassan and Saad, 1996). El-Rayis *et al.* (1996) showed that considerably higher concentrations of copper and zinc are recorded near the outlet of the Western Harbour. El-Mex Bay is considered an important fishing ground and  $2190 \times 10^6 \text{ m}^3$  a year are discharged from El-Mex pumping station to the west of the harbour which could be introduced into the harbour under the effect of a westerly wind (Nessim and Tadros, 1988). The Eastern Harbour receives annually about  $962 \times 10^6 \text{ m}^3$  and raw sewage from the main sewage outfall (Kayet Bey) is situated in its vicinity. The Eastern area lies between Kayet Bey outfall and Gleem is affected mainly by sewage discharged from the main sewer at Kayet Bey.

The bottom sediments of these sites are continually accumulating trace and major elements and they are a record of the long term input of materials. These elements when discharged to the marine environment will be transported by prevailing currents and removed by either physical, chemical or biological processes. Elements are picked up by particulate or organic matter and settle at the bottom. Therefore, the aim of the present work is an attempt to study some trace metal concentrations (copper, cadmium, iron, lead, zinc and chromium) in the surficial sediment of the coastal zone of Alexandria, as well as to evaluate the extent of pollution by heavy metal load due to the material of anthropogenic trace metals, which may affect the availability of metals. Partial extraction is an indication of the relative binding strength for these metals that is obtained by extraction with hydrochloric acid. Louma and Bryan (1981) have shown that this extractant provides useful information for assessment of the fraction of total metal concentration in sediments available for biological uptake.

## MATERIALS AND METHODS

Surficial sediment samples were collected along Alexandrian coast during 1995 (Fig. 1). Eight sampling locations (I to VIII) were chosen to represent different sedimentary environments taking into account the influence of the urban and industrial wastes in front of El-Dekheila Harbour (stations II and III), El-Mex Bay (stations I and IV), Western Harbour (station V), Kayet Bey, Eastern Harbour (station VI), El-Ibrahimiya and Glem (stations VII and VIII). The sediments were dried to constant weight at room temperature. Some physical and chemical analysis (organic carbon, total nitrogen, grain-size distribution and inorganic carbon as calcium carbonate) were carried out. Following Oregoni and Aston (1984), sediment samples were digested in a dried teflon beaker with the acid mixture ( $\text{HNO}_3/\text{HClO}_4/\text{HF}$ , 3:2:1) and evaporated to near dryness at  $80^\circ\text{C}$ . After complete digestion, 5 ml of 0.1 M hydrochloric acid were added at room temperature and the residue was transferred to a 25 ml volumetric flask with extra hydrochloric acid (0.1 M). Trace metals in these solutions were measured using Atomic Absorption Spectrophotometer (Perkin-Elmer 2380).

Organic carbon content was estimated using the wet oxidation method (Nelson and Sommers, 1982). According to the Bremner and Mulvaney (1982) method, the total nitrogen content was determined. Inorganic carbon (total carbonate) content was evaluated from the weight loss after treatment with 0.2 M hydrochloric acid. Grain size distribution was determined by wet sieving of sand and by pipette technique for silt and clay fractions (Folk, 1974). To assess the influence of trace elements in sediments on the environment, the hydrochloric acid was used to extract the metals due to the anthropogenic components (Louma and Bryan, 1981). One gram of dried (50°C) sediment of each sample was shaken for 2 h with 10 ml hydrochloric acid, 1 N, and the amount of metal in the supernatant, which was removed with centrifugation (5000 r.p.m for 15 minutes), was measured.

## RESULTS AND DISCUSSION

Table I shows physical and chemical properties of the surficial sediments which are used in the present study. It is clear that the total organic carbon ranged between 0.07 and 2.55%.

Also, the predominant sediment type is the coarse fraction, percentage of the fraction reached up to 93% with some exception at sites II, V and VI, where the mud content was up to 49.3%, 63.5% and 35.7%, respectively.

TABLE I Physical and chemical properties of the surficial sediment samples

Site	Organic carbon %	Total nitrogen %	C/N Ratio	CaCO <sub>3</sub> %	Grain size distribution			Textural class
					Sand	Silt	Clay	
I	0.488	0.059	8	77	93.6	4.2	2.2	sandy
II	0.338	0.013	26	87	50.7	44.3	5.0	sandy loam
III	0.225	0.045	5	82	97.3	2.3	0.4	sandy
IV	0.113	0.043	3	85	98.9	1.1	—	sandy
V	2.550	0.252	10	85	36.5	54.0	9.5	silty loam
VI	1.200	0.232	5	60	64.3	25.5	10.2	sandy loam
VII	0.263	0.063	4	89	97.5	2.5	—	sandy
VIII	0.075	0.038	2	76	98.3	1.7	—	sandy

TABLE II Total concentration of trace metals, extractable, residual fractions ( $\mu\text{g g}^{-1}$ ) and surficial enrichment. Res. = Residual = T.M. - EXT., S.D. = Standard Deviation, EXT. = Extractable Conc, S.E.F. = Surficial Enrichment

Sites	Copper		Cadmium		Zinc		Lead								
	T.M.	EXT.	Res.	S.E.F.	T.M.	EXT.	Res.	S.E.F.	T.M.	EXT.	Res.	S.E.F.			
I	10.0	0.63	9.27	2.5	18.75	5.0	13.25	125	40.0	3.26	36.74	2.0	239.6	17.8	221.8
II	17.5	0.63	16.87	4.0	16.25	5.5	10.75	108	35.63	0.68	34.95	1.8	270.8	21.4	249.4
III	5.0	1.25	3.75	1.2	17.5	6.5	11.0	117	31.88	4.11	27.77	1.6	166.7	16.6	150.1
IV	7.5	0.63	6.87	2.0	20.0	5.5	14.6	133	36.25	3.54	32.71	1.8	208.3	15.2	193.1
V	40	1.25	38.75	10.0	15.0	5.0	10.0	100	91.88	21.74	70.14	4.6	218.8	17.2	201.6
VI	42.5	1.88	40.62	10.0	16.3	6.0	10.3	109	109.38	6.79	102.59	5.5	375.0	18.0	357.0
VII	7.50	1.25	6.25	1.9	16.3	6.0	10.3	109	34.38	5.44	28.94	1.8	260.4	16.4	244
VIII	5.0	1.25	3.75	1.2	18.75	4.5	14.25	125	36.25	2.99	33.26	1.8	156.3	20.1	136.2
Mean	16.9	1.1	12.0	4.1	17.4	5.6	11.8	115	52.0	6.1	45.9	2.8	237.0	17.8	219.2
$\pm$	$\pm$	$\pm$	$\pm$	$\pm$	$\pm$	$\pm$	$\pm$	$\pm$	$\pm$	$\pm$	$\pm$	$\pm$	$\pm$	$\pm$	$\pm$
S.D.	15.6	0.4	11.6	3.7	1.7	0.6	1.9	11.1	30.5	6.6	26.6	1.9	69	2.0	68.8

### **Total Content, Leachable and Residual Fractions of Trace Metals**

As shown in Table II, the results revealed that the total concentration of trace metals (copper, zinc, iron, lead and chromium) in surficial sediments tended to decrease away from El-Mex Bay to the Eastern Harbour towards the sea as the decreasing influence of waste disposal. Metal distribution in surficial sediments of the study area show varying and different behaviour influenced by urbanisation processes. Total metal concentration in the sediments vary in the range of 5–42.5 for copper, 15–20 for cadmium, 31.9–109.4 for zinc, 1500–2917 for iron, 156.3–375 for lead and 25–137 for chromium (all  $\text{mg kg}^{-1}$ ) for chromium. Trace metals content markedly increased in the sediments of stations V and VI; this may be related to the deposition of sediment. These stations had relatively high levels of fine particles (clay, 10%) and increase in organic carbon (2.55% in sector V and 1.2% in sector VI); These values (Tab. I) of organic carbon and total nitrogen may be due to the discharged wastes and phytoplankton activities. The data in Table II indicate that the area away from sites V and VI had markedly less metal contamination with the exception of the total content of cadmium and Cd-extract with hydrochloric acid. The results show that similar levels of total cadmium concentration and Cd-extract were found in the study area and this may be attributed to higher cadmium level in overlying sediments. The leachable trace metal concentration in hydrochloric acid and residual fractions of the total content are listed in Table II. It is evident that the highest content of leachable or residual cadmium was found in the sediment with a higher percentage in the extractable fraction. The most striking feature is the predominance of the residual fraction for all metals except cadmium, where the acid leachable cadmium reached up to 37% of the total content (Fig. 2). Alloway (1990) noted that adsorption processes rather than mineral precipitation or organic complexation control the distribution of cadmium between the soluble and solid phases in polluted soils. Heavy metal sulphides are practically insoluble at neutral pH. Iron, manganese and cadmium sulphide are readily soluble in hydrochloric acid, whereas copper, lead and mercury sulphides are only soluble in oxidizing acids, such as nitric acid (Förstner and Wittmann, 1981). Engler and Patrick (1975) stated that under reducing conditions in reduced soils and sediments containing

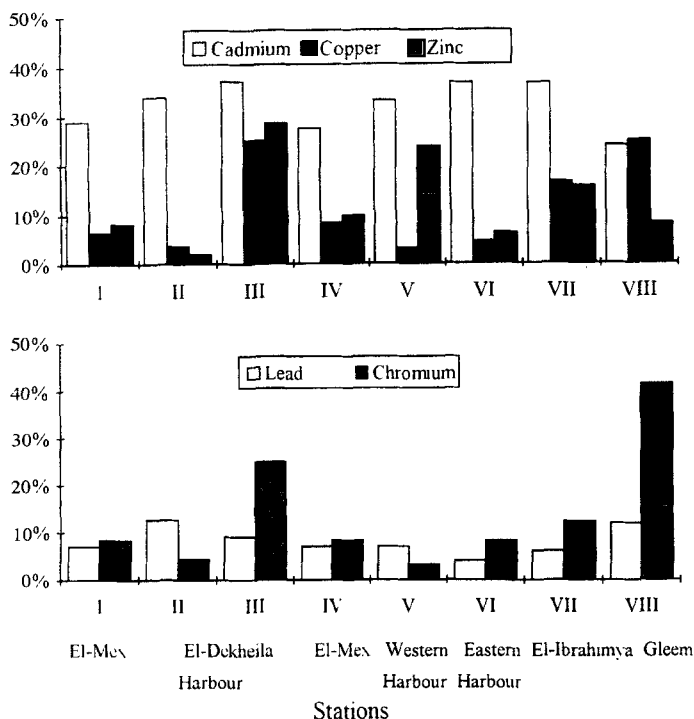


FIGURE 2 Relative amounts of trace metals in leacheable fraction.

sulphides, the precipitation of insoluble metal sulphide could be important in controlling the soluble levels of toxic metals. Nessim (1994) showed that the cadmium concentration extracted with hydrochloric acid are nearly homogeneous in the Western and Eastern Harbours with an average of 4.3 ppm. A higher concentration of total cadmium was found in the Western Harbour sediments, where this was 7 to 64  $\mu\text{g g}^{-1}$  (El-Sayed *et al.*, 1988); cadmium comes to the study area with the industrial waste waters. Amounts of cadmium accumulate in the deposits through contaminated materials such as use of coal and oil, cement, chemical plants and tanneries. Precipitates of cadmium phosphates could be expected to form in soils containing elevated cadmium levels, especially at higher pH values (Lindsay, 1979). The average of total phosphorus in the



Western and Eastern Harbours sediments is 188 and 298 ppm (Nessim, 1994).

### Statistical Analysis

To validate the trace metals association with the different constituents, the statistical evaluations of the analytic data were made. As shown in Table III, there is a highly significant positive correlation between the total content of metals (copper, zinc, iron, chromium) with the fine particles, other than lead. The association of these metals with organic carbon is related to its importance as micronutrients (significant correlation between  $r = 0.80$  and  $r = 0.86$ ); this may reflect the role of organic materials in partitioning of trace metals. It is evident from the results (Tab. III) that there is highly positive correlation between these metals and the total iron. This may suggest that copper, zinc, chromium and other elements in polluted waters are scavenged by iron oxides present in bottom sediment (Lu and Chen, 1977). The correlation analysis shows that the total zinc is strongly correlated with the total copper ( $r = 0.96$ ). This was found, in agreement with the finding of El-Sayed (1993) for Lake Edku sediments, where he suggested that copper and zinc are incorporated in some mineral form. There is a positive correlation between leachable zinc, copper and organic carbon content ( $r = 0.94$  and  $0.38$ , respectively). The results showed that more than 95% of the iron was found in the residual fraction and the correlation analysis revealed that the total iron (Tab. III) associated with clay and organic matter, suggest that the iron occurs either as a lithogenic or an anthropomorphic effect. Cadmium had negative correlation with some physical and chemical parameters; this may be attributed to its chemistry in natural waters and appears to be dominated by inorganic forms and its low tendency to form organic complexes (Bernhard *et al.*, 1975). On the other hand, Nessim (1994) suggested a certain complexation between cadmium and carbohydrate contents in the Eastern Harbour where he found a positive correlation between both.

According to Förstner and Wittmann (1981), the anthropogenic input of heavy metals is directly proportional to the concentration of these metals in the exchangeable form of the sediments affected by the polluted waters.

TABLE III Correlation coefficient ( $r$ ) between trace metals and some physical and chemical parameters of  
 T. N. = Total Nitrogen, EXT. = Extractable Concentration, O. C. = Organic Carbon, Res. = Residual co

	T.N.		O.C		CaCO <sub>3</sub>		Silt		Clay		Copper		Cadmium		Zinc		
	T	Res	T	Ext	T	Res	T	Ext	T	Res	T	Ext	T	Res	T	Ext	
T.N.	1																
O.C	0.91	1															
CaCO <sub>3</sub>	-	0.77	1														
Silt	-	0.84	-	1													
Clay	0.86	0.84	-	0.83	1												
T.Cu	0.92	0.86	-	0.77	0.98	1											
Ext. Cu	0.66	-	-0.63	-	-	1											
Res. Cu	0.92	0.87	-	0.78	0.89	0.999	1										
T.Cd	-	0.68	-	-0.76	-0.7	-0.68	-	-0.68	1								
Res.Cd	-	-	-	-	-	-	-	-	0.94	1							
T.Zn	0.96	0.82	-	-	0.92	0.96	0.67	0.96	-	-	1						
Ext.Zn	0.82	0.94	-	-	-	0.68	-	0.68	-	-	0.66	1					
Res.Zn	0.90	0.70	-0.73	-	0.90	0.94	0.69	0.93	-	-	0.98	-	1				
T.Fe	0.89	0.8	-	-	0.84	0.88	-	0.88	-	-	0.91	0.68	0.87				
Res.Fe	0.90	0.81	-	-	0.86	0.90	-	0.89	-	-	0.91	0.68	0.88	0.			
Ext.Fe	-	-	-	-	-	-	-	-	-	-	-	-	-	-			
T.Pb	-	-	-	-	0.66	-	-	0.66	-	-	-	-	-	-	0.63	-	0.72
T.Cr	0.86	0.98	-	0.81	0.83	0.85	-	0.85	-0.76	-0.61	0.77	0.91	0.66	0.			
Ext.Cr	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Res.Cr	0.84	0.97	-	0.82	0.83	0.85	-	0.85	-0.75	-0.61	0.76	0.89	0.65	0.			

The relative amount of the anthropogenic trace metals fraction (in the leachable fraction) to the total elements in the surficial sediments for the study area is presented in (Fig. 2). The results showed that the percentage of trace metals (copper, zinc, lead, iron and chromium) in the leachable fraction ranged from 0.43% to 25% but was important for cadmium where it reached about 37% of the total cadmium in the sediments of the area.

### Pollution Index

To fulfil the objectives of the study, the Surficial Enrichment Factor (SEF) of metals in the surficial sediments of the study area has been calculated (as a pollution index) as the ratio of metal concentration in the sample to the same metal concentration of the natural levels. The background levels of trace metals suggested by Whitehead *et al.* (1984) for the Mediterranean sediments are likely to be 15 for chromium, 0.15 for cadmium and 25 for lead (all  $\mu\text{g g}^{-1}$ ). Elsokkary and Müller (1990) suggested that the enrichment factor has been computed as the ratio of metal content in the sediment sample to the metal concentration in the shale material. Recently, the average composition of shale has been adopted as the standard material. Trace metal concentration of shale materials are 95 for zinc; 90 for chromium; 45 for copper; 20 for lead; 19 for cobalt and 0.3 for cadmium (all  $\mu\text{g g}^{-1}$ ). Most carbonate rocks show a dilution of trace metals with the corresponding shale levels. The concentrations of zinc ( $20 \mu\text{g g}^{-1}$ ) and copper ( $4 \mu\text{g g}^{-1}$ ) (Förstner and Wittmann, 1981).

The total content of carbonate in the sediments of the study area was between 60 to 89%. According to the above results, we could consider the values of each trace metal in the Mediterranean sediments and carbonate rocks as the background level for the study area. The average concentration of copper (17), cadmium (17), zinc (52), lead (237) and chromium (55) (all  $\text{mg kg}^{-1}$ ) are compared with natural background values, the enrichment factors for the sediments are ranged between 3 and 4-fold for copper, chromium and zinc. The results showed that the highest index reached 9-fold for lead and 113-fold for cadmium. These high factors are attributed to the anthropogenic inputs from the surrounding area.

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