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Accumulation and distribution of heavy metals in surface sediments of a semi-enclosed basin in the southeastern Mediterranean Sea, Egypt

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Abstract

The distribution, enrichment and accumulation of heavy metals in the surficial sediments of the Alexandria City Eastern Harbour (Mediterranean coast of Egypt) were investigated. Surface sediments (in the <63mm fraction) collected from 12 sites representing the entire area of the harbour, were analyzed by AAS for Cd, Cu, Zn, Cr, Pb and Al. Metal contents were compared with literature data to assess the pollution status of sediments. Enrichment factors (EFs) and the geoaccumulation Index (Igeo) were calculated as a criterion of possible contamination.

Keywords: Heavy metals; Eastern harbour; Enrichment factor; Geoaccumulation index.

Introduction

Heavy metals in marine sediments have both a natural and anthropogenic origin: distribution and accumulation are influenced by sediment texture, mineralogical composition, adsorption and desorption processes and physical transport. Metals participate in various biogeochemical mechanisms, have significant mobility, can affect the ecosystems through bioaccumulation processes and are potentially toxic for the environment and for human life (MANAHAN, 2000). Sediment contamination poses one of the worst environmental problems in marine ecosystems, acting as sinks and sources of contaminants in aquatic systems. Sediment analysis plays an important role in assessing the pollution status of the marine environment (MÜCHA *et al.,* 2003, PEKEY, 2006). Heavy metals have been discharged into the world's rivers, harbours and estuaries as a result of rapid industrialization (CHEN *et al.,* 2004). Chromium (Cr VI) is classified as priority pollutant by the United States Environmental Protection Agency (US EPA) with a carcinogenicity classification A (human carcinogen), while Cd and Pb are classified in the same list with a carcinogenicity classification B (probable human carcinogen) (US EPA, 1999).

The Mediterranean Sea is an area where sediments have different geochemical composition. The Eastern Harbour of Alexandria (EH) is located in the south-eastern Mediterranean Sea between latitudes 31° 12′ – 31° 13′ N and longitudes 29° 53′ - 29° 54′ E (Fig. 1); it is a semi-enclosed basin (mean depth 6m), and has been strongly affected by urbanization (EL-RAYIS *et al.,* 1997, EL-SABROUTI *et al.,* 1997 and ABDALLAH & ABDALLAH 2007). The Harbour has a surface area of about 2.53 km^2; accordingly its volume is about $15.2x10^6$ m^3. It is sheltered from the sea by an artificial breakwater leaving two openings (left and right). The left opening is the main navigation entrance to the harbour (300 m width). Through these openings the exchange of water between the harbour and Mediterranean water takes place.

Sources of pollution include untreated domestic discharges through several submerged minor sewage outfalls distributed along the harbour coast. There are various small industries such as: photo development shops, car cleaning and repairing, some foodstuff plants, gas stations, small dairy plants and some foundries. Also the harbour water receives additional waste effluents from fishing ships and the shipyard situated on its western side. Other wastewater discharges occur through two marine outfalls lying at the outer sides of the harbour, the Qait Bey and Silsila marine outfalls (EL-RAYIS *et al.,* 2003).

The importance of this harbour relates to the discovery of ancient buildings on the peninsula of Timonium and Antirhodos Island (located in the eastern part of the harbour) and artificial dykes constructed by the Ptolemies and by Marcus Antonius. In addition, about 1000 different artifacts including columns, basins, sphinx statues, and parts of obelisks with hieroglyphs and ceramics were discovered during the excavations. This basin is also considered as one of the main fishing grounds for the city of Alexandria and its adjacent areas.

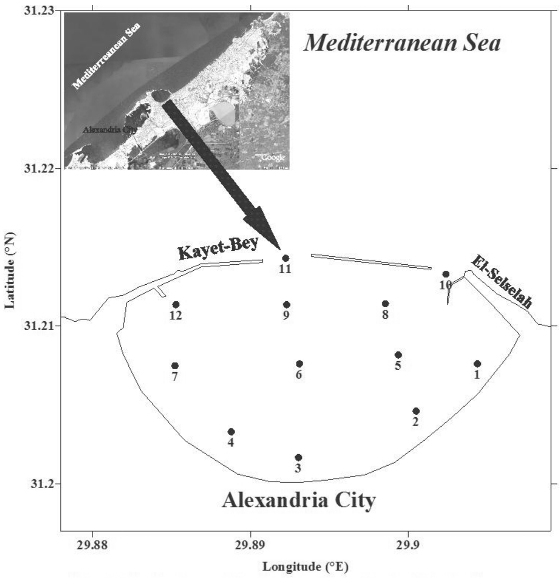

Fig. 1: Study area with the location of sampling stations.

A study of the distribution, enrichment and accumulation of heavy metals in the Eastern Harbour sediments is important for the assessment of the possible influence of anthropogenic activities on the harbour environment. The main objectives of the present study are to assess the heavy metal status of sediment samples from the harbour area in the context of the specific impact of the minor sewers, using the enrichment factor (EF) and to study the spatial distribution of Al, Zn, Cr, Cu and Cd contents; the geoaccumulation index (I_{geo}) has been calculated in order to assess the sediments' heavy metal enrichment and to establish if metal contents represent background levels for the Mediterranean Sea.

Materials and Methods

Sampling

Surficial sediment samples were collected during June 2006 by Van Veen grab from twelve stations (Fig.1), representing the entire area of the harbour (2.53 km^2) including the harbour entrance (station 11) and its outlet (station 10).

Sample analysis

After sampling, sediments were stored in plastic bags and placed in a cooler at 4AC, then transported to the laboratory for analysis. Samples were dried in an oven at 50AC for 3-4 days. Subsequently, they were lightly ground in an agate mortar for homogenization, sieved to pass <63 mm (MORILLO *et al.,* 2004) and prepared for analysis. The powdered and dried sediments were digested in a mixture of HF-$HClO_4$-HNO_3 (LORING & RANTALA, 1992) and brought into solution in 0.5M HCl (12 ml) using Milli Q water. Samples were analyzed on a flame AAS (Varian Techtron-Model 1250). Blanks were included in each batch of analysis. Calibration standards were regularly performed to evaluate the accuracy of the analytical method.

The accuracy of the analytical procedure was checked using a triplicate analysis of certified reference material (BCSS-1) from the National Research Council of Canada.

Analytical results indicate a good agreement between the certified and measured values (Table 1) and metal recovery being practically complete for most of them.

Results and Discussion

The main component of elements in sediments is aluminosilicate material. If there were no anthropogenic sources, concentrations of elements should have been explained by this source. However, composition of sediment is modified by contributions from various man-made sources. The degree of the modification in the chemical composition of sediments may be different at each sampling point due to different magnitude of source contributions at each station (ATGIN *et al.,* 2000).

Concentrations and averages of five metals in the surface sediment from Alexandria Eastern Harbour (E.H) are shown in Table (2). The extent of sediment

Table 1
Metals extracted from standard reference material (BCSS-1, n= 3).

Concentration	Pb	Cu	Cr	Cd	Zn
Metals[a] Extracted	22.70	18.5	123	0.30	119
Metals[b] Extracted	23.30	17.9	118	0.34	111
Recovery (%)	102	97	96	113	93

[a] Certified values corresponding to the total extraction of metals from the standard reference material (BCSS-1).
[b] Values of the metals extracted from the standard reference material BCSS-1 in this study.

Table 2
Descriptive statistics of heavy metals contents in the surficialsediments of the Eastern Harbour.

Elements	Range	Mean	Median	SD
Zn	83.4-3168.7	1588.59	1689.35	104.5
Cu	23.0-117.1	53.44	33.90	23.9
Cr	N.D-39.0	27.91	31.03	11.3
Cd	0.08-3.11	0.79	0.29	0.2
Pb	37.0-154.0	82.50	74.50	33.5

contamination was assessed using the enrichment factor (EF) and the geo-accumulation index (Igeo). EF is a good tool to differentiate between anthropogenic and naturally occurring sources of metals (REDDY *et al.,* 2004; SELVARAJ *et al.,* 2004, ADAMO *et al.,* 2005; VALD'ES *et al.,* 2005). An enrichment factor (EF) technique is used in the area of atmospheric aerosols, sediments, soil and solid wastes to determine the degree of modification in the composition (PEKEY, 2006).

The widely used element to normalize the metals in sediments is Al, the predominant content of coastal sediments. The EF is defined as:

$$EF = (x/Al)_{sediment}/(x/Al)_{crust}$$

where x/Al is the ratio of the heavy metal (x) to the Al. EF values were interpreted as suggested by Birth (2003) for the metals studied with respect to crust average (TAYLOR, 1964). EF < 1 indicates no enrichment, EF < 3 is minor enrichment, EF = 3–5 is moderate enrichment, EF = 5–10 is moderate to severe enrichment, EF = 10–25 is severe enrichment, EF = 25–50 is very severe enrichment, and EF > 50 is extremely severe enrichment.

The minimum, moderate and maximum enrichment factors were calculated for all analyzed metals in this study (Table 3). Chromium showing EF<1 fall in the group of elements without enrichment in the study area. As Copper showing EFs ranging from no enrichment to moderate enrichment (at station 12, as shown in Fig. 2). On the other hand, high EF values (35.1 for Zn, 34.7 for Cd and 9.1 for Pb) were found in the sediments of stations 3, 12 and 4, in the vicinity of small sewers which carry mixed waste discharge from nearby industries and domestic sewage (stations 3 and 4), while station (12) lies in the vicinity of shipyards and the anchorage of fishing boats. The EF values for Zn were >10 (11.0 to 35.12) in most stations (Fig. 2) which indicates the high degree of Zn contamination (severe enrichment). Cd had the second highest EF values (e.g., 1.3 to 34.7; Fig. 2) suggesting moderate to severe enrichment among the metals studied. The third highest EF values were for Pb (2.4 to 9.1). Zinc, Cd and Pb are known as the markers of paint industries (YASAR *et al.,* 2001, LIN *et al.,* 202).

The geoaccumulation index (I_{geo}) for the metals studied were calculated using the Müller (1979) expression:

$$I_{geo} = \log_2[C_n/1.5B_n]$$

Where C_n is the measured concentration of the examined metal 'n' in sediments and Bn is the background concentration of the same metal. It is very difficult to establish B_n values for sediments in the

Mediterranean Sea owing to geochemical variability of various areas and different anthropogenic impacts (BUCCOLIERI *et al.,* 2006). In this work, Bn value has been taken equal to metal concentrations determined by Buccolieri *et al.,* 2006 in the Taranto Gulf (Ionian Sea, south Italy).

Based on the I_{geo} data and Müller's geo-accumulation indexes, the contamination level with respect to each metal at 12 stations is ranked in Table (4). Among five metals studied, the I_{geo} of Zn was ranked from strong to very strong class (I_{geo} class = 4-5) for sediments in the inner (in the vicinity of minor sewers) and the middle sections of the harbour. Zero to medium class of Zn were observed for sediments in the outer section of the harbour. Whereas I_{geo} of Cd (second abundance metal in the E.H sediment) was ranked from (4-5) for sediments in the south and western parts of the harbour, where the minor sewers and shipyards are located. Moderate to strong I_{geo} of Cd were observed for sediments from the harbour entrance. This might indicate that the E.H has heavy accumulations of Zn and Cd metals, which apparently come from sewers that include

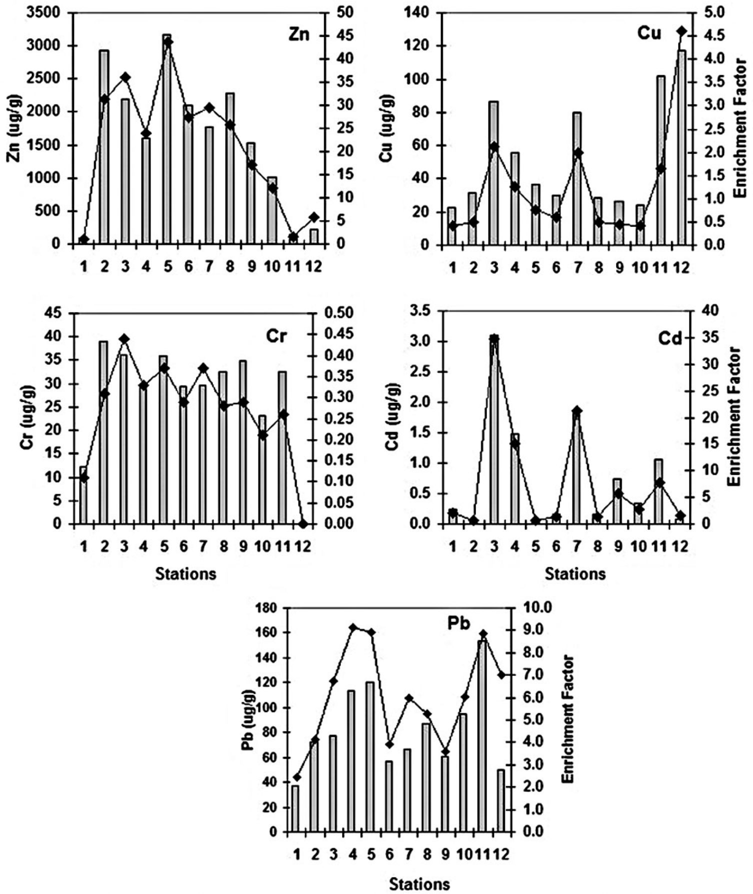

Fig. 2: Heavy metal contents (bar chart) and Enrichment Factor (scatter plot with connect line).

Table 3
Enrichment Factor (EF) values of trace metals for each station studied at the Eastern Harbour.

	Stations											
Metal	**1**	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**	**10**	**11**	**12**
	Enrichment Factor											
Zn	1.02	31.30	35.90	24.10	35.12	27.30	29.40	25.90	17.10	12.10	1.80	5.70
Cu	0.42	1.00	2.10	1.20	0.75	0.59	2.00	0.50	0.44	0.43	1.60	4.60
Cr	0.11	0.31	0.44	0.33	0.37	0.30	0.40	0.30	0.30	0.21	0.30	0.10
Cd	2.20	1.60	34.70	15.20	1.78	1.50	21.20	1.30	5.70	2.70	7.80	1.50
Pb	2.43	4.11	6.76	9.12	8.91	3.93	5.96	5.27	3.60	6.02	8.87	7.03

Table 4
***Igeo* classes of trace metals for each station at the Eastern Harbour.**

	Stations											
Metal	**1**	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**	**10**	**11**	**12**
	Enrichment Factor											
Zn	0	5	4	4	5	4	4	4	4	3	0	1
Cu	0	0	1	0	0	0	1	0	0	0	1	1
Cr	0	0	0	0	0	0	0	0	0	0	0	0
Cd	1	0	5	4	0	0	4	0	3	1	0	3
Pb	0	0	0	1	1	0	0	0	0	1	1	0

1 = Non, 2 = Non to Medium, 3 = Moderately to strong, 4 = Strongly polluted
5 = Strong to very strong

industrial wastes in addition to the outside source (station 11, the entrance of the E.H, had 1.06 mg/g Cd).

Comparison with other studies

The present data were compared with results obtained from various sources (Table 5) to gather preliminary information about the level of pollution in the Eastern Harbour. Data were also compared with marine sediment quality standards, SQS, (WDOE, 1995) and background concentrations (TAYLOR, 1964 , SALOMONS & FÖRSTNER, 1984). When the present data were compared against elemental background compositions, it was observed that they were not contaminated in Cr and Cu, however, other elements, Cd, Zn and Pb, with greater anthropogenic inputs, were observed to be enriched in the harbour sediment samples. Zinc values were higher than the State of Washington SQS values, but concentrations of other elements were lower than the SQS values. Copper and Cr concentrations were at levels comparable to unpolluted areas reported in the literature, but the concentrations of Cd, Pb and Zn were similar to those in polluted areas (Table 5).

Distribution maps of elements

The distributions of metal concentrations in sediment samples collected from different sites in the harbour are given as

Table 5
Trace elements concentrations (mg/g) from various sources.

Location	Cd	Cu	Zn	Cr	Pb
Eastern Harbour [a]					
Range (median)	0.083 – 3.1(0.8)	23.0 – 117.1(33.9)	83.4 – 3168(1689.3)	N.D – 39.0 (31.0)	37 – 154 (82.5)
Izmit Bay,Turkey [b]	2.5 – 9.5 (4.9)	24.5 – 102.4 (67.6)	44.0 –1900 (930)	38.9 – 112.4 (74.3)	55.2 – 172.0 (102)
Mean crust [c]	0.11	50	75	100	14
Mean sediment [d]	0.17	33	95	72	19
Sediment management Standards [e]	5.1	390	410	260	450
Southern Baltic Sea, Poland [f]	0.81	12.6	60.1	28.7	31.5
Koahsiung Harbour, Taiwan [g]	0.1 – 6.8	5 – 946	52 – 1369	0.2 – 900	9.5 - 470
Harbour of Ceuta, Spain [h]	N.D	5 – 865	29 – 695	13 – 381	10 - 516
Montevideo Harbour, Uruguay [i]	<1.0 – 1.6	58 – 135	174 – 491	79 – 253	44 - 128

N.D : Not Determined
[a] This study
[b] Pekey (2006)
[c] Taylor (1968)
[d] Salomons and Forstner (1984)
[e] WDOE (1995)
[f] Szefer *et al* (1996)
[g] Chen *et al* (2007)
[h] Guerra-Garcia and Garcia-Gomez (2005)
[i] Muniz *et al* (2004)

contour maps. Developing a pollution map for each element measure in sediment samples thus assesses the impact of the sewers on the harbour. The distribution patterns of six elements (Al, Zn, Cu, Cr, Cd and Pb), whose concentrations were measured by AAS, were depicted using a Geographical Information System (GIS) ArchView GIS 3.2a software. Examining Figure 3, we observed that Al (soil-related element) displays different distribution from pollution-derived elements. This is expected, since soil-related elements such as Al exist in the aluminosilicate matrix of sediments (ATGIN *et al.,* 2000, KUMAR *et al.,* 2001). Chromium and Cu are used as markers for industries using heavy metals (GALLEGO *et al.,* 2002, LOSKA *et al.,* 2004). These elements point to the mixed sewage discharges into the harbour through several sewers located along the southern edge of the harbour.

Cadmium, Pb and Zn are elements with similar properties; Fig. (3) shows the quite similar patterns of distribution of Cd, Pb and Zn. As mentioned before, these elements are known as the markers of paint industries, many of which are located in the study area.In addition the harbour has several shipyards along its western side.

Conclusion

Surface sediment samples collected from twelve stations representing the entire area of the Eastern Harbour of Alexandria were analyzed using AAS. Examining the general properties of sediment data from the Eastern Harbour, it was found that Zn represents the highest median content, followed by Pb. According to calculations of enrichment factors, Pb and Cd are of moderately severe enrichment, while Zn has the highest level of enrichment (severe enrichment). Regarding other elements, Cr is at background levels and Cu is of minor enrichment.

The distribution of the concentration of metals gives information about sources of pollution in the area; Al displays a distribution differing from pollution-derived elements. Furthermore, a similar pattern of distribution shared by Cr and Cu indicates that mixed sewage wastes affect the area. Finally, similar distribution patterns for Cd, Zn and Pb with high EF point to the operation of numerous shipyards (construction and paint) in the same area.

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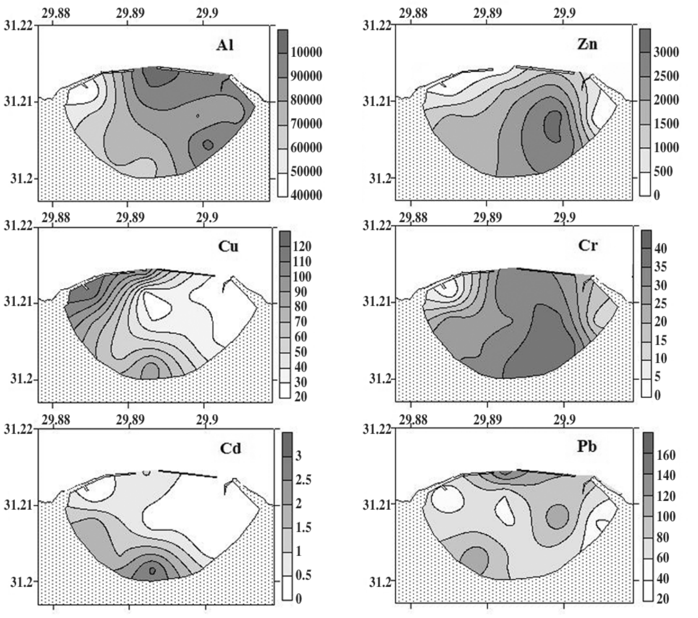

Fig. 3: Spatial distribution of Al, Zn, Cu, Cr, Cd and Pb (μg/g dry weight) in surface sediments.

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