Factor analysis of sediments in the Alexandria western Harbour, Egypt

Harbour Factor analysis Heavy metals Organic Texture Port Analyse factorielle Métaux lourdes Organique Texture

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ABSTRACT	The Western Harbour of Alexandria is the main trade harbour along the Mediter- ranean coast of Egypt. Its basin receives about $6 \times 10^6 \text{ m}^3 \text{ d}^{-1}$ of untreated industrial (Chlor-alkali, cement, oil), agricultural and domestic wastes. The harbour sediments are highly contamined by various organic and inorganic contaminants. Heavy metals (Fe, Mn, Zn, Cu and Cd), nutrient components (C-N-P), organic carbon, sulphur and other chemical constituents were assessed in the harbour sediments and its surrounding shelf deposits. R-mode factor analysis was employed to classify the raw data objectively in order to interpret the different associations and interactions of the textural and chemical parameters.						
	Fine calcareous (51.8% by weight) deposits cover the harbour basin, these deposits are rich in organic carbon ($\simeq 5.39\%$) and nitrogen ($\simeq 1.4\%$), while phosphorous and sulphur average 0.03 and 0.36% respectively. Heavy metals are also high in these deposits, their average concentrations are as follows: 1.35% Fe, 345.10 ⁻⁶ %Cu, 274.10 ⁻⁶ %Mn, 232.10 ⁻⁶ %Zn and 25.10 ⁻⁶ %Cd. It is noticeable that the levels of these contaminants decrease in the harbour surroundings. Four factors explain 76% of the total variance in the harbour area, they are: organic factor, copper-magnesium factor, textural factor and cadmium-nitrogen factor. Another four factors explain 85% of the total variance in the harbour approaches: textural factor, magnesium-copper-nitrogen factor, cadmium factor and zinc-mang- anese-copper factor.						
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RÉSUMÉ	Analyse factorielle des sédiments du port occidental d'Alexandrie, Égypte						
	Alexandrie est le principal port de commerce de la côte méditerranéenne d'Égypte. Son bassin occidental reçoit journellement 6.10^6 m^3 de déchets non traités d'origine domestique, agricole et industrielle (alcalino-chlorés, ciments, produits pétroliers). Divers produits organiques et inorganiques polluent fortement les sédiments du port. Ceux-ci et les dépôts du plateau continental environnant contiennent des métaux lourds (Fe, Mn, Zn, Cu et Cd), des sels nutritifs (C-N-P), du carbone organique, du sulfure et d'autres composés chimiques. Les données brutes ont été classées objective- ment par analyse factorielle en mode-R pour permettre d'interpréter les différentes associations et interactions entre la texture du sédiment et les paramètres chimiques. Le bassin portuaire est recouvert de fins dépôts calcaires (51,8% en poids) riches en carbone organique (~5,39%) et en azote (~1,4%), avec du phosphore (0,03%) et du soufre (0,36%). Les concentrations moyennes en métaux lourds y sont élevées: Fe (1,35%), Cu(345.10 ⁻⁶ %), Mn(274.10 ⁻⁶ %), Zn (232.10 ⁻⁶ %) et Cd(25.10 ⁻⁶ %). Les teneurs en polluants sont moindres autour du port. Dans la zone portuaire, quatre facteurs représentent 76% de la variance totale: matière organique, cuivre-magnésium, texture du sédiment et cadmium-azote. Aux approches du port, quatre autres facteurs représentent 85% de la variance totale: texture, magnésium-cuivre-azote, cadmium et zinc-manganèse-cuivre.						

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INTRODUCTION

The western harbour of Alexandria is the main trade harbour along the Mediterranean coast of Egypt; at present, it handles about 90% of the foreign trade of the country.

As a result of the progressive urbanization and industrialization of the Alexandria region, the coastal waters in general and the western harbour in particular receive considerable amounts $(12 \times 10^6 \text{ m}^3 \text{ d}^{-1})$ of untreated industrial, agricultural and domestic wastes (Salem, Sharkawi, 1981). These wastes are mostly derived from the effluent from the El-Mex pumping station to the west of the harbour area, amounting to $6 \times 10^6 \text{ m}^3 \text{ d}^{-1}$. The effluent consists of overflow $(0.5 \times 10^6 \text{ m}^3 \text{ d}^{-1})$ from lake Maryut (a coastal lagoon heavily polluted mostly by domestic and industrial wastes), and drainage water from the El-Umum drain $(5.5 \times 10^6 \text{ m}^3 \text{ d}^{-1})$. Releases from El-Noubariya canal into the harbour amount to $90 \times 10^3 \text{ m}^3 \text{ d}^{-1}$. Misr chemical industries (chlor-alkali plant) releases $3500 \text{ m}^3 \text{ d}^{-1}$ of wastes into the harbour. Portland cement factories discharge into the harbour region an unestimated quantity of wastes. Minor amounts of industrial wastes (about $2200 \text{ m}^3 \text{ d}^{-1}$) are directly released to the harbour from the tanneries.

Since the harbour basin is sheltered, it favours the entrapment of the wastes introduced from land-based sources as well as from the harbour due to shipping activities.

Most of the harbour basins all over the world are suffering from drastic contamination problems because of their geological setting, being mostly semi-closed, badly ventilated and recipients for various pollutants. Examples of reported works on harbour sediment contamination are those of: Klein *et al.* (1974) on New



Figure 1

Area of study and location of sediment samples (A: tanneries and small industries; B: oil refineries; C: cement industry; O: sewage outlet).

York harbour; Boyden (1975) on Poole harbour; Nieuwenhuise *et al.* (1978) on Charleston harbour and El-Sayed *et al.* (1980) on the eastern harbour of Alexandria.

Preliminary studies were conducted on the texture and the concentration of organic carbon in a few samples from the western harbour of Alexandria by Steuer (1935), El-Awady (1972) and El-Wakeel and El-Sayed (1978). Recently, El-Wakeel *et al.* (1984) attempted a quantitative approach to study the heavy-metal contamination in the sediments of the western harbour. However, none of the previous studies have clearly defined the major characteristics, nor types and association of contaminants in the harbour sediments.

The present paper presents the results of the textural and chemical characteristics of the western harbour sediments and their surrounding shelf deposits which were discriminated on the basis of several parameters. R-mode factor analysis is employed to discuss the results of this study; it provides a powerful approach to the interpretation of a wide variety of environmental parameters in a rapid and explicit way.

WESTERN HARBOUR SETTING

The western harbour lies to the west of the city of Alexandria along the Mediterranean coast of Egypt. It covers an area of about 31 km^2 (Fig. 1); generally, it is a shallow water body of about 7 m average depth. The harbour is, to a great extent, sheltered and comprises shallow inner and outer basins, though the western extremity of the outer basin is connected to the open sea by a narrow opening.

The harbour was naturally formed during the Pre-Holocene subsidence of the coast and the subsequent transgression of the sea (Butzer, 1960).

Apart from waste solids, little amounts of sediments are now deposited on the harbour bottom. On the other hand, the continental shelf surrounding the harbour is covered by calcareous marine deposits (El-Wakeel, El-Sayed, 1978).

MATERIALS AND METHODS

Sample collection and analysis

Forty-seven surface sediment samples were collected from the western harbour of Alexandria and its surroundings (Fig. 1), using a van Veen grab sampler which gives a minimum of disturbance. Hard ground patches prevented sediment collection at a few stations. A small amount of the uppermost layers of the collected samples (ca. 0-2 cm or occasionally 0-5 cm) was carefully removed to prevent metallic contamination, placed in polyethylene bags and refrigerated until returned to the laboratory. Most of the collected samples are of very fine grains, dark grey to black in colour with an occasional hydrogen sulphide odour.

Grain-size analysis and textural parameters (Mz: mean size and sorting δ_1) were determined according to Folk (1974).

A representative portion of the sample (gravels were discarded if present) was washed, air-dried and ground to pass a 100 mesh screen for the determination of the required chemical parameters. Nutrient components (C-N-P) were determined according to the methods described by El-Wakeel and Riley (1957), Vogel (1953) and Murphy and Riley (1962), respectively. Total sulphur was gravimetrically determined according to Easton (1972). Total carbonates were measured gasometrically, while calcium and magnesium were estimated according to Riley (1958).

Heavy-metal concentrations (Fe, Mn, Cu, Zn and Cd) were determined in the pretreated samples for the chemical analysis.

The samples were first digested (strong attack) using a mixture of nitric and perchloric acids (1:1). Measurements of the heavy-metal concentrations were carried out in duplicate using a Shimadzu AAS Model AA-360-11. The necessary precautions were taken to prevent interference and contamination during the different stages of the analysis. Internal standards were introduced within the sediment matrix; the coefficient of variation was found to be: Fe, 5%; Mn, 3%; Cu, 1%; Zn, 3%; and Cd, 8%.

Data analysis (R-mode factor analysis)

In the present study, the raw data were classified objectively using factor analysis. The purpose of factor analysis is to reduce the complexity within the similarity matrix of a multivariate data collection, transforming it into a simpler and more easily interpreted factor matrix.

The factor analysis technique starts with the establishment of a correlation coefficient matrix (M, M) of variables from the data matrix having dimensions N and M, denoting number of samples, N, and number of variables, M. This step is followed by the calculation of the eigenvector matrix (V) which represents the magnitudes and directions of variables in space, and the eigenvalues (E) which represent their corresponding variances.

The final step includes the rotation of the principal factor (varimax rotation technique), to achieve a simple structure leading to the rotated factor matrix (see Davis, 1973 and Jöreskog *et al.*, 1978 for detailed explanation).

RESULTS AND DISCUSSION

Sediment texture and distribution

The bottom of the western harbour is mostly covered by mud and sandy-mud deposits, except some scattered sand and gravel patches in the inner harbour (Fig. 2a). The coarse sediments present the *in situ* bioclastics, whereas fine deposits are mostly of terrigenous origin. The average mean size (Mz) of the harbour sediments is $5.45 \emptyset$, indicating the fineness of these sediments relative to the harbour surroundings whose average mean size is $1.68 \emptyset$. The inner harbour sediments are moderately to poorly sorted, while the outer harbour is dominated by very poorly sorted sediments. The



Figure 2

a) distribution of sediments in the harbour and its surroundings; b) distribution of carbonates.

average sorting value in the harbour sediments is $2.29 \varnothing$. On the other hand, the sediments of the harbour approaches are mostly moderately sorted (average $1.01 \varnothing$).

The sediment distribution in the harbour is mostly controlled by the inflowing N to NE bottom currents (average velocity $15-20 \text{ cm s}^{-1}$), and the outflowing S to SW surface currents (Sharaf El-Din, Farag, 1981).

Chemistry of the sediments

Total carbonates

The total carbonate content of the harbour sediments ranges between 20 and 65%, and averages 51.8%. These values are relatively lower than those of the sediments,

in the surrounding areas (range 70-96%, average 75.5%; Fig. 2b). The shelf sediments off Alexandria are generally high in carbonate content (average 75%; El-Wakeel, El-Sayed, 1978).

Nutrient components

Organic carbon

Organic carbon-rich sediments cover the entire harbour (W.H.) basin (range from 3 to 17%; average 5.39%), whereas sediments of low organic-carbon content (range 0.13-2.7%; average 0.97%) cover the harbour's surroundings (Fig. 3*a*). Sediments around the coal quay have extremely high organic-carbon value (17%). The organic carbon content of the western harbour sediments is higher than that of the sediments of the eastern harbour of Alexandria (El-Sayed *et al.*, 1980) and of Charlotte harbour sediments (Huang, Goodell, 1967), whereas it is slightly lower than in Boston harbour sediments (Mencher *et al.*, 1968).

It is noticeable that high organic carbon in the western harbour sediments is not incorporated in the clay fraction, but in the silt fraction for which the correlation coefficient (r) between these two parameters is 0.44.

Kjeldahl nitrogen

The nitrogen content in the western harbour sediments ranges from 0.6 to 4.2% and averages 1.43%, and is generally higher than in the sediments outside the harbour region (range 0.06-0.2%, average 0.1%; Fig. 3b). The spatial distribution of nitrogen in the harbour sediments does not coincide with that of organic carbon. There is insignificant correlation between these two components (r=0.06) in the harbour sediments, whereas they are highly correlated in the sediments surrounding the harbour (r=0.72).

Total phosphorus

Sediments from the western and the eastern harbour of Alexandria (previously studied by El-Sayed *et al.*, 1980), have nearly similar phosphorous levels, which average 0.03%. Relatively low phosphorus characterizes the sediments of the harbour surrroundings (average 0.014%; Fig. 3 c). Phosphorus is highly correlated with silt covering the harbour basin (r=0.76), because of adsorption on this fraction (Jitts, 1959).

Total sulphur

High sulphur content characterizes the harbour sediments (range 0.4-1.0%; average 0.36%), compared to its concentration in the harbour's surrounding shelf sediments (range 0.02-0.1% and average 0.09%; Fig. 3*d*).

Heavy metals

Iron ranges from 0.5 to 2.9% in the western harbour sediments with an average of 1.35%. These concentrations decrease in the surrounding shelf sediments to 0.17-0.4% (Fig. 4*a*).

The shelf sediments off Alexandria are characterized by relatively low iron content (El-Sayed, 1981).

Copper ranges between 30 and 1890.10^{-6} % in the western harbour sediments, averaging 345.10^{-6} %;



Figure 3 a) distribution of organic carbon; b) distribution of nitrogen; c) distribution of total phosphorus; d) distribution of sulphur.

lower concentrations (100-300. 10^{-6} %) characterize the sediments in the harbour surroundings (Fig. 4 b). These concentrations are higher relative to that in the sediments of the eastern harbour (27. 10^{-6} %; El-Sayed et al., 1980), and in Poole harbour (35. 10^{-6} %; Boyden, 1975). However, high copper concentrations (4800. 10^{-6} %) characterize the sediments of New Bedford harbour (Stoffers et al., 1977).

Manganese concentration ranges between 154 and 400. 10^{-6} % and averages 274. 10^{-6} % in the harbour sediments, but it tends to decrease in the sediments of the harbour surroundings ($\simeq 193.10^{-6}$ %; Fig. 4c). These concentrations are generally higher than those in the sediments of the eastern harbour of Alexandria ($\simeq 95.10^{-6}$ %; El-Sayed *et al.*, 1980), and in the sediments of Poole harbour as well ($\simeq 177.10^{-6}$ %; Boyden, 1975).

Zinc is high in the sediments of the western harbour

(23 to 474. 10^{-6} %; $\simeq 232. 10^{-6}$ %), whereas the sediments of the surrounding shelf have low zinc values ($\simeq 68. 10^{-6}$ %; Fig. 4 d). Lower zinc concentrations were found in the sediments of Poole harbour (82-217. 10^{-6} %; Boyden, 1975); extremely high zinc concentrations characterize the sediments of New Bedford harbour (1550. 10^{-6} %; Stoffers *et al.*, 1977).

Cadmium is generally high in the sediments of the western harbour and in the surroundings. The concentration ranges between 7 and $64.10^{-6}\%$ and $\simeq 25.10^{-6}\%$ in the harbour sediments, whereas it ranges between 3 and 58.10⁻⁶% in the surrounding shelf sediments (Fig. 4e). The sediments of the eastern harbour of Alexandria, about 5km to the east of the western harbour and less affected by pollution, are also polluted by cadmium (average $3.10^{-6}\%$; this cadmium is of non-lithogenous origin (El-Rayis *et al.*, 1986). In Poole harbour's sediments, cadmium ranges from 1 to $10.10^{-6}\%$ (Boyden, 1975). The average cadmium

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content in New Bedford harbour is 52.10^{-6} %; whereas the maximum amounts of cadmium enriched in surface sediments (130.10⁻⁶%) is about 100 times the background level of the metal measured at a 100 cm depth in a core sample (Stoffers *et al.*, 1977).

Interpretation of the isolated factors

Based on the test of significance, four factors were

extracted in respect of the harbour area, represented by twenty-seven samples; their significance value is 0.323. At the harbour approaches, another four factors were extracted based on the significance value (0.378) for twenty samples. These factors account for about 76 and 85% of the total variance among the variables in the harbour area and its surroundings, respectively. Table 1

Correlation matrix of the various parameters measured in the harbour area (level of significance 0.32 at P = 0.05).

1/-*	1.00												· · · · · · · · · · · · · · · · · · ·			
IVIZ*	. 1.00															
σI**	00	1.00														
С	0.43	0.19	1.00													
Ν	0.13	0.20	0.06	1.00												
Р	0.59	14	0.42	0.22	1.00											
CaO	33	08	57	24	50	1.00										
MgO	28	0.20	11	02	68	0.28	1.00									
Sand	84	24	52	23	66	0.57	0.31	1.00								
Silt	0.62	30	0.44	0.19	0.76	34	52	65	1.00							
Clay	0.66	0.39	0.17	0.03	0.07	23	0.13	56	15	1.00						
S	0.24	0.12	0.79	0.14	0.41	51	13	32	0.35	00	1.00					
Fe	0.44	0.39	0.64	0.27	0.50	70	05	60	0.26	0.41	0.61	1.00				
Cu	19	0.27	0.11	06	62	02	0.61	0.13	40	0.18	05	0.17	1.00			
Mn	0.62	0.09	0.49	0.12	0.61	68	33	74	0.40	0.50	0.39	0.78	0.03	1.00		
Zn	0.29	0.35	0.83	0.22	0.36	73	06	51	0.31	0.18	0.63	0.75	0.29	0.56	1.00	
Cd	04	0.01	03	0.34	0.06	0.01	17	11	0.20	19	0.09	0.06	0.06	0.10	0.03	1.00

Similarity matrix of variables measured in sediments of the harbour area.

Mean size.

** Sorting.

Table 2

Correlation matrix of the various parameters measured in the harbour surroundings (level of significance 0.38 at P=0.05).

Mz*	1.00															
σI**	0.59	1.00														
С	0.79	0.85	1.00													
N	0.53	0.69	0.72	1.00												
Р	0.83	0.75	0.81	0.39	1.00											
CaO	35	64	60	73	28	1.00										
MgO	0.09	0.06	0.11	0.17	00	55	1.00									
Sand	97	53	79	51	79	0.30	10	1.00								
Silt	0.96	0.42	0.71	0.43	0.74	22	0.11	99	1.00							
Clay	0.91	0.79	0.90	0.59	0.91	48	0.00	87	0.81	1.00						
S	0.83	0.65	0.73	0.46	0.82	27	0.00	80	0.76	0.85	1.00					
Fe	0.78	0.84	0.85	0.72	0.75	54	03	75	0.69	0.87	0.71	1.00				
Cu	0.09	0.20	0.38	0.65	17	66	0.34	16	0.10	0.09	<i>—.</i> 04	0.22	1.00			
Mn	0.68	0.77	0.85	0.65	0.74	59	0.15	71	0.62	0.80	0.68	0.79	0.37	1.00		
Zn	0.20	0.41	0.49	0.38	0.30	24	0.11	27	0.18	0.28	0.41	0.24	0.42	0.61	1.00	
Cd	31	12	23	0.00	30	07	0.02	0.33	33	25	44	10	0.09	0.01	02	1.00

Similarity matrix of variables measured in sediments of the approaches to the western harbour area

* Mean size.

** Sorting.

Table 3

Tables 1 and 2 present the correlation matrices of the various parameters measured in the harbour and its surroundings, respectively. The varimax rotated factor matrices in the harbour area and its surroundings are shown in Tables 3 and 4.

The diagrammatic presentation of results of the factor analysis inside and outside the harbour are shown in Figure 5.

Table 4

The varimax rotated factor matrix in the harbour surroundings (level of significance 0.36 at P = 0.05).

The varimax rotated factor matrix in the harbour area (level of significance 0.33 at P = 0.05).

	1	2	3	4
Mz*	_	-0.3768	-0.8109	
σI**	-	0.5535	-0.3332	-
С	0.8945	-	_	-
N	_	-	_	0.7963
P	0.4033	-0.7789	-0.3445	_
CaO	-0.7375	_		_
MgO		0.7914	-	-
Sand	-0.4077	-	0.7718	-
Silt	0.3526	-0.7603	-	-
Clay	-	-	-0.9086	_
S	0.8436	-	_	-
Fe	0.7623	-	-0.4573	-
Cu	-	0.8079	-	-
Mn	0.5447	-	-0.6301	-
Zn	0.9085	_	-	-
Cd		-		0.8038

Varimax rotated factor matrix harbour area values less than: .323: are ommitted.

Rows = variables. Columns = factors.

* Mean size.

** Sorting.

	1 ·	2	3	4
Mz**	0.9222			
σI**	0.7788	_	-	_
С	0.8580	_	-	_
N	0.5740	0.5390	-	_
Р	0.9137	-	_	_
CaO	-0.4016	-0.7982	_	_
MgO	-	0.8062	_	_
Sand	-0.8813	_	-	-
Silt	0.8380	-	0.3974	_
Clay	0.9702	_	_	-
ร่	0.8297	-	_	_
Fe	0.9119	-	_	
Cu	_	0.7811	-	0.4097
Mn	0.7636	_	_	0.4523
Zn	_	-	_	0.9257
Cd	_	-	-0.7723	

Varimax rotated factor matrix harbour approaches values less than: .378: are ommitted. Rows = variables.

Columns = factors.

** Sorting.

^{*} Mean size.



Figure 5

Diagrammatic presentation of results of factor analysis for the harbour area (A) and its surroundings (B).

The harbour area

Factor 1

Statistically, this factor accounts for 39.25% of the total variance among the variables. It is characterized by the association of organic carbon, zinc, sulphur, iron, manganese, phosphorus and silt; and the inverse association is of calcium and sand. It represents, therefore, an organic factor in which the organic carbon controls the other species and indicates either adsorption onto organic particles (Harding, Brown, 1976 and Armstrong *et al.*, 1976) and/or the formation of organometal complexes (Rashid, 1971).

The association of organic carbon, sulphur, phosphorus, heavy metals and the silt fraction of sediments has been noted by several authors and indicating the mutual affinities among those elements (Pezetta, Iskandar, 1975). This association may lead to conclude that these elements may act in a synergetic manner.

The possible origin of this factors is the enrichement of some elements along with the sewage wastes (Harding, Brown, 1976 and El-Sayed *et al.*, 1980), and the control of the silt-size coal particles on the abundance and distribution of organic carbon, sulphur and the heavy metals.

Factor 2

This factor accounts for 17.63% of the total variance and shows an association of copper, magnesium and sorting; an inverse association is also revealed for phosphorus, silt and mean size.

The strong relationship between copper and magnesium could not be accounted for on a chemical basis; magnesium belongs to the chemical group I, whereas copper belongs to group IV; therefore, the co-precipitation of both elements is excluded. On the other hand, substitution behaviour is chemically impossible because their respective atomic radii are different. The possible direct source of copper to the harbour sediments is the wastes reaching the harbour area which is loaded by 23.2 kg d^{-1} of dissolved copper and 106.9 kg d^{-1} of particulate copper (El-Rayis, Saad, 1986). Copper is also enriched in the western harbour sediments by the direct input of antifouling paints rich in copper and cupric oxide (Goldberg, 1976; El-Sayed *et al.*, 1980). Copper is also high in the air in the El-Mex area surrounding the harbour; it is estimated to be about $0.03 \,\mu \text{gm}^{-3}$ (El-Dakhakhny *et al.*, 1986); therefore, copper in the air could be considered as an additional contributor. The association of copper and magnesium with silt strongly suggests that these two elements are incorporated into the silt fraction, possibly by adsorption.

The inverse association of phosphorus and silt revealed that phosphorus is strongly related to the silt fraction, whereas it tends to decrease in the clay and sand fractions, as noted by Jitts (1959) and El-Sayed *et al.* (1980).

Factor 3

Factor 3 accounts for 10.87% of the total variance. It shows the strong association of clay, mean size, manganese, iron, phosphorus and sorting. The most obvious character of this association is that clay (textural) affects the concentration of manganese, iron and phosphorus in sediments. It indicates the adsorption of these elements on clays, which have high volume-to-surface ratios. The ability of clays to scavenge heavy metals has been noted by Armstrong *et al.* (1976) and Harding and Brown (1976).

Manganese is enormously high in the outflow of Maryut Lake, which in turn affects the western harbour through the discharge point of El-Umum Drain. The estimated discharges of manganese (in dissolved and particulate forms) on a daily basis are 45.8 and 745.9 kg, respectively (El-Rayis, Saad, 1986).

Factor 4

This factor is principally a cadmium-nitrogen factor; it accounts for 8.43% of the total variance. The relation between these two parameters may reflects their similar input source, or most likely their mutual chemical adherence (Collinson, Shimp, 1972; Pezetta, Iskandar, 1975). Alexeyev (1971) pointed out that cadmium ions tend to form amine complexes in presence of ammonia in solution. Shannon *et al.* (1974) and Prakash (1976) noted that the presence of NTA (nitrilotriacetic acid) in sewage discharges leads to the formation of metal-NTA complexes. This complex is mostly present in the adsorbed form in sediments.

It is therefore assumed that the organic source of nitrogen is the sewage (enriched with metals) and other types of wastes discharged into and around the harbour area. These wastes contain great amounts of metals, sulphide and ammonia (Salem, Sharkawi, 1981).

Cadmium reaches the harbour area as one of the elements discharged with waste waters; it has been estimated that the amounts of dissolved and particulate forms of cadmium reaching the western harbour daily are 5.05 and 5.47 kg, respectively (El-Rayis, Saad, 1986). This high amount, however, is lower than that

affecting the New York harbour (52.2 t/year; Klein et al., 1974). Additional amounts of cadmium accumulate on the harbour's bottom through contamination with extraneous materials such as cement, colorants or combustion of coal and oil. It is worth mentioning that the western harbour is surrounded by cement factories, oil refineries, chemical plants and tanneries.

The environment is easily contaminated by one of the transitional metals, cadmium, via the atmosphere. Duce et al. (1974) reported that cadmium is one of the elements enriched in the eolian particulates relative to the average crustal material by one to four orders of magnitude. Cadmium is emitted in high quantities from the combustion of coal and the production of cements; its emitted quantity to the atmosphere by the cement industry is about 80 t/year (Goldberg, 1976).

Heavy metals were assessed in the air around the western harbour of Alexandria in the El-Mex industrial area. The concentration of some metals were as follows: Fe, $1.39 \,\mu gm^{-3}$, Cu, $0.03 \,\mu gm^{-3}$, and Zn, $2.51 \,\mu gm^{-3}$. Unfortunately, cadmium was not determined (El-Dakhakhni *et al.*, 1986). However, cadmium is closely associated with zinc geochemically. This association stems from their similar chemical properties, being in the same periodic group. Cadmium gets into waterways from zinc mining areas, which are not present around the western harbour, or from industrial uses such as metal plating and the use of CdS as an orange pigment (Fergusson, 1982).

El-Rayis *et al.* (1986) noticed that the origin of cadmium in the eastern harbour (5 km eastward of the western harbour) is almost 100% non-lithogenous, but is mostly related to man's activity.

The harbour surroundings (shelf)

Factor 1

This factor accounts for 56.6% of the total variance. It is characterized by the strong association of textural parameters (clay, silt, mean size and sorting) with nutrient components (C-N-P) and Fe-Mn. The inverse association is indicated by sand and calcium. This factor is considered as a fine-grained textural factor, where silt and clay contents greatly affect the concentrations of some organic and heavy-metal constituents. Krauskopf (1967) noted that high organic-matter content appears to follow high clay percentage; a relation which is common in most marine sedimentary environments. Heavy metals are enriched in clays and organic matter by precipitation as metallic coatings, incorporation in crystalline structure and adsorption on cation exchange sites (Gibbs, 1973; Armstrong *et al.*, 1976).

The high loadings of manganese and iron represent the possible occurrence of an iron-manganese hydroxide phase, which in turn is related to the oxidation potential factor (Spencer *et al.*, 1969). Iron and manganese are the major metal loads of the drainage from Lake Maryut to the harbour region; the concentrations of dissolved iron and manganese affecting the harbour are 64 and 45.8 kg d^{-1} , respectively. These two metals in particulate form are disposed in the harbour area in the amounts of 1738 and 745 kg d⁻¹, respectively (El-

Rayis, Saad, 1986). Additionally, the sewage outlets open directly in the harbour and affect the sediments.

Factor 2

It accounts for 15.72% of the total variance. The first association is presented by the magnesium, copper and nitrogen, whereas the second inverse association is indicated by the negative loadings on calcium. The coppernitrogen association might suggest the formation of a copper amine complex. According to Alexeyev (1971), copper in alkaline media tends to form amine complexes with ammonia; as the pH of the media decreases, copper may return to solution or may precipitate in other forms. Copper can also exist in the form of Cu-NTA which is enhanced by the presence of Mg⁺⁺, whereas excess Ca⁺⁺ increases the degradation of this NTA complex (Huber, Popp, 1972).

Factor 3

The variance explained by this factor is 7.33%. It is purely a cadmium factor. It shows that cadmium incorporated in the bottom sediments surrounding the harbour, especially as shown in the high concentrations observed, is mainly due to extraneous source and ultimately is not a consequence of any chemical process in the area. Cadmium therefore provides rather good evidence of the direct influence of atmospheric and waste pollution in the harbour region. Its origin has been thoroughly discussed beforehand.

Factor 4

This factor accounts for 6.07% of the variance and is characterized by the association of zinc, manganese and copper. Although these three elements belong to two different groups (manganese and zinc in group III, copper in group IV), their possible coprecipitation as hydroxide under the same Eh and pH conditions is obvious (Alexeyev, 1971; El-Sayed, 1981).

The common origin of these elements is the waste waters discharged into the harbour region; this water is loaded with immense quantities of these pollutants. Their association in domestic sewage affecting the eastern harbour of Alexandria was noticed by El-Sayed *et al.* (1980).

CONCLUSIONS

The western harbour of Alexandria receives high quantities of different contaminants derived from several land-based sources installed around it. The contamination of the harbour's sediments by heavy metals and nutrient components is primarily due to the uncontrolled discharge of untreated wastes into the harbour basin, as well as the influence of eolian particulates rich in some hazardous metals and as a consequence of the shipping activites within the harbour. The contaminants are gradually diluted in the shelf sediments surrounding the harbour due to the relative proximity from the direct waste discharging outlets, and the mixing with marine sediments.

Factor analysis enable the definition of the types of

contaminants and their association and interaction in the sediments of the harbour and its surroundings. Organic carbon and silt/clay fractions control most of the metal associations.

Sediment contamination will increase and further deteriorate the area with eventual onset of euxenic conditions, unless alternative methods of waste disposal are introduced.

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