Speciation of Trace Metals in Coastal Sediments of El-Mex Bay South Mediterranean Sea–West of Alexandria (Egypt)

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Abstract Sediments of El-Mex Bay estuary on the southern Mediterranean Sea have been analyzed for trace metals after sediment fractionation by sequential leaching. A sequential extraction procedure was applied to identify forms of Mn, Cu, Cd, Cr, Zn and Fe. The five steps of the sequential extraction procedure partitioned metals into: CH_3COONH_4 extractable (F1); NaOAC carbonate extractable (F2); $NH_2OH.HCl/CH_3COOH$ reducible extractable (F3); $H_2O_2–HNO_3$ organic extractable (F4) and $NHO_3/HClO_4/HF$ acid soluble residue (F5). Extracted concentrations of trace metals analyzed after all five steps, were found to be (μg/g) for Mn: 1930.2, Cu: 165.3, Cd: 60.9, Cr: 386.3, Zn: 2351.3 and Fe: 10895. Most of elements were found in reducible fraction except Fe found in acid soluble residue, characterizing stable compounds in sediments. Labile (non-residual) fractions of trace elements (sum of the first four fractions) were analyzed because they are more bioavailable than the residual amount. Correlation analysis was used to understand and visualize the associations between the labile fractions of trace metals and certain forms, since Fe-and Mn-oxides play an important role in trace metals sorption within aquatic systems, especially within El-Mex Bay sediments that characterized by varying metal bioavailability.

Keywords Trace metals · Pollution · Sediment · Fractions · Labile · El-Mex Bay

1 Introduction

Estuary is a precious coastal site, subject to high demand for a variety of uses: as location of harbors and ports, human settlements, recreational areas and as biologically highly productive fishery ground (Prohić and Kniewald 1987). Disposal of sewage and pollutants often results in a degradation of environmental quality. Estuary is, thus, an important stage in the global sedimentary cycle. Sediments are often the sinks of metal contaminants in aquatic system (Förstner 1989).

Contamination of sediments by metals and organic compounds is now widespread and well documented in numerous Egyptian coastal waters and lakes (Saad and Hemeda 1982; El-Rayis et al. 1996; Tayel 1995 and Nessim et al. 1997). However no attempts have been made to evaluate the solid speciation of heavy metals in sediments in provenance of El-Mex Bay morphology and hydrology.

El-Mex Bay, lies in the western part of Alexandria coast between longitude 29° 45′ and 29° 54′ E and

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latitude 31° 07′ and 31° 15′ N (Fig. 1), and extends for about 7 km between EL-Agami (west) and the Alexandria commercial Western Harbor, W.H., (east) with maximum depth 20 m. The Bay is one of Alexandria coasts but it differs in having several industrial plants that directly discharge their effluents into it. These are petrochemical, cement, chemicals, tanneries, industrial dyes, ink, petroleum refining, meat processing, and fish production beside the Alexandria

iron and steel factory (Rifaat et al. 1996). The last is recently constructed in its western, El-Dekhaila, seaside (Fig. 1). In addition, the Bay is an estuarine zone of huge agricultural drain called Omoum Drain its discharge rate $2{,}547.7 \times 10^{6}$ m^{3}/year. The downstream part of the last drain receives considerable amounts of Alexandria domestic and industrial wastes prior discharging to the bay at a site lies just west of the Western Harbor.

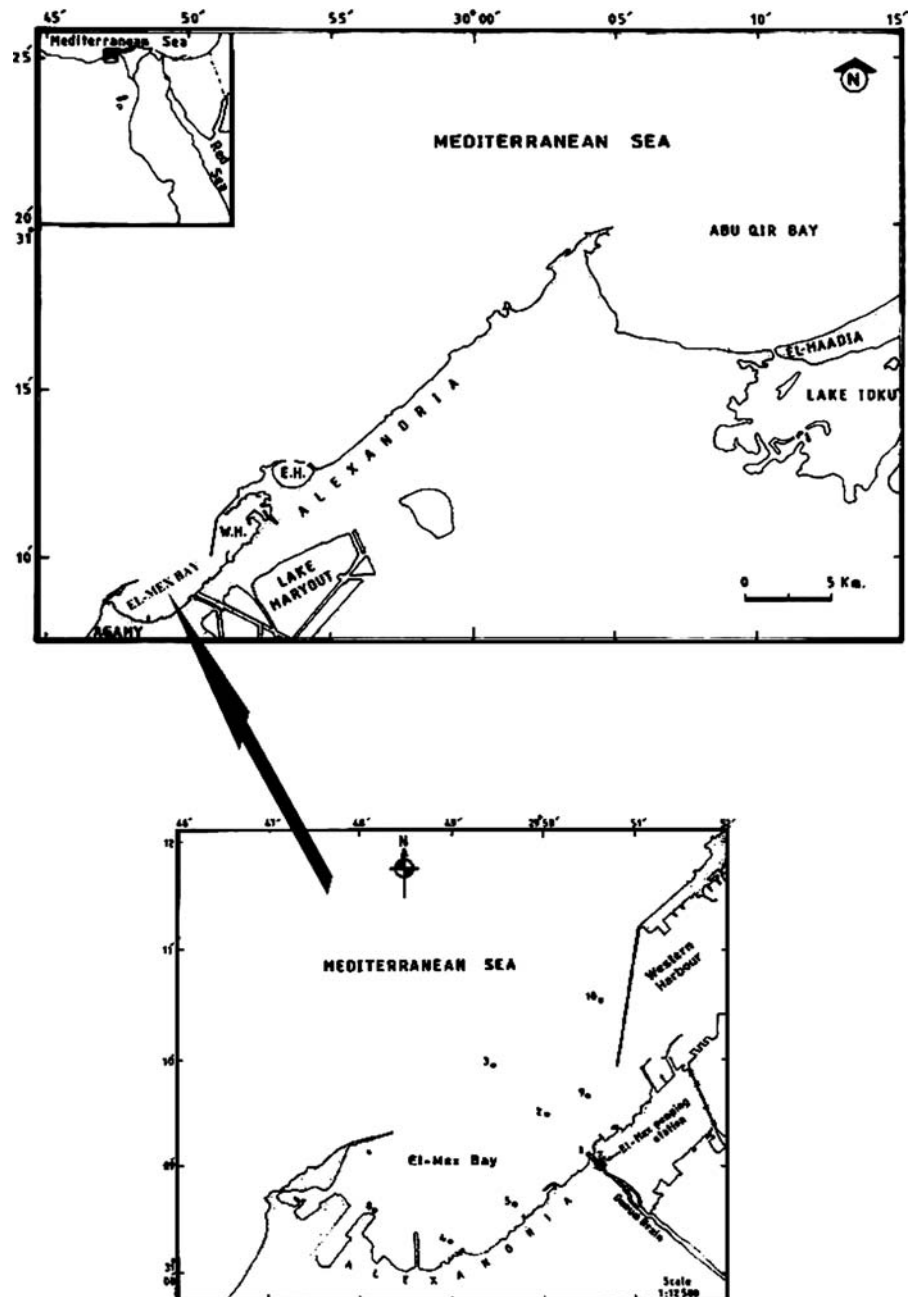**Fig. 1** Sampling locations in El-Mex Bay

Table 1 Detection limits for fractions metal concentrations

Metal	Detection limit (µg/g)				
	F1	F2	F3	F4	F5
Fe	0.2	0.3	0.2	0.1	0.5
Mn	0.1	0.4	0.3	0.4	0.5
Cu	0.2	0.1	0.2	0.1	0.2
Cd	0.1	0.8	1.0	0.3	0.1
Cr	0.4	0.1	0.3	0.4	0.4
Zn	0.1	0.1	0.5	0.4	0.3

Under prevailing hydrographic conditions and a sheltered geographical position, EL-Mex Bay estuary is two-layered estuary, the fresh water from the drain spreads in the estuary after mixing with seawater as surface brackish layer that overlies the other layer of almost proper Mediterranean seawater (El-Gindy et al. 1986).

The bottom sediments of the bay are generally medium to very coarse sand except at the area near the entrance of the western harbor where fine to coarse silts dominant.

The surplus of metal contaminants introduced into the aquatic system as anthropogenic input usually exist in relatively unstable chemical forms and is not incorporated into crystal lattices of minerals, but tends to accumulate at exchangeable sites of the sediments (Förstner et al. 1982). In addition, the principal problems in this environment, according to Förstner and Salomons (1980) are:

(a) The potential availability of the contaminants in the sediments for aquatic life (bioavailability)
(b) The problem of remobilization, whether it occurs and under circumstances

The mentioned problems cannot be satisfactory solved by trace metals analysis of the bulk sample alone. Use of total metal concentrations as a criterion to assess the potential effects of sediments contamination, implies that all chemical forms of a given metal have equal impacts on the environment, which is highly improbable (Tessier et al. 1979). Sequential extraction procedures, as opposed to bulk sample analysis, allow for the differentiation of the relative binding strengths of the trace metals to the various solid phases by successive leaching with chemicals of increasing strength and selectivity (Kersten and Förstner 1985). This procedure provides much more data on the origin of pollutants, their reaction pathways, biological and physico-chemical availability and possible remobilization, than does bulk sample analysis. Therefor the aim of this study is to establish partitioning patterns of heavy metals in estuarine sediments originating in a huge drain catchment area.

2 Materials and Methods

Alexandria is an industrial town (it is the second largest city in Egypt and it has about 40% of the total Egyptian industrial activities) located on the southern coast of the Mediterranean Sea and north of Egypt. El-Mex Bay is situated to the west of Alexandria, its sediments mostly consist in sand, the mean size of the bottom sediment ranges between 0.82 and 1.97φ with exception in site 9, and its sediment consists of sandy mud. Eight sediment samples covered all the bay were sampled as four samples at the front of outfall of the land-based sources in the bay, two sites at the central part and two sites from the offshore sediments. The Van Veen Grab sampler was

Table 2 Distribution of Manganese in sediment fractions (µg g^{-1})

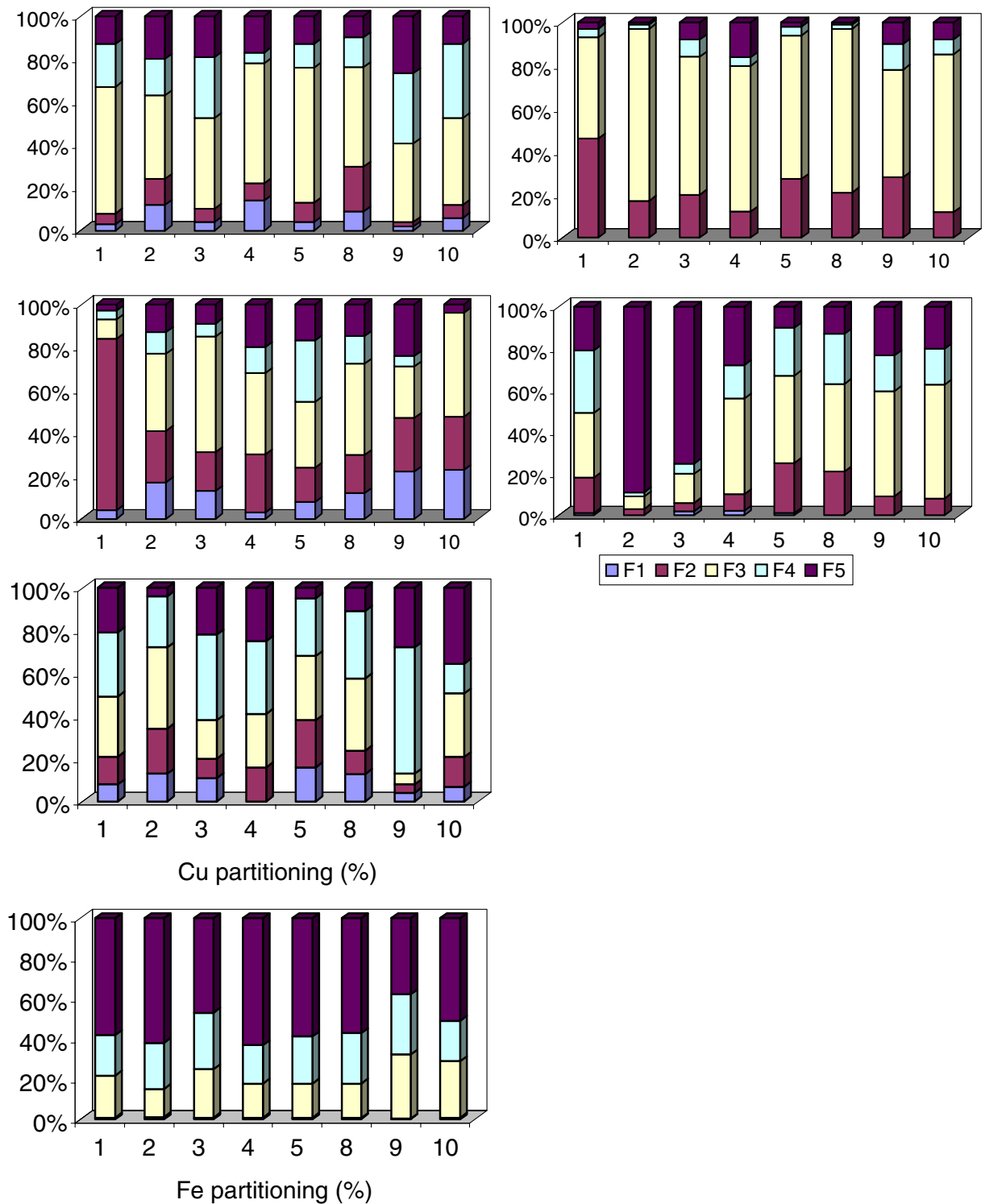| Sample	Total concentration	Exchangeable fraction (F1)		Carbonate fraction (F2)		Iron and manganese oxides fraction (F3)		Organic/sulphide fraction (F4)		Residual fraction (F5)	
		Conc.	%	Conc.	%	Conc.	%	Conc.	%	Conc.	%
1	30.5	0	0	99.1	33	188.6	62	9.3	3	6.5	2
2	179	0	0	30.6	17	142.7	79	4.3	2	1.3	1
3	269	1	<1	53.2	20	172.4	64	21.8	8	21.5	8
4	155	0	0	18.1	12	104.1	67	6.9	4	25.3	16
5	252.7	0	0	68	27	168.9	66	10.9	4	4.9	2
8	132	0	0	28.1	21	100.1	76	3.0	2	1.1	1
9	433	0	0	119.6	28	218.1	50	49.9	12	45.2	10
10	206	0	0	23.7	12	151.5	74	15.1	7	15.7	8

Fig. 2 Percent contribution of each geochemical fraction to total metal concentration at each sample.

Table 3 Distribution of Iron in sediment fractions ($\mu g\ g^{-1}$)

Sample	Total concentration	Exchangeable fraction (F1)		Carbonate fraction (F2)		Iron and manganese oxides fraction (F3)		Organic/sulphide fraction (F4)		Residual fraction (F5)	
		Conc.	%	Conc.	%	Conc.	%	Conc.	%	Conc.	%
1	780	2.1	0.3	4.3	0.5	163.8	21	157	20	453	58
2	709	2.5	0.4	4.9	0.7	99.6	14	160.8	23	441	62
3	1614	6.9	0.4	7.9	0.5	391.3	24	449	28	759	47
4	1623	6.7	0.4	5.8	0.4	280.2	17	311	19	1019	63
5	810	3.1	0.4	3.6	0.4	137.5	17	190	24	476	59
8	774	1.0	0.1	4.3	0.6	130.0	17	195	25	444	57
9	3063	2.8	0.1	5.3	0.2	983.5	32	906	30	1165	38
10	1522	5.5	0.4	4.3	0.3	411.0	27	313	20	788.5	52

used to collect a large amount of sediments; a sample was taken from the center with a polyethylene spoon to avoid contamination by the metallic parts of the sampler. Samples were then stored in plastic cups that were cleaned by 1:1 HCl and 1:1 HNO$_3$ and were stored frozen at 4°C until analysis. They dried at 85°C for 48 h in forced air oven, and were subsequently ground in agate mortar, homogenized and sieved. Cu, Cd. Cr, Zn, Mn and Fe were fractionated from sediment samples using the sequential leaching technique modified by Prohić and Kniewald (1987) from the original paper by Tessier et al. (1979). In order to define the fractions of the trace metals (exchangeable, carbonate, Mn- and Fe-oxides (reducible), organic/sulphidic and acid soluble (residual) fraction) and explore the metals bioavailability, the following five steps were used in the sequential extraction procedure:

Step 1   (F1) – exchangeable metals. The dried and sieved sediment sample was first extracted

with 1 M CH$_3$COONH$_4$ (pH 7) by shaking for 3 h.

Step 2   (F2) – metals bound to carbonate. The solid residue from step 1 was leached with 1 M NaOAc (pH 5) with acetic acid (HOAc) by shaking for 5 h.

Step 3   (F3) – metals bound to reducible phases (Fe-Mn-oxides). The solid residue from step 2 was extracted with 1 M NH$_2$OH.HCl in 25% (v/v) HOAc by shaking for 4 h.

Step 4   (F4) – metals bound to organic matter and sulphide. The residue from step 3 was extracted at 85°C for 12 h with 30% H$_2$O$_2$ (adjusted to pH 2 by addition of HNO$_3$), followed by cooling and extracted with 1 M CH$_3$COONH$_4$.

Step 5   (F5) – metals fraction bound to acid soluble residue. The solid residue from step 4 was digested at 120°C with an NHO$_3$–HClO$_4$–HF mixture according to the procedure

Table 4 Distribution of copper in sediment fractions ($\mu g\ g^{-1}$)

| Sample	Total concentration	Exchangeable fraction (F1)		Carbonate fraction (F2)		Iron and manganese oxides fraction (F3)		Organic/sulphide fraction (F4)		Residual fraction (F5)	
		Conc.	%	Conc.	%	Conc.	%	Conc.	%	Conc.	%
1	18.2	1.5	8	2.4	13	5.0	28	5.5	30	3.8	21
2	12.6	1.7	13	2.7	21	4.8	38	2.9	24	0.46	4
3	28.4	3.1	11	2.7	9	5.1	18	11.2	40	6.3	22
4	12.7	0.0	0	2.1	16	3.1	25	4.4	34	3.1	2.5
5	13.8	2.2	16	3.1	22	4.1	30	3.7	27	0.6	5
8	11.5	1.5	13	1.2	11	3.9	34	3.7	32	1.2	11
9	52.2	2.2	4	2.2	4	2.5	5	30.6	59	14.6	28
10	15.9	1.1	7	2.2	14	4.8	30	2.2	14	5.8	36
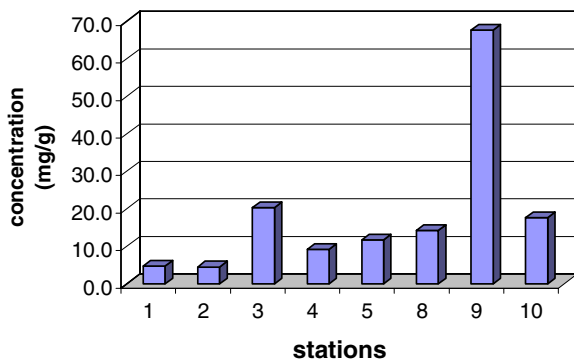
Fig. 3 Concentration of OC% in sediments of different stations along El-Mex Bay.

described by Tessier et al. (1979) for total metal analysis. Metal concentrations in all extracts were analyzed by atomic absorption spectroscopy (Varian Techtron – Model 1250 spectrophotometer, equipped with a hydride vapor system). Detection limits for the metal extracts are shown in Table 1. External standard solutions were prepared from 1,000 mg/l stock metal solutions. The precision of the metal analysis controlled by duplicate samples with the relative standard deviations of means of duplicate measurements less than 10%.

Values equal or smaller than the detection limits were arbitrarily taken as the half of detection limit as allows the use of these values for further statistical analysis (Reimann and Filzmoser 2000).

3 Results and Discussion

The mean size of the bottom sediments of El-Mex Bay ranges between 0.82 and 2.73φ with an average 1.59φ. Medium sand mostly occupies the inner and central parts of the Bay and represents about 65% of the total samples. The area near the entrance of the Western Harbour was covered by fine sand. The outer margin of the Bay is covered by coarse sand (stations 3 and 10). The sediments of the Bay are derived from the mechanical breakdown of the coastal and bottom platforms by means of current and wave action (El-Sabarouti et al. 1997). The present work is in agreement with Rifaat (1982) and El-Sayed et al. (1988), they reported that almost sediments in El-Mex Bay are classified as sand to gravelly sand (coarse–very coarse texture). According to Folk's (1965), the majority of samples (63%) are moderately sorted and about 37% of samples are poorly sorted.

3.1 Manganese Mn

The percentage of Mn in the exchangeable fraction is depleted (0%) as shown in Table 2 and Fig. 2. The depletion of Mn in the solid phase below the Eh oxidation limit of the sediment is followed by a rise in dissolved Mn in the interstitial waters as well as a Mn release into the waters above the sediments (Bonatti et al. 1971; Prohić and Kniewald 1987). The carbonate fraction has an even greater percentage of Mn (12–46%) as the ionic radii of Mn^{2+} and Ca^{2+} ions are similar, the Mn^{2+} ion can substitute the Ca^{2+}

Table 5 Distribution of Cadmium in sediment fractions ($\mu g\ g^{-1}$)

Sample	Total Concentration	Exchangeable Fraction (F1)		Carbonate Fraction (F2)		Iron and Manganese Oxides Fraction (F3)		Organic/sulphide Fraction (F4)		Residual fraction (F5)	
		Conc.	%	Conc.	%	Conc.	%	Conc.	%	Conc.	%
1	11.9	1.7	15	3.1	26	4.1	34	1.6	14	1.4	12
2	11.0	1.9	17	2.6	24	3.9	36	1.1	10	1.4	13
3	4.3	0.5	13	0.8	18	2.3	54	0.3	6	0.4	9
4	6.8	0.2	3	1.8	27	2.6	38	0.8	12	1.4	20
5	8.3	0.7	8	1.3	16	2.5	31	2.4	29	1.4	17
8	7.9	0.9	12	1.4	18	3.4	43	1.0	13	1.2	15
9	6.4	1.4	22	1.6	25	1.6	25	0.3	5	1.5	23
10	4.3	0.9	21	1.1	25	2.1	49	0.0	0	0.2	5

Table 6 Distribution of chromium in sediment fractions ($\mu g\ g^{-1}$)

Sample	Total concentration	Exchangeable fraction (F1)		Carbonate fraction (F2)		Iron and manganese oxides fraction (F3)		Organic/sulphide fraction (F4)		Residual fraction (F5)	
		Conc.	%	Conc.	%	Conc.	%	Conc.	%	Conc.	%
1	36.3	1.2	3	1.9	5	21.3	59	7.1	20	4.7	13
2	33.6	4.1	12	4.1	12	13.7	41	6.1	18	5.6	17
3	40.9	1.8	4	2.5	6	17.3	42	11.4	28	7.9	19
4	34.7	4.7	14	2.8	8	19.5	56	1.7	5	5.9	17
5	38.9	1.6	4	3.3	9	24.4	63	4.4	11	5.2	13
8	27.6	2.4	9	5.8	21	13.0	47	3.8	14	2.6	10
9	114.9	1.9	2	2.3	2	42.2	37	37.5	33	31	27
10	59.4	3.4	6	3.6	6	24.2	41	20.6	35	7.6	13

ion in the crystal lattice of $CaCO_3$ giving up to 4% (by weight) of $MnCO_3$ (Pingitore 1978). Deurer et al. (1978) pointed out that, there is an average increase in Mn content in sediments with a higher percentage of the carbonate fraction. The percentage of Mn in the Fe- and Mn-oxides fraction, F3, is high, the range being 47–79%. The upper range limit refers to the sample at the middle part of the bay (station 2). Thus Mn can be present in this sample either as Mn-oxides or hydroxides. Mn mobilized after peroxide treatment probably belongs to the sulphidic fraction. Low Mn content in the residual fraction, F5, was appearing.

3.2 Iron Fe

A negligible percentage of Fe was extracted as the exchangeable and carbonate fractions (less than 1% of the extracted Fe, also reported by Tüzen 2003). Most of Fe (38–63% of total Fe extractions) was associated with the residual fraction, F5, (Table 3, Fig. 2). The residue fraction appeared to 54.5% of the total

extractions, whereas the Fe- and Mn-oxide (reducible) fraction increased slightly to 32%. These results confirm that acidified hydroxylamine solution preferentially reduces Mn-oxides than Fe-oxides. Iron was mostly concentrated in the acid soluble fraction, F5, in sediments as crystalline Fe-oxides are dissolved by acid (Fig. 2). Indicating that Fe originates from geochemical background rather than anthropogenic source. Also Tüzen (2003) reported that, the largest amount of iron associated with the residual fraction in some sediments.

3.3 Copper Cu

According to the results presented in Table 4, Cu is primarily bound to organic/sulphide fraction, F4, (39% of the total extractions); this is confirmed by observations of other authors (Salomons and Förstner, 1984) indicating the strong complexing affinity of organic matter with Cu. This feature may result from a large flux of organic matter to the bottom sediments

Table 7 Distribution of zinc in sediment fractions ($\mu g\ g^{-1}$)

Sample	Total concentration	Exchangeable fraction (F1)		Carbonate fraction (F2)		Iron and manganese oxides fraction (F3)		Organic/sulphide fraction (F4)		Residual fraction (F5)	
		Conc.	%	Conc.	%	Conc.	%	Conc.	%	Conc.	%
1	172.7	1.2	1	28.7	17	54.0	31	52.5	30	36.3	21
2	506.1	1.2	<1	16.3	3	30.3	6	7.6	2	450.6	89
3	592.3	10.3	2	22.4	4	81.1	14	27.3	5	451.2	76
4	253.9	4.2	2	20.5	8	115.9	46	41.0	16	72.2	28
5	121.8	0.9	<1	29.4	24	51.5	42	27.4	23	12.5	10
8	89.3	0.0	0	18.8	21	37.2	42	21.7	24	11.6	13
9	414.2	1.6	<1	37.9	9	207.5	50	70.8	17	96.4	23
10	201.0	0.8	<1	16.4	8	108.6	54	34.4	17	40.8	20

as reflected by OC distribution (Fig. 3). In addition, the dominance of organic fraction in labile fractions suggests that the organically bound materials such humic and fluvic may be easily available for biological uptake. The acid soluble residue, F5, was the next most important fraction in the sediments as far as Cu is concerned (22%) followed by the reducible fraction (20%); the carbonate bound (11%) and the exchangeable fraction (8%) Fig. 2.

3.4 Cadmium Cd

Cadmium speciation was more or less affected by its concentration in the sediments. The percentage Cd in the easily exchangeable, carbonate, organic and residual fractions was increased with increasing Cd concentration. In contrast, Cd distribution in the reducible fraction decreased with increasing Cd

concentration. In the present study, most of Cd was associated with the reducible (Fe- and Mn-oxides) fraction (37%) followed by carbonate bound (23%) fraction, but Cd in the exchangeable and residual fractions was dominant at lower concentrations (Table 5 and Fig. 2).

Thus partitioning of the metals into geochemical fractions leads to different conclusions regarding the level of contamination of each site. Cement factory is located within 500 m of El-Mex Bay shore and has been shown to result in extremely high levels of air borne Cd pollution in this area. The cement production contains about 2 ppm Cd (WHO 1992). Nriagu and Pacyna (1988) pointed out that, the atmospheric fallout of Cd to fresh and marine waters represents a major input of Cd at the global level. A GESAMP study of the Mediterranean Sea indicated that this source is comparable in magnitude to the total river

Table 8 Comparisons of total metals content ($\mu g\ g^{-1}$) of marine surface sediments from various geographical regions with the present study

	Cu	Cd	Cr	Zn	Mn	Fe
Syrian coast, Mediterranean Sea[a]	–	–	380	–	–	–
Harbour of Ceuta, Spain[b]	5–865	–	13–381	296–695	–	–
Danube Sediments[c]	27	–	–	72.8	656	26734
Floodplain lake, Netherlands[d]	39–118	0–10.4	–	255–915	387–1039	16000–32000
Semarang Estuary, Indonesia[e]	33–72	–	29–96	84–259	–	30500
Gulf of Aqaba, Jordan[f]	5.6–23.6	–	4.5–44	15–173	–	–
Arabian Sea, Pakistan[g]	24.40	–	32.3	50–108	–	–
Huanghe Estuary, China[h]	21.98	–	63.7	71.3	438.5	19000
Hokuriku, Japan[i]	24.80	0.23	68.7	126	–	–
Krka River estuary, Adriatic sea[j]	10–95	–	30–105	32–72	700–2400	–
Abu-Qir Bay, Mediterranean Sea, Egypt[k]	38–561	–	–	118–1779	800–2520	12920–14480
El-Mex Bay, Mediterranean Sea, Egypt[l]	44.6	1.51	–	60.7	143.8	1771
El-Mex Bay, Mediterranean Sea, Egypt[m]	11.5–52.2	4.3–11.9	27.6–114.9	89.3–592.3	132–433	709–3063

[a] Othman et al. (2000)

[b] Guerra-Garcia and Garcia-Gomez (2005)

[c] Relić et al. (2004)

[d] Griethuysen et al. (2005)

[e] Takarina et al. (2004)

[f] Abu-Hilal (1993)

[g] Tariq et al. (1993)

[h] Zhang et al. (1988)

[i] Ohta et al. (2004)

[j] Prohić and Kniewald (1987)

[k] Faragallah (2004)

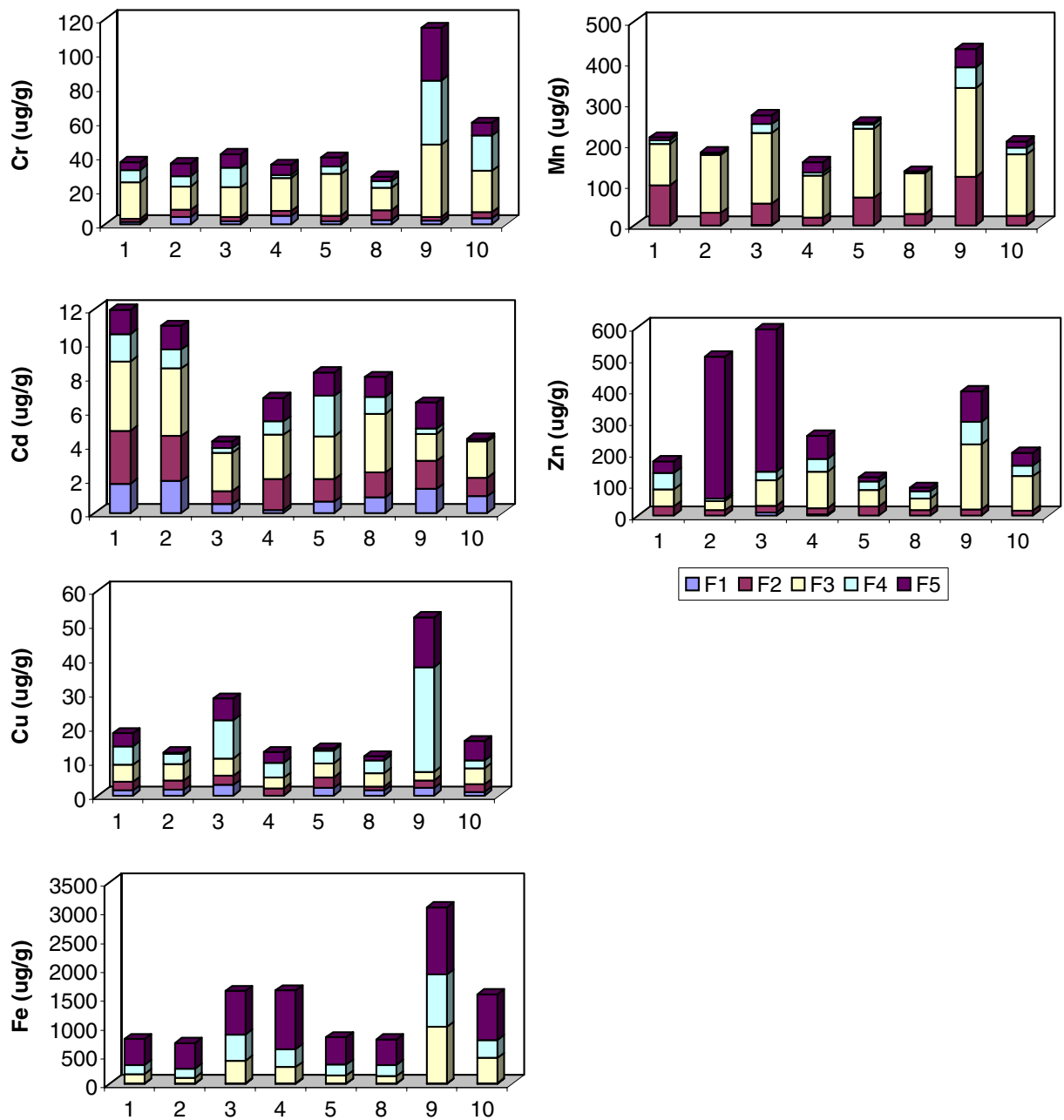[l] El-Rayis et al. (1996)

[m] Present study

Fig. 4 Concentration of Cr, Cd, Cu, Fe, Mn and Fe in each geochemical fraction by site.

input of Cd to the region (GESAMP 1985). Another source of Cd in the investigated area, the huge amounts of agricultural wastes carried by Omoum Drain to El-Mex Bay containing phosphate fertilizers (El-Rayis and Abdallah 2005), as one of the contaminants entering the Bay sediments, are also impacting the marine environment (phosphate fertilizers contain from 10 to 200 ppm Cd, WHO 1992).

Table 9 The percentage of labile fractions of the studied metals

Metal	L12 (%)	L123 (%)	L1234 (%)
Mn	23	87	94
Fe	0.6	24	49
Cu	19	39	78
Cd	36	73	85

Table 10 Correlation coefficient between extracted concentrations of Mn and Fe in F3, L12, L123 and L1234 fractions

		F3	L12	L123	L1234
Mn	F3				
	L12	0.889[a]			
	L123	0.974[a]	0.970[a]		
	L1234	0.972[a]	0.958[a]	0.993[a]	
Fe	F3				
	L12	0.244			
	L123	1.000[a]	0.254		
	L1234	0.996[a]	0.269	0.996[a]	

[a] Correlation is significant at the 0.01 level

3.5 Chromium Cr

More than 45% of Cr concentrations was extracted in the reducible step, F3, of the analyzed samples (Table 6). At much higher Cr concentration (about 114.9 μg/g), the exchangeable and carbonate fractions appeared to decrease, whereas the Fe- and Mn-oxides fraction is increased. In the analyzed sediments, Cr was associated in decreasing amount in the: reducible>organic>acid soluble residue>carbonate bound>exchangeable fractions of the analyzed sediments.

Cr pollution was evident in El-Mex Bay sediments especially at the entrance of the Western Harbor of Alexandria. The high concentration of labile and organic Cr found in site 9 suggests elevated levels of Cr in marine sediment of the entrance or mouth of the Western Harbor originates from leather tanning industries. There are more than10 tanners located near El-Mex area and discharging its wastes directly in this Harbour. Therefor, the water exchange between the Harbour and El-Mex Bay led to increase Cr levels at site 9. Cr contamination of marine and freshwater environment by leather tanning industries has been documented in many parts of the world (Ireland: Walsh and O'Halloran 1998; Brazil: Jordao et al. 1997; India: Khwaja et al. 2001 and Indonesia: Takarina et al. 2004).

3.6 Zinc Zn

Zinc mostly partitioning in the Fe- and Mn-oxides reducible and in the residual fractions, whereas in the carbonate and organic matter fractions slightly decreased with increasing concentrations in the sediments. On the other hand, smaller fractions of Zn were detected

in the easily exchangeable fraction (<2%). Residual fraction is the second most abundant in Zn with percent concentrations of the metal in the range 10–89% (Table 7 and Fig. 2). Generally, Zn level in the residual fraction is higher than the levels of Cu, Cd and Cr. This may be understandable from the point of view that "detritus" Zn is an important fraction of the total Zn concentration in these estuarine sediments. In addition, the acid soluble residual fraction at stations 2 and 3 covered about 38% of the total amount of Zn and reflected these stations were not heavily contaminated with Zn. This may indicate that although the total Zn levels of sediments in these stations were higher than the rest of the stations in terms of total Zn, only a small amount of Zn concentration (8%) were most likely due to anthropogenic input and this seems to pose less impact to living organisms in the sediments. Since it is mainly due to geological processes under natural field conditions. Similar results were reported for some sediments (Li et al. 2000; Weisz et al. 2000)

Total sediment transport in El-Mex Bay by Omoum Drain is about 48,661 ton/year compared to 167,094 ton/year for many land-based sources as Misr for Chemicals Co., Alexandria for Petroleum Refinery Co. and Sodium Bicarbonate Co. The total metal content of El-Mex Bay sediments fell within the range of concentrations reported in different geographical regions (Table 8). Comparison of Cu, Cd, Zn, Mn and Fe content of El-Mex Bay sediments based on El-Rayis et al. (1996), the recent study on this area, with the present data suggests an elevation in total metals content in El-Mex sediments relative to off shore values.

Table 11 Correlation coefficients between F3 of Mn and Fe and L123 fraction of Cu, Cd, Cr and Zn

		F3			L123		
		Mn	Fe	Cu	Cd	Cr	Zn
F3	Mn						
	Fe	0.608[a]					
L123	Cu	0.508	−0.115				
	Cd	0.025	−0.451	−0.087			
	Cr	0.609[a]	0.881[b]	−0.235	−0.345		
	Zn	0.533[a]	0.959[b]	−0.225	−0.485	0.895[b]	

[a] Correlation is significant at the 0.05 level

[b] Correlation is significant at the 0.01 level

Geochemical speciation of six heavy metals for all sites is represented in Fig. 4. The sample at the entrance of the Alexandria Commercial Harbour, namely Western Harbour, W.H, (site 9) had high concentrations of nearly all metals relative to the other sites. This peak was oftentimes associated with the reducible fraction. As this site receives dumped wastes from the ship traffic to and from the W.H. In addition the sediments of the nearby W.H are rich in organic matter content being 4.3 and 8.9% for the outer and inner Harbour, respectively (El Wakeel and El Sayed 1978).

The labile fractions of the investigated metals were calculated as follows: the exchangeable added to carbonate fraction as L12, L12 added to reducible fraction as L123, and L123 added to organic mater and sulphide fraction as L1234. The percentages of the studied metals in the labile fractions were shown in Table 9.

The most mobile metal was Mn (L123) followed by Cd, Cr then Cu. After the second steps (F2) of the experimental procedure, all the metals were under 50% of the total extractable amount. After the reducible step (F3) most of the metals showed significant increase in the percentage of the total extractable amount. In contrary with Relić et al. (2004) among all the metals, a significant increase in the percentages was observed after the organic step of the procedure. The organic fraction accounted for less than 25% of total heavy metal content in El-Mex Bay except in the case of the highly Cu contaminated (site 9).

4 Correlation Analysis

The Pearson correlation coefficient (r) between the extracted concentrations of Mn and Fe in the reducible step (F3) as well as their non-residual fractions are shown in Table 10.

The high degree of correlation between the Mn extracted in the reducible step (F3) on the procedure and its labile fractions (L12, L123, L1234) could indicate that the Mn extracted by hydroxylamine could be from the dissolution and extraction of Mn-oxides (Pickering 1986). The high correlation ($r=0.972$) between F3 and the total amount of extracted Mn confirms that the concentration of this metal extracted by hydroxylamine hydrochloride determines that "fate" of Mn in El-Mex Bay sediments. In this form, Mn-Oxides could be one of the most important scavengers of trace metals.

On the other hand, there is positive correlation between the iron extracted in the reducible step (F3) and the amount of this element extracted in the L123 and L1234 labile fractions. The low correlation coefficient between L12 and L123, L1234 fractions of Fe could indicate the existence of one form of Fe-oxides. Also these results suggest that partly Fe-oxides, besides the dominant Mn-oxides, could be scavengers for the trace metals in the L123 labile fraction (Pickering 1986).

The Pearson correlation coefficient (r) between the extracted concentrations of Mn and Fe in the reducible step (F3) and the amounts of Cu, Cd, Cr

Table 12 Correlation coefficient between F3 of Mn and Fe and L123 and L1234 fractions of Cu, Cd, Cr and Zn

		F3		L123				L1234			
		Mn	Fe	Cu	Cd	Cr	Zn	Cu	Cd	Cr	Zn
F3	Mn										
	Fe	0.608[a]									
L123	Cu	0.508	−0.115								
	Cd	0.025	−0.451	−0.087							
	Cr	0.609[a]	0.881[b]	−0.235	−0.345						
	Zn	0.533	0.959[b]	−0.225	−0.485	0.895[b]					
L1234	Cu	0.773[b]	0.891[b]	0.138	−0.275	0.746[b]	0.810[b]				
	Cd	0.015	−0.566	−0.019	0.956[b]	−0.372	−0.567	−0.336			
	Cr	0.680[a]	0.946[b]	−0.103	−0.335	0.953[b]	0.890[b]	0.821[b]	−0.427		
	Zn	0.569	0.940[b]	−0.218	−0.416	0.894[b]	0.991[b]	0.807[b]	−0.491	0.880[b]	

[a] Correlation is significant at the 0.05 level

[b] Correlation is significant at the 0.01 level

and Zn in the L123 non-residual fractions are shown in Table 11.

There are positive correlation between Cr and Zn in the L123 labile fraction and the amount of Fe extracted in the reducible step. These results could indicate that there are two different substrates for the investigated trace metals. The significant positive correlation between Cr and Zn in the L123 fraction indicates an association of these metals.

The correlation between concentrations of Mn and Fe in reducible step (F3) and between Cu, Cd, Cr and Zn in L123 and L1234 fractions are shown in Table 12.

There are positive correlation between Mn extracted in the reducible step (F3) and Cu, Cr and Zn in the L123 and L1234 fractions, the non-residual fraction (L1234) of Cu, Cr and Zn are also associated with each other (Table 12). There are positive correlations between Fe in (F3) and Zn and Cr from the L123 and L1234 fractions. The labile fractions L123 and L1234 of Cd, Cr and Zn are highly correlated with each other. This could be explained by the fact that a negligible amount of Cd, Cr and Zn had been extracted after the fourth step of the procedure, so there were no significant differences between those two labile fractions.

This study establishes a baseline for heavy metals speciation in El-Mex Bay estuary in the north coast of Egypt on the Mediterranean Sea and identifies Cr, Cu, Cd, Zn, Mn and Fe as contaminants in the coastal sediments. Analysis of the speciation of the various heavy metals allowed for identification of potential pollution sources that would have otherwise been missed in this area of only total metal content was known.

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