

Fractionation and assessment of heavy metals in the Mediterranean Sea sediments of Tripoli Port (Libya) and El-Mex Bay (Egypt)

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Abstract

The state of heavy metal pollution and the mobility of Fe, Mn, Cu, Zn, Ni, Cd and Cr were studied in two different regions in the Mediterranean Sea, one represent Tripoli Port (Libya) and the other represent El-Mex Bay (Egypt). Three surface sediment samples were collected from each region. Methods used to characterize heavy metals in solid phase of the sediments include physical fractionation and chemical extraction. Chemical extraction schemes are most frequently used approach to fractionate trace metals in sediments. High Cu concentration associated with organic fraction was recorded in the study area reached to 16.5 % of the total Cu. Zn is the most labile metal, mainly bound to non-residual fraction; it is presented in the first extraction stages, (ranged from 43 to 70 %). Also, Cd revealed that about 50 % of the total content is bounded to the labile form in the sediments of El Mex Bay. This indicates that Cd and Zn is mainly high risk of mobility. The risk assessment code of Fe and Cu showed low risk, while Mn, Zn and Cd ranged from low risk to medium risk to aquatic environment of the study area.

Keywords: Sediment, geoaccumulation index, heavy metals, Libya

I. Introduction

Libya is a large landscape country in North Africa with a total area of 1.5 M km². Libya is an oil producing country whose economy depends on the oil and gas industry. The oil and gas revenues account for more than 90% of the country's income. The oil and gas facilities are scattered all over the country, on-shore and off-shore, in which water demands for quality and quantity are very high. (Al-Hengari et al., 2007). Pollution resulting from land based sources and human activities are mainly occurring at the vicinity of large coastal cities, and are concentrated on rather few urban/industrial centres on the coastal zone. Trace metals are one of the serious pollutants in environment because of their toxicity and bioaccumulation problems (Tam and Wong 2000). Sediments represent one of the ultimate sinks for trace metals discharged into the environment (Bryan and Langston, 1992), they can absorb persistent and toxic chemicals levels many times higher than its concentration in water column (Mucha et al., 2003; Yuan et al., 2004 and Rodriguez et al., 2009).

El-Mex bay is lying on the Mediterranean Sea and is considered as one of the main fishing grounds. It has surface area of about 19.4 km², and mean depth of about 10 m (Labib, 1997). It receives a heavy load of agricultural, municipal and industrial wastewaters (7×10^9 m³/year) via El-Umum Drain (EL-Rayis and Abdulah, 2006). In addition to direct discharge from five main industries, Chemical, Chloro alkali, Tanneries, Cement, and Petroleum, besides additional amount of municipal wastewater from the main sewer of Alexandria (Mikhail et al., 2001). The elevation in levels of trace metals concentrations in marine environment is a worldwide problem and the discharge of trace metal wastes has many obvious impacts on water, sediments, and biota, led to decrease in productivity, and increase in exposure of humans to harmful substances. The toxicity, bioavailability, bioaccumulation, biodegradability, persistence, mobility, solubility, extractability and many other critical properties is found to depend on the form and nature of the chemical species (Lores and Pennock, 1998). Single and sequential extraction schemes were developed in the early 1980s with the aims of assessing trace-element bioavailability to plants and of studying the environmental accessibility of trace metals (Tessier et al., 1979; Ure et al., 1993). Many different schemes were developed in

the past 30 years, as illustrated by a huge number of publications in the international scientific literature schemes.

The aim of this study was to evaluate the magnitude of the different forms of heavy metals in the sediment of Tripoli Port (Libya) and El-Mex Bay (Egypt)

II. Materials and Methods

II.1. Collection and preparation of samples

Six surface sediment samples were collected from two different regions in the Mediterranean Sea, one represent Tripoli Port (Libya) and the other represent El-Mex Bay (Egypt). Three samples were collected from each region. (Fig 1). Plastic spatula was used for sample collection; use of metal tools was avoided. The surface sediment samples were taken from 0-10 cm and quickly packed in airtight polythene bags. Sub-samples of the material were oven dried at 50°C for 24 h and sieved (aperture 125 µm). The lower particle size fraction was homogenized by grinding in an agate mortar and stored in glass bottles for chemical analyses.

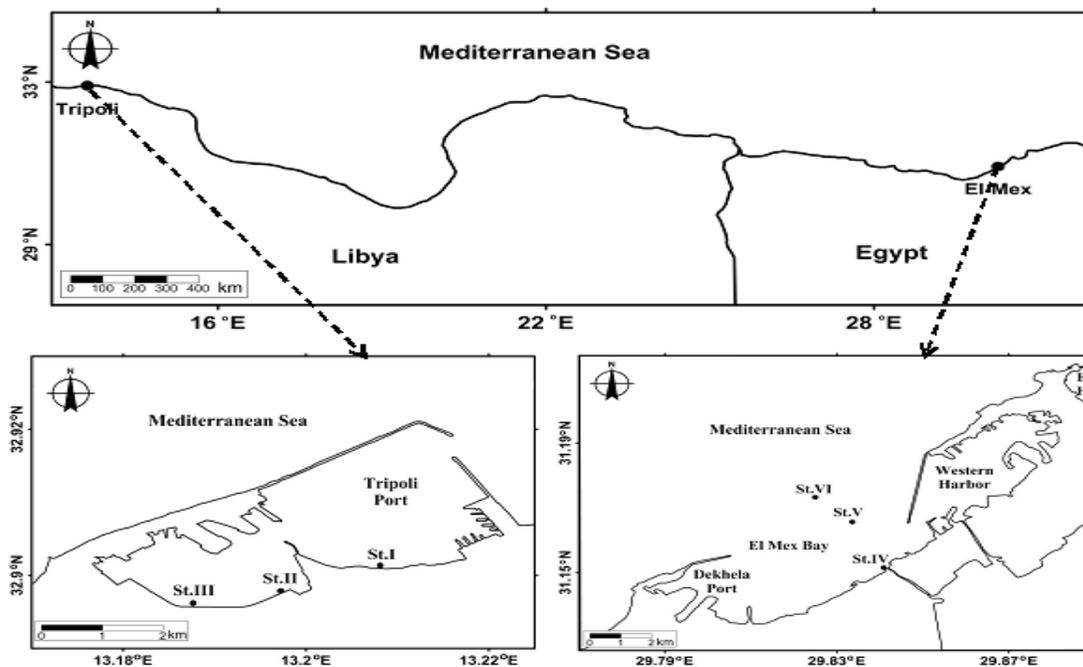


Figure 1. Sampling Stations

II.2. Methods of Analysis

The sample was divided into two portions. The first portion was prepared for determination of total calcium carbonates were measured volumetrically as percent

CaCO₃ by a simple water calcimeter apparatus (Black, 1965). Granulometric analyses have been made using standard sieve and pipette analysis techniques (Folk 1974). Total organic carbon (Org C) content of samples were determined by oxidation with acidified K₂Cr₂O₇ and back titration with ferrous ammonium sulphate, essentially as described by Gaudette et al. (1974). The percentage of organic matter was calculated by multiplying total organic carbon percentage by 1.8. For total trace metals analysis, the powder samples (0.3g) were digested with HNO₃, HF, Aqua regia (HNO₃: HCl) and HClO₄ in a previously cleaned and dried Teflon beaker, then evaporated to near dryness at 80 °C. After complete digestion, the residue was transferred to a 25ml volumetric flask with 0.1 M HCl. (Loring and Rantala, 1992).

The second portion was subjected to sequential extraction studies as the following:

Sequential extractions which were performed according to Tessier et al. (1979) and Shuman (1985) as follows:

- a. The exchangeable fraction is extracted by 1M sodium acetate solution at pH 8.2 at room temperature for one hour with continuous agitation.
- b. The fraction bound to carbonate is extracted from residue (a) with sodium acetate solution at pH 5.0 for one hour at room temperature with continuous agitation.
- c. The fraction bound to iron-manganese oxides is extracted from residue (b) with 0.05 M hydroxylamine hydrochloride in 25% (v/v) acetic acid; this step is performed at 70°C with occasional agitation for six hours.
- d. The fraction bound to organic matter is obtained according to Gupta and Chen (1975).
- e. The residual fraction is computed as the difference between the total element concentration (from 1) and the sum of the other determined fractions (i.e. from a to d).

The samples were separately analyzed by using Parkin Elmer atomic absorption spectrophotometer (2830). The concentrations of trace metals were determined in μg^{-1} .

II.3. Quality control studies

All chemicals and reagents were of analytical reagent grade quality (Sigma-Aldrich, USA). Millipore water was used throughout all the experiments. Before use, all glass and plastic ware were soaked in 10 % HNO₃ for 24 h. The washing was completed with Millipore water rinse. Method validation and quality control samples were done using a

reference material (HISS-1, National Research of Council of Canada; Table1). The detection limits were calculated by six determinations in one batch of synthetic sea water (close or less than $1\mu\text{g/l}$). The precision was agreed to be within 10%. The variation coefficients were 1.3–6% for Fe; 2.5–8.2% for Mn; 2.6–8.9% for Zn; 2.8–11.3% for Cu; 2.1-7.5 for Pb; 3.5-8.21 for Cd; 2.0-9.0 for Co; 2.5-8.37 for Ni and 2.4–9.4% for Cr. Natural sample was analyzed in duplicate in each of six batches of samples after spiking by a known concentration from the standard reference material. The same natural sample was analyzed without spiking. The percentages of recovery for spiked samples were used to determine the accuracy. The recoveries of metal spikes added to the sediments studied were 102% for Fe; 97% for Mn; 95% for Cu; 103% for Zn; 94% for Cd.

Table 1. The concentrations for different metals (mg kg⁻¹) in the reference materials (HISS-1, National research of Council of Canada).

Metal	Found	Certified
Fe	0.242 ± 0.09	0.236 ± 0.017
Mn	60.95 ± 4.2	61.24 ± 2.30
Zn	4.70 ± 0.79	4.60 ± 1.21
Cu	2.15 ± 0.37	2.08 ± 0.08
Cd	0.024 ± 0.09	0.022 ± 0.028

III. Results and discussion

III. 1. Sediments Characterization

Grain Size, Total Organic Matter (TOM) and Carbonate (CaCO₃)

The results of grain size analysis, total organic matter (TOM) and carbonate content (CaCO₃) of the studied sediments are listed in Table2. The data revealed that the sediments collected from the present investigated area were composed mainly of sand varied between 89 and 94% in Tripoli Port sediment while it ranged from 80 to 98 % in El-Mex Bay sediments. The distribution of silt clay percentage in marine sediments of Tripoli Port and El-Mex Bay were (6.0-10.0%) and (2.0-19.0 %), respectively.

The organic matter in sediments, expressed as total organic carbon (TOC) represents an important reservoir for the global carbon cycle (Weston and Joye, 2005). It is linked with early diagenesis and plays an important role in the ocean chemistry (Lee, 1994). At the global scale, the storage of organic matter (in terms of TOC) mirrors the distribution

pattern of phytoplankton biomass (Seiter *et al.*, 2004). The organic matter contents in Tripoli Port region varied between 0.82% and 1.05 % while in El-Mex Bay region ranged from 0.41 % to 2.39 %. The content of organic-matter is lower in Tripoli Port region (Libya) comparing with those reported in El-Mex Bay region (Egypt); this may be related to the lower primary productivity and inferior conditions for organic matter preservation. The highest value (around 2 %) was recorded at El-Mex Bay region (Egypt), reflecting high rate of organic matter accumulation from the domestic drainage water. According to Mueller and Suess (1979), the ratio between the recycled and accumulated organic matter in sediments is controlled by the bulk sedimentation rate.

Table 2. Grain size analysis, organic matter, calcium carbonate and total heavy metals concentration in the sediments

Regions	St.	O.M %	CaCO ₃ %	Sand %	Silt+ Clay %	Total metals concentration (µg/g)				
						Fe	Mn	Cu	Zn	Cd
Tripoli Port Lypia	I	1.05	32.47	94.00	6.00	220.23	118.7	10.07	12.12	1.28
	II	0.94	30.54	92.30	7.70	217.42	117.9	9.09	11.59	1.24
	III	0.82	30.78	89.60	10.40	202.62	115.2	9.14	15.06	1.16
	Ave.					213.42	117.3	9.43	12.92	1.23
	±SD					7.7	1.5	0.5	1.5	0.4
El-Mex Bay (Alexandria) Egypt	IV	2.39	37.88	88.00	12.00	2624.9	291.7	48.17	110.4	2.25
	V	1.51	50.90	80.20	19.80	2058.3	250.1	12.17	78.42	1.58
	VI	0.41	55.63	98.00	2.00	1524.9	865.9	13.92	43.83	1.94
	Ave.					2069.37	469.2	24.75	77.55	1.92
	±SD					1039	265	14	39	0.3

The carbonate content in sediments (expressed as percent CaCO₃) varied between 30.0% and 32.0 % in Tripoli Port region (Table2). These values are lower than those reported in El-Mex Bay region (Egypt), ranged from 37.0 to 55.0 %. The carbonate contents of the sediment in El-Mex Bay region may be related to the biogenic calcareous components which are found to be sufficient in the sediment fractions to form such CaCO₃ percentages, also indicate varying influences of bioproductivity, and post-depositional carbonate solution. It is evident that the shells of organisms are the principle contributors of carbonate in sediments. A direct significant correlation ($r = 0.60$) with the carbonate fraction and organic matter content, this may be attributed to the presence of carbonate debris in sand size fraction.

III.2. Total heavy metals distribution in the sediments

In recent decades, industrial and technological advancements have led to the gradual increase of heavy metal concentrations (Ives and Cardinale, 2004). As such, this phenomenon of trace metals being present in the environment at high concentrations causes deleterious effects on various terrestrial creatures and human beings (Jain, 2004; Bradl, 2005; Walker et al., 2006; Spurgeon *et al.*, 2008). The regional variations of the total concentrations of the investigated trace metals (Fe, Mn, Zn, Cu, Ni, Cr and Cd), in marine sediments of the study area are given in Table 2.

The distribution of total Fe concentrations in the sediments of the study area revealed that the level of Fe in El-Mex Bay region (Egypt) ($2069.4 \pm 1039 \mu\text{g g}^{-1}$) is higher than those recorded in Tripoli Port region ($213.4 \pm 7.70 \mu\text{g g}^{-1}$), due to the effect of industrial activities in the surrounding area of El-Mex Bay. The total concentration of Fe in Tripoli Port region is lower 10 times than that reported in sediment of El-Mex Bay of Alexandria Egypt. The results of the total Mn concentration in sediment samples showed that the minimum average Mn concentration recorded in Tripoli Port region ($117.3 \pm 1.50 \mu\text{g g}^{-1}$) and the maximum average Mn concentration recorded in El-Mex Bay region ($469.2 \pm 265.0 \mu\text{g g}^{-1}$). The variability of Mn content may be attributed to the sediment texture of the samples.

The total Cu concentrations in the present study ranged from 9.43 ± 0.5 in Tripoli Port to $24.8 \pm 14.0 \mu\text{g g}^{-1}$ in El-Mex Bay sediments. The average Cu concentration in the present study was lower than that recorded in the bottom sediment of the Rybnik Reservoir in Poland ($451.74 \mu\text{g g}^{-1}$ dry wt.) (Loska and Weichula, 2003). The total concentration of Cu is lower comparing with Damietta Harbor sediments recorded by El-Gharapawy (2009) (the average of Cu concentration equals $44.36 \pm 25.75 \mu\text{g g}^{-1}$). The average concentration of Cu in the study area is lower 10 to 24 times comparing with the results of Euvaikos Gulf (240 mg kg^{-1}) reported by Dassenakis *et al.* (2003). The results of the average of total Zn concentrations in the sediments of the study area ranged from 12.9 ± 1.5 to $77.6 \pm 39.0 \mu\text{g g}^{-1}$ for Tripoli Port and El-Mex Bay sediments, respectively. The total concentration of Zn is very low comparing with Damietta Harbor sediments recorded by El-Gharapawy (2009) (the average of Zn concentration equals $146.05 \pm 53.96 \mu\text{g g}^{-1}$), the average concentration of Zn in the study area is lower 10 times comparing with the results of Tripoli Port

($12.9 \pm 1.5 \mu\text{g g}^{-1}$). As shown in Table 2, the distribution of total Cd concentration in the study area ranged from 1.16 to $2.25 \mu\text{g g}^{-1}$ at all the sites. The concentration of Cd in this study showed values lower in Tripoli port sediments (ave.; $1.23 \pm 0.05 \mu\text{g g}^{-1}$) than in El-Mex Bay sediments (ave.; $1.92 \pm 0.64 \mu\text{g g}^{-1}$).

Fractionation of Heavy Metals:

Iron Fractionation (Fe):

Fe was mostly concentrated in the residual fraction, although it was found in other fractions. The greater percentage of Fe in the residual fraction ranged between 73.7 % at station IV and 82.6 % at station VI in El Mex Bay sediments (Table 3, Fig.2). This reflects the greater tendency of Fe to be in the lattice structure of the sediment. Several authors have observed that the majority of Fe content was found in the residual fraction (Pardo et al., 1993). The sum of all fractions content, except residual in Tripoli Port and El Mex Bay sediments ranged from $47.05 \pm 1.44 \mu\text{g/g}$ to $445.86 \pm 241.73 \mu\text{g/g}$, these values represented 22.0 % of the total Fe content of the two regions. Among the non-residual fractions, the organic fraction constitutes the greatest amount of Fe in Tripoli Port sediments. Its mean content reached to $19.17 \pm 2.15 \mu\text{g/g}$. Organic matter plays an important role in trapping through the direct adsorption, complexation processes and the formation of insoluble sulphides. The amount of Fe present in Fe–Mn oxides fraction associated with the sediments of El Mex Bay was the greatest ($237.13 \pm 137.9 \mu\text{g/g}$) compared with those found Tripoli Port sediments. The relative percentage of exchangeable represented less than 1% of the total iron content; the carbonate form ranged from 5 to 8 % in the study area (Fig. 2).

Table3. Fe concentrations ($\mu\text{g g}^{-1}$) in each fraction of Tripoli port and El-Mex Bay sediments – Mediterranean Sea.

Sites	St.	F1	F2	F3	F4	Sum Fractions	Residual	Total
Tripoli Port	I	2.45	11.44	14.21	18.5	46.60	173.72	220.32
Lypia	II	2.77	10.62	15.22	16.94	45.55	171.87	217.42
	III	1.98	10.32	14.61	22.08	48.99	153.69	202.68
El-Mex Bay	IV	12.34	251.40	381.30	44.40	689.40	1935.50	2624.90
(Alexandria)	V	10.11	110.30	228.60	34.40	383.45	1674.85	2058.30
Egypt	VI	8.55	128.60	101.50	26.04	264.72	1260.18	1524.90

Mn fractionation (Mn):

Mn is mostly concentrated in the residual fraction, it represent more than 65% of the total concentration from stations I-III (in Tripoli Port, while in El-Mex Bay it reached more than 90%). The other important phase of Mn is non-residual form. Mn associations with different fractions in the two regions are given in Table 4 and Fig. 2. The average Mn content in the five fractions of the study area (Table 4) can be arranged in the following order: Residual (240.0 µg/g; 81.90%) > Carbonate (19.03 µg/g, 6.50%) > Fe-Mn oxides (17.49 µg/g, 6.0 %) > Organic form (9.12 µg/g, 3.1%) > Exchangeable (7.47 µg/g, 2.69 %). The relative percentage of Mn about the fractionation revealed similarity in exchangeable fraction for the two regions of the study area, very small amounts of Mn (< 3 %) were found in the exchangeable fraction for all samples. This indicates the low contribution of Mn by anthropogenic activities. The concentrations of Mn associated with carbonate were relatively high in the sediments of the study area, representing 6.5 % of the total Mn (Fig. 2). The metal in the exchangeable and carbonate fractions are considered to be weakly bound and may equilibrate with the aqueous phase, thus becoming more bioavailability (Fytianos et al., 1995). Caplat et al., (2005) found that Mn is mainly present in the acid-soluble fraction (carbonate form) and showed significant affinity for the residual fraction (up to 50%). Mn bound with both Fe-Mn oxides and organic fractions was low; representing 9 % of the total Mn. In general, Mn can be presented as oxides, hydroxides or in association with iron oxides / hydroxides, Mn ions can be adsorbed and / or partially ion-exchanged on the surface of MnO₂ and they can be environmentally mobile in certain conditions (Weisz et al., 2000). Mn, also, bound to carbonates or specifically adsorbed and bound to organic matter and sulfides (Dong et al., 1998). The relative percentage of Mn associated with residual fraction is high, more than 81%. The high concentration of Mn in the residual fraction may be due to the variation in mineralogical composition of sediments of the study area.

Copper fractionation (Cu):

Cu in the non-residual fraction (Fig. 2 and Table 5) is concentrated in the organic fraction than in other forms indicating its association with organic phase. The exchangeable fraction is detected in the study area (0.27 µg/g, 1.54% of the total Cu). The average values

of Cu in the five fractions of the study area are shown in Table 5. They are arranged as follows: residual (12.93 $\mu\text{g/g}$, 75.3%) > organic form (2.84 $\mu\text{g/g}$, 16.50%) > Fe-Mn oxides (0.60 $\mu\text{g/g}$, 3.5%) \approx carbonate (0.54 $\mu\text{g/g}$, 3.20%) > exchangeable (0.27 $\mu\text{g/g}$, 1.54%).

Table 4. Mn concentrations ($\mu\text{g g}^{-1}$) in each fraction of Tripoli port and El-Mex Bay sediments – Mediterranean Sea.

Sites	St.	F1	F2	F3	F4	Sum Fractions	Residual	Total
Tripoli Port	I	3.24	12.95	12.26	8.42	36.87	81.87	118.74
Lypia	II	3.24	17.50	12.12	7.28	40.14	77.79	117.93
	III	3.12	15.54	13.78	6.64	39.08	76.11	115.19
El-Mex Bay	IV	22.16	25.24	26.74	12.56	86.70	205.05	291.75
(Alexandria)	V	7.41	24.20	24.38	9.68	65.67	184.41	250.08
Egypt	VI	5.64	18.77	15.64	10.14	50.19	815.73	865.92

The high concentration of Cu associated with organic fraction was recorded in the study area around 16.5 % of the total Cu. Sediment samples are characterized by relatively high organic matter percentage, ranged from 0.4 to 2.39 %. This indicates that Cu occurs in the forms of organic complexes. Cu is preferentially retained in organic matter by complexation rather than by ion exchange (Balasoiu et al., 2001; Wu et al., 1999). As expected from a number of previous studies on polluted sediments (Li et al., 2001; Wu et al., 1999) extractable Cu is mainly associated with the oxidizable phase, where it is likely to occur as organically complex metal species. This behavior can be explained by the well-known high affinity of Cu to humic substances, which are chemically very active in Cu complexation (Pardo et al., 1993; Marin et al., 1997). Rapin et al., (1983) reported that Cu is mostly bound to the organic matter/sulfide fraction (70–80%) in marine sediment in highly polluted area of Villefranche Bay. On the other hand, most of the Cu is presented in the residual fraction (75 % of the total Cu). The higher association with the residual fraction indicates its low bioavailability (Kotoky et al., 2003). The percentage of metal in the residual fraction can not be easily released to the environment since the metal is about to crystal lattice. Several investigators have demonstrated that the sorption of Cu on to hydrous Fe–Mn oxides is due to co-precipitation of Cu in the Fe–Mn oxide lattice (El-Sikaily et al., 2005). The low Cu content in the exchangeable (1.54%) and carbonate fraction (3.2 %) in the present study indicates that the bioavailability of Cu to the sediments may be less.

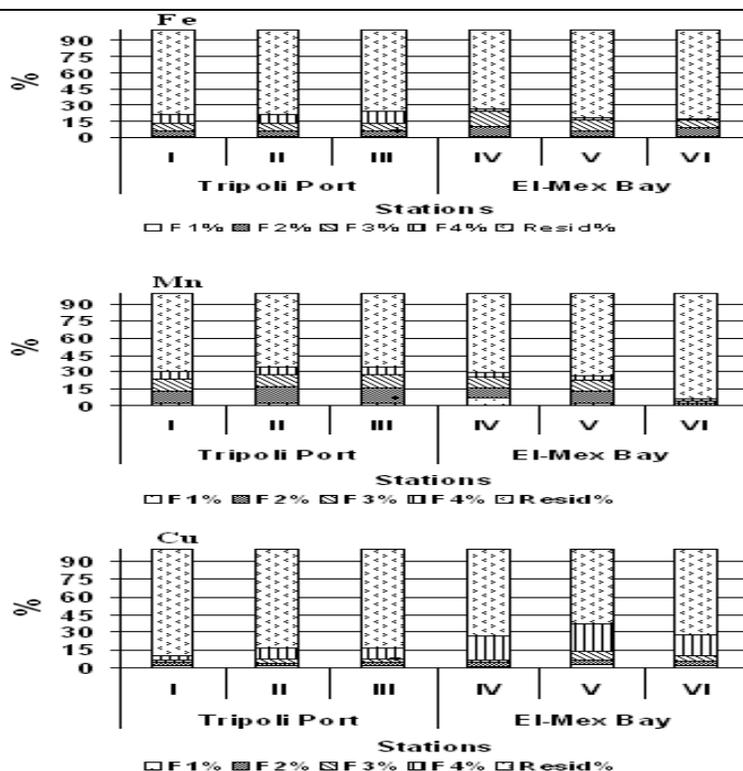


Figure 2. Percentage of Fe, Mn and Cu in each fraction, to the total content of Tripoli port and El-Mex Bay sediments – Mediterranean Sea.

Table 5. Cu concentrations ($\mu\text{g g}^{-1}$) in each fraction of Tripoli port and El-Mex Bay sediments – Mediterranean Sea.

Sites	St.	F1	F2	F3	F4	Sum Fractions	Residual	Total
Tripoli Port	I	0.14	0.29	0.26	0.36	1.05	9.02	10.07
Lypia	II	0.12	0.22	0.32	0.88	1.54	7.55	9.09
	III	0.21	0.24	0.24	0.86	1.55	7.59	9.14
El-Mex Bay	IV	0.51	1.55	1.30	9.50	12.86	35.81	48.67
(Alexandria)	V	0.36	0.50	0.86	2.80	4.52	7.65	12.17
Egypt	VI	0.25	0.45	0.62	2.62	3.94	9.98	13.92

Zn fractionation (Zn):

Zn reveals that a major part is found to be associated with Fe-Mn oxides and organic phases compared to exchangeable and carbonate phases. Zn in oxides and organic fractions constitute about between 30% of the total Zn at stations III and VI and reaching to 56% of the total Zn at station V. Zn bound to exchangeable fraction is very low (3% of the total content except station IV reached to 13 % of total Zn). The associations of Zn with the

different fractions are given in Table6 & Fig.3. The average values of Zn concentration in the five fractions of the two regions are shown in Table . They are arranged as follows: residual (18.91µg/g, 41.80%) > Fe-Mn oxides (13.54 µg/g, 29.90 %) > carbonate (5.28 µg/g, 11.70%) > exchangeable (4.07µg/g, 9.00%)> organic form (3.42µg/g, 7.60%).

Zn is the most labile metal, recovered in the first extraction stages, and is associated with the non-residual fraction of sediment. Zinc is mainly bound to non-residual fractions Caplat et al., (2005). As shown in Fig.3, the results revealed high level of Zn concentration is obtained in the non-residual fractions (labile form); it ranged from 43 to 70 %. Fe-Mn oxides and organic fractions were reported to be an important carrier of Zn for the aquatic environment in sediments, this in agreement with that reported by Fernandes (1997). Zn-bounded to the oxide form about 30 % of the total Zn, adsorption Zn in the oxides fraction has higher stability constant than carbonate fraction (Fernandes, 1997; Li et al., 2001). The percentage of Zn associated with residual fractions was similar in the sediments of Tripoli Port and El Mex Bay. Generally, The results of Zn geochemical association forms indicate that more than 50 % of the total Zn was recorded in the non-residual fraction, which increased potential Zn mobility and bioavailability, this may be possible by disposal of untreated sewage wastes from domestic drainage and human activities in the area.

Table 6. Zn concentrations ($\mu\text{g g}^{-1}$) in each fraction of Tripoli port and El-Mex Bay sediments – Mediterranean Sea.

Sites	St.	F1	F2	F3	F4	Sum Fractions	Residual	Total
Tripoli Port	I	0.43	1.41	3.82	0.98	6.64	5.48	12.12
Lypia	II	0.50	2.71	2.08	1.90	7.19	4.40	11.59
	III	0.41	2.10	2.52	1.68	6.71	8.35	15.06
El-Mex Bay	IV	15.34	15.01	25.82	8.20	64.37	45.98	110.35
(Alexandria)	V	4.95	4.03	39.94	5.90	54.82	23.60	78.42
Egypt	VI	2.80	6.43	7.06	1.88	18.17	25.66	43.83

Cadmium Fractionation (Cd):

Cd in the environment may be derived from either natural or anthropogenic sources. Natural sources include geological weathering and volcanic emissions. Cd and its compounds may enter the environment at any point from the inputs of industrial effluents, sewage sludge, domestic wastes, and pigments. In the present study area a major part of Cd

is concentrated in the residual fraction varied from 0.69 $\mu\text{g/g}$ at station V to 1.31 $\mu\text{g/g}$ at station VI. The next important phase of Cd concentration is in the non-residual fraction (labile form). The associations of Cd with different fractions are shown in Fig.3& Table7. As shown in Table the average values of the five fractions of the study area arranged in the following order: Residual (1.00 $\mu\text{g/g}$; 63.5%) > Fe-Mn oxides (0.18 $\mu\text{g/g}$, 11.20 %) \simeq Organic form (0.21 $\mu\text{g/g}$, 13.00%) > Carbonate (0.11 $\mu\text{g/g}$, 7.00%)> Exchangeable (0.08 $\mu\text{g/g}$, 4.8%).

As shown in Fig. 3, the results revealed that about 50 % of the total content of Cd is bounded to the labile form (non-residual fraction) in the sediments of El Mex Bay (stations IV-VI). This indicates that Cd is mainly discharged from urban wastes and it is high risk of mobility. In Tripoli Port sediments (Stations I-III), the labile concentration of Cd (non-residual fraction) represented about 23 % of the total Cd content, which most of Cd concentrations are associated with residual fraction and it is considered as low risk of

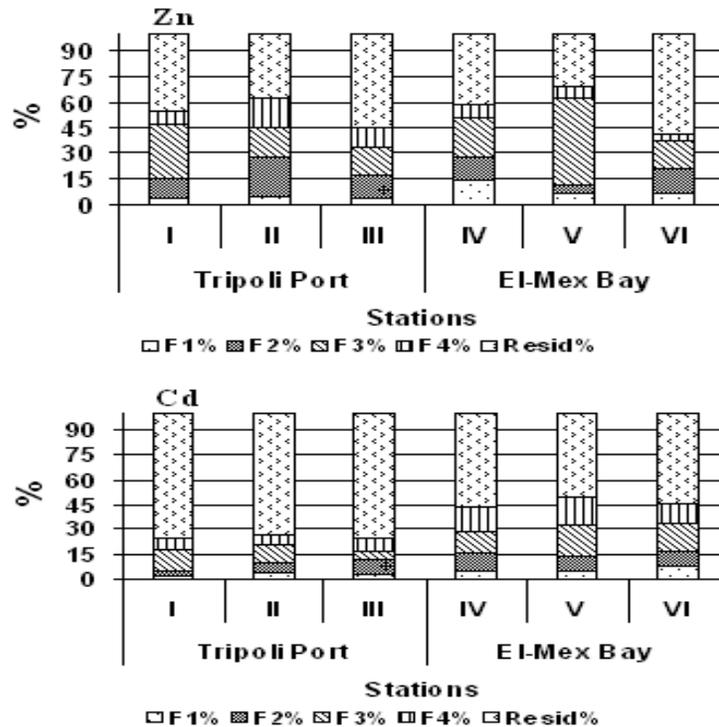


Figure 3. Percentage of Zn and Cd in each fraction, to the total content of Tripoli port and El-Mex Bay sediments – Mediterranean Sea.

mobility (Filgueiras et al., 2004). The data obtained in the exchangeable fraction of Cd are similar in the all sediments ($0.08 \pm 0.05 \mu\text{g/g}$). This indicates that Cd is highly distributed in the study area. The low amounts of Cd in the exchangeable fraction (Table 7) indicate that Cd is from lithogenic source. The average concentration of Cd associated with carbonate is $0.11 \pm 0.07 \mu\text{g/g}$. Cd associated with exchangeable and carbonate fractions are considered to be weakly bound and may equilibrate with the aqueous phase, and so becoming more bioavailability (Dong et al., 1998). These data could reflect the dangerous of Cd in El Mex Bay area. Also, Cd bound to organic fraction and Fe-Mn oxides fraction which is high polluted in El Mex Bay area (more than 30% of the total Cd). Organic matter and Fe-Mn oxide have high scavenging affect on Cd and may provide a sink for Cd (Dong et al., 1998; Yu et al., 2001).

Table 7. Cd concentrations ($\mu\text{g g}^{-1}$) in each fraction of Tripoli port and El-Mex Bay sediments – Mediterranean Sea.

Sites	St.	F1	F2	F3	F4	Sum Fractions	Residual	Total
Tripoli Port	I	0.02	0.02	0.12	0.06	0.22	1.06	1.28
Lypia	II	0.03	0.05	0.1	0.04	0.22	1.02	1.24
	III	0.03	0.08	0.04	0.08	0.23	0.93	1.16
El-Mex Bay	I	0.17	0.23	0.38	0.48	1.26	0.99	2.25
(Alexandria)	II	0.11	0.16	0.22	0.4	0.89	0.69	1.58
Egypt	III	0.09	0.12	0.2	0.22	0.63	1.31	1.94

Risk Assessment Code (RAC):

According to the RAC (Perin et al., 1985; Singh et al., 2005), the metals in the sediments are bound with different strengths to the fractions. The RAC assesses the availability of metals in solution by applying a scale of the relative percentage in the exchangeable and carbonate fractions. This classification is tabulated in Table 8. It is evident from the results of the fractionation studies that the metals in the sediments are bound to different fractions with different strengths. The strength values can, therefore, give a clear indication of sediment reactivity, which in turn assess the risk connected with the presence of metals in an aquatic environment. This criterion of RAC as given below indicates that sediment which can release in exchangeable and carbonate fractions, less

than 1% of the total metal will be considered safe for the environment. On the contrary, sediment releasing in the same fraction more than 50% of the total metal has to be considered highly dangerous and can easily enter the food chain (Jain, 2004). The risk assessment code of Fe and Cu showed low risk, while Mn, Zn and Cd ranged from low risk to medium risk to aquatic environment of the study area.

Table 8. Risk assessment Code (RAC)

Risk	Criteria (%)	Present study % of Exchangeable + Carbonate				
		Fe	Mn	Cu	Zn	Cd
No risk	< 1	2.8 -	5.9 - 8.9	3.7 - 7.1	11.5-	3.1 -17.1
Low risk	1 - 10	17.6			27.7	
Medium risk	11 - 30					
High risk	31 - 50					
Very high risk	> 50					

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Sequential extraction of Fe, Mn, Cu, Zn, and Cd in sediments of Tripoli port and El Mex Bay indicated that the exchangeable Cu fraction was very low from the study area and small amounts of Fe, Mn and Zn were found in this fraction for all samples (< 3 % of the total). This indicates the lower effect of the anthropogenic material on the distribution of Fe, Mn, Zn and Cu content. The low content of these metals in the exchangeable fraction showed low bioavailability. Large amounts of Zn extracted from the exchangeable and carbonate fractions indicated its anthropogenic source which represented from 11.8 to 27.7 % of total concentration. It is clear from the results that the residual fraction is the most important fraction. Among this fraction, Fe and Mn were represented more than 80 % from the total content for each metals.

References

Al-Hengari, S., Al-Hengari, M.El-Bousiffi, W.El-Moudir (2007). Libyan Petroleum Institute experience in evaluation of desalination plants in the Libyan oil sector. *Desalination* 206:633–652

Balasoïu, C.F., Zagury, G.J. and Deschenes, L. (2001). Partitioning and speciation of chromium, copper, and arsenic in CCA-contaminated soils: influence of soil composition" *Sci. Total Environ.* 280, pp. 239–255.

Black C. A. (1965). *Methods of Soil Analysis*: Amer. Soc. Agron., Madison, Wisconsin, pp. 562- 1389

- Bradl, H. B. (2005). Heavy metals in the environment: Origin, interaction, and remediation. Amsterdam: Elsevier.
- Bryan, G. and Langston, W. (1992). Bioavailability, accumulation and effects of heavy metals in sediments with special reference to nited Kingdom estuaries: a review. *Environmental Pollution* 76: 9–131.
- Caplat C., Texier H., Barillier D., and Lelievre C. (2005) Heavy metals mobility in harbour contaminated sediments *Marine Pollution Bulletin*, 50: 504 -11.
- Dassenakis M., Andrianos H., Depiazi G., Konstantas A., Karabela M., Sakelari A and Skoullou M., (2003). The use of various methods for the study of metal pollution in marine sediments, the case of Euvoikos Gulf, Greece, *Applied Geochemistry* 18 : 781 – 794.
- Dong, D., Zhu, X., Yang, B., and Liu M., (1998) Evaluation of sampling and analytical errors in the determination of manganese in soils, *Microchemical Journal*, 59: 356–363.
- El- Gharapawy, S.M. (2009). Assessment of Some Heavy Metals in the Bottom Sediments in Damietta Harbor Egypt. A Thesis Mansoura University, Damietta Faculty of Sciences Environmental Sciences Department. PP 255.
- EL-Rayis OA, Abdallah MAM. (2006). Contribution of Nutrients and some Trace Metals from a Huge Egyptian Drain to the SE-Mediterranean Sea, west of Alexandria. *Mediterranean Mar. Sci.*, 7(1):79-86.
- El-Sikaily, A., Khaled, A., and El-Nemr, A., (2005). Leachable and total nine heavy metals in muddy and study sediment collected from Suez Gulf, *Egyptian Journal of Aquatic Research* 31:99-119.
- Fernandes, H. M., (1997) Heavy metal distribution in sediments and ecological risk assessments: the role the digenetic processes in reducing metal toxicity in bottom sediments, *Environmental Pollution*, 97:317-325.
- Filgueiras, A.V., Lavilla, I., and Bendicho, C., (2004) Evaluation of distribution, mobility and binding behaviour of heavy metals in surficial sediments of Louro River (Galicia, Spain) using chemometric analysis: a case study, *Science of the Total Environment*, 330:115 –129.
- Folk, K.L. (1974) Petrography of sedimentary rocks. Univ. Texas, Henphill, Austin, Tex, 182B.
- Fytianos, K., Bovolenta, S., and Muntau, H., (1995) Assessment of metal mobility from sediment of Lake Vogoritisi" *Journal Environmental Science and Health*, **A30** (6), pp.1169- 1190.
- Gaudette, H.E., W.R. Flight, L. Toner and W. Folger, (1974) An inexpensive titration method for the determination of organic carbon in recent sediments. *J. Sedimentary Petrol.*, 4: 249-253.
- Gupta, S.K. and Chen, K.V. (1975) Partitioning of trace metals in selective chemical fractions of near shore sediments. *Environ. Lett.*, 10 129-158.
- Ives, A. R. and Cardinale, B. (2004). Food-web interactions govern the resistance of communities after nonrandom extinctions. *Nature*, 429, 174–177.
- Jain C.K. Singhal D.C. and Sharma M.K. (2004). Adsorption of zinc on bed sediment of River Hindon: adsorption models and kinetics, *Journal of Hazardous Materials B114*: 231-239.
- Jain, C.K., (2004). Metal fractionation study on bed sediments of River Yamuna, India" *Water Research*, 38: 569-578.

- Kotoky, P., Bora, B. J., Baruah, N. K., Baruah, J., Baruah P., and Borah, G. C., (2003) Chemical fractionation of heavy metals in soils around oil installations, *Assam Chemical Speciation and Bioavailability*, 15(4): 115-126.
- Labib W. (1997). Eutrophication in mex bay (Alexandria, Egypt) Environmental Studies And Statistical Approach. B. Nat. Inst. Oceanogr. Fish. ARE., 23: 49-68.
- Lee, C., (1994) Controls on carbon preservation – New perspectives: *Chemical Geology*, 114, 285-288.
- Li, X; Shen, Z., Wai, O. W. H., and Li, Y. S., (2001). Chemical forms of Pb, Zn and Cu in the sediment Profiles of the Preal River estuary" *Marine Pollution Bulletin*, 42, (3),pp. 215-223.
- Lores E, Pennock J. (1998). The effect of salinity on binding of Cd, Cr, Cu and Zn to dissolved organic matter, *Chemosphere*, 37: 861-874.
- Loring, D. H. and Rantala, R. T. T., (1992). Manual for geochemical analysis of marine sediments and suspended particulate matter, *Earth Science Reviews* 32, pp.235-283.
- Loska, K. and D. Weichula. (2003). Application of principal component analysis for the estimation of source of heavy metal contamination in surface sediments from the Rybnik Reservoir. *Chemosphere*, 51, 723–733.
- Marin, B., Valladon, M., Polve, M., and Monaco, A., (1997). Reproducibility testing of a sequential extraction scheme for the determination of trace metal speciation in a marine reference sediment by inductively coupled plasma-mass spectrometry, *Analytica Chimica Acta*, 342, pp.91 – 112.
- Mikhail SK, Gergis WL, Siam EE. (2001). Transport Processes In A Heavy Eutrophic Marine Bay, Alexandria (Egypt), Applying Environmental Impact Assessment (EIA) Model. *Egypt. J. Hospital Med.*, 4: 84-96.
- Mucha, A. P., Vasconcelos, M.T.S.D. and Bordalo, A.A. (2003). Macro benthic community in the Doura Estuary: relations with trace metals and sediment characteristics. *Environmental Pollution*, vol. 121, pp. 169-180.
- Mueller, P.J. and Suess, E.: (1979). Productivity, sedimentation rate and sedimentary organic matter in the oceans, 1. organic carbon preservation. *Deep Sea Research* 26: 1347 – 1362
- Oregioni, B. and Aston, S.R. (1984). The determination of selected trace metals in marine sediments by flame-atomic absorption spectrophotometry. IAEA Monaco Laboratory. Internal Report UNEP, March, 1986, *Reference Methods for Marine Pollution Studies*, No. 38.
- Pardo, R., Barrado, E., Castrillejo, Y., Velasco, M. A., and Vega, M., (1993). Study of the contents and speciation of heavy metals in River sediments by factor analysis" *Analytical Letters*, 26, pp.1719–39.
- Perin, G., Craboledda, L., Lucchese, M., Cirillo, R., Dotta, L., Zanetta, M. L., and Oro, A.A., (1985). Heavy metal speciation in the sediments of northern Adriatic sea. A new approach for environmental toxicity determination. In: Lakkas, T.D. (Ed.), *Heavy Metals in the Environment*, vol. 2. CEP Consultants, Edinburgh.
- Rapin, F., Membrine, G. P., Förstner, U., and Gracia, J. L., (1983). Heavy metals in marine sediment phases determined by sequential chemical extraction and their inter-action with interstitial water" *Environmental Technology Letters*, 4, pp.387–396.
- Rodriguez L., Ruiz E., Alonso-Azcarate J. and Rincon J. (2009). Heavy metal distribution and chemical speciation in tailings and soils around a Pb–Zn mine in Spain. *Journal of Environmental Management* 90: 1106-1116.

-
- Seiter, K., Hensen, C., Schröter J., Zabel, M., (2004). Organic carbon in surface sediments – defining regional provinces: Deep-Sea Research I, 51, 2001–2026.
- Shuman, L.M. (1985). Fractionation method for soil microelements. *Soil Sci.*, 11-22.
- Singh, K. P., Mohan, D., Singh, V. K., and Malik A., (2005) Studies on distribution and fractionation of heavy metals in Gomti river sediments—a tributary of the Ganges, India" *Journal of Hydrology*, 312, pp. 14-27.
- Spurgeon, D. J., Rowland, P., Ainsworth, G., Rothery, P., Long, S., and Black, H. I. J. (2008). Geographical and pedological drivers of distribution and risks to soil fauna of seven metals (Cd, Cu, Cr, Ni, Pb, V, and Zn) in British soils. *Environmental Pollution*, 153, 273–283.
- Tam, N. F. Y., & Wong, Y. S. (2000). Spatial variation of heavy metals in surface sediments of Hong Kong mangrove swamps. *Environmental Pollution*, 110(2), 195–205.
- Tessier, A., Campbell, P.G.C. and Bisson, M. (1979). Sequential extraction procedure for the speciation of particulate trace metals. *Anal. Chem.*, 51: 844-851.
- Ure, A. M., Quevauviller, V., Muntau, H., & Griepink, B. (1993). Speciation of heavy metals in solids and harmonization of extraction techniques undertaken under the auspices of the BCR of the Commission of the European Communities. *International Journal of Environmental Analytical Chemistry*, 51, 135.
- Walker, C. H., Hopkin, S. P., Sibly, R.M., & Peakall, D. B. (2006). *Principles of ecotoxicology* (3rd edn). London: Taylor & Francis.
- Weisz, M., Polyák, K., and Hlavay, J., (2000). Fractionation of elements in sediment samples collected in rivers and harbors at Lake Balaton and its catchment area *Microchemical Journal*, 67, pp. 207-217.
- Weston, N.B., Joye, S.B., (2005). Temperature-driven decoupling of key phases of organic matter degradation in marine sediments: PNAS, 102, 17036–17040.
- Wu, J., Laird, D.A. and Thompson, M.L., (1999). Sorption and desorption of copper on soil clay components, *J. Envir. Qual.*, 28, pp. 334–338.
- Yu, K.C., Tsai, L. G., Chen, S. H., and Ho, S. T., (2001). Correlation analyses on binding behavior of heavy metals with sediment matrices. *Water Research*, 35, (10), pp. 2417 - 2428.
- Yuan C., Shi J., He B., Liu J., Liang L. and Jiang G. (2004). Speciation of Heavy Metals in Marine Sediments from the East China Sea by ICP-MS with Sequential Extraction. *Environmental International* 30: 769-783.