Mobility and risk assessment of heavy metals by sequential extraction in coastal sediment south Mediterranean Sea, Egypt

Maha Ahmed Mohamed Abdallah[1] · Adel Amer Mohamed[2]

Abstract

The chemical speciation of metals (Cd, Zn, Cu, and Fe) for coastal marine sediment samples collected from ten locations in the Western Harbour (main harbour) in Egypt and has been studied in two surveys which were determined using the four-step sequential extraction procedure. A sequential extraction technique was used to quantify exchangeable, oxides (reducible), organic/sulphidic, and acid-soluble (residual) fraction. It was noticed that Cd and Zn have the highest capability to be released from the sediment, more mobile and bioavailable, by the simple ion exchange mechanism in the W.H than Cu and Fe which were present at higher percentages in the acid-soluble fraction, meaning that these two metals were strongly bound to the sediments. Considering the percentage of metals extracted in the most labile fractions (F1 + F2 + F3), the order of mobility (from most to least bioavailable) was: Cd (94%) > Zn (64%) > Cu (22%) > Fe (3.5%). Risk assessment code (RAC) analysis indicated that the sediments show no risk for Fe and a low risk for Cu and low-to-medium risks for Zn and medium-to-high risks for Cd with RAC values greater than 11% and 30%, respectively, indicating a substantial risk of metal mobilization from sediments across the entire study region.

Keywords Sediment · Metals · Bioavailability · Risk assessment · Western Harbour · Egypt

1 Introduction

Heavy metal pollution is a widespread environmental problem due to the persistent and non-biodegradable properties of these contaminants [27]. Sediments are the largest reservoir and a major source of metals in the marine environment and play an important role in the transport and storage of potentially hazardous metals. The increase in the concentrations of metals, including those that are biologically essential, can exert toxic effects. Large amounts of metals waste are commonly generated from industrial processes and discharged into the environment. These anthropogenic metal discharges result from industrial activities such as plating, tanning, and corrosion inhibition [15]. It is now recognized that the determination of the total concentrations of metals in sediments is not sufficient to be able to predict the capacity

for mobilization of these elements. In addition, the determination of total element does not give accurate estimate of the likely environmental impact. The environmental behavior of heavy metals is decisively dependent on its chemical form, which influences mobility, bioavailability, and toxicity to organisms. Consequently, there is considerable interest in understanding the associations of these elements with the solid phase [18, 23]. Metal speciation occurring in the sediments is in turn expected to influence metal bioavailability, and thereby metal content in biota, in particular in the soft tissues of fish and mussels [26].

Heavy metal speciation in environmental media using sequential extraction techniques might provide much useful information regarding the chemical nature or potential mobility and bioavailability of a particular element, which consequently can offer a more realistic estimate of actual environmental impact. The principle of this procedure is based on the selective extraction of heavy metals in different physicochemical fractions of a material using specific solvents [25]. These procedures have been widely used for determining specific chemical forms of heavy metals in a range of environmental media, including sediments. Sediment samples are subjected to sequential extraction

✉ Maha Ahmed Mohamed Abdallah
   mahaahmed7@ymail.com

1 Marine Pollution Lab, National Institute of Oceanography and Fisheries, Alexandria, Egypt

2 Marine Chemistry Lab, National Institute of Oceanography and Fisheries, Suez, Egypt

using chemicals of decreasing pH and increasing oxidizing strength to remove the operationally defined host fractions corresponding to the exchangeable, carbonate, reducible, organic sulfide phases, and the residual phase. The potential ecological risk of each heavy metal in sediments is determined by its total content and speciation.

Harbours are key structures of great economic and social importance in coastal areas. In future decades, harbours are expected to grow in both number and size due to worldwide changes in business practices and the globalization of commerce [24]. These changes are likely to increase the adoption of procedures that maintain harbour functionality to become increasingly important in the management of coastal areas [5]. In this environment, heavy metals discharged from sources such as industrial and sewage effluents may accumulate in bottom sediment as the suspended particles on which they are adsorbed settle out [10]. Although the Western Harbour of Egypt (W.H) is economically one of the most important harbours on the Mediterranean Sea, it is one of the least studies. Being situated in a semitropical area and almost completely surrounded by land and artificial breakwaters. In addition to the aquatic inputs through several activities inside the Western Harbour and the land-based sources represented in Noubaria navigation canal, Mahmoudia canal, and some sewers, W.H is also exposed to atmospheric pollution from the same activities that cause aquatic pollution as several industries surrounding it. The pollutants from those different sources made the harbour become one of the most polluted coastal in Egypt [3, 4]. The objectives of this study were focused on the study of the concentration, distribution, and mobility of cadmium, zinc, copper, and iron in the surface sediments of the main harbour of Egypt (W.H) and to use this information to determine the main geochemical processes controlling the mobility of the studied metals within the harbour.

2 Materials and methods

2.1 Study area

The Western Harbour (W.H) of Egypt (Lat. 31°12′N, Long. 29°53′E) in Alexandria is the largest and oldest harbour on the Egyptian Mediterranean coast (Fig. 1); at present; it handles about 75% of the foreign trade of the country. It is a shallow, semi-elliptical, and semi-enclosed basin with an area of 31 km^2; in general, it is a shallow water body of about 7 m average depth.

However, a deeper basin is located in the outer part of the harbour (the main part of the harbour), where water depths of up to 20 m are observed and the predominant currents flow is anticlockwise. The harbour is connected to the open sea by a narrow mouth called "El Boughaz", which protects the bay from the prevailing NW winds and renders the harbour a safe anchorage.

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. The Western Harbour has received considerable amounts of treated and untreated industrial, agricultural, and domestic wastes [7]. Amounts of industrial wastes include a chlor-alkali plant and cement factories discharge unknown quantities of wastes indirectly into the harbour through the exchange between the W.H and El Mex Bay in addition to some tanneries. The Western Harbour also receiving external pollutants (agricultural wastes) from Omoum drain via El Mex Bay [1, 2]. Because the harbour is a semi-closed basin with restricted water circulation, it may serve as an entrapment of the wastes introduced from land-based sources as well as from the harbour itself due to shipping activities, these activities may also impact its ecological functioning.

2.2 Sampling and chemical analysis

Surface sediment samples (0–5 cm) were collected from ten sites representing all the W.H area from ten stations (Fig. 1). Samples were collected with a van Veen grab sampler and the upper 3–5 cm of sediment removed with a PTFE spatula. 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.

The dried sediment samples were subsequently ground in agate mortar, homogenized, and sieved. Cd, Zn, Cu, and Fe were fractionated from sediment samples using the sequential leaching technique modified by Prohić and Kniewald [17] from the original paper by Tessier et al. [21], to define the fractions of the trace metals [exchangeable, oxides (reducible), organic/sulphidic and acid-soluble (residual) fraction]. Metal concentrations in all extracts were analyzed by atomic absorption spectroscopy (Varian Techtron—Model 1250 spectrophotometer, equipped with a hydride vapor system). External standard solutions were prepared from 1000 mg l^{-1} stock metal solutions. The precision of the metal analysis is controlled by duplicate samples with the relative standard deviations of means of duplicate measurements less than 10%.

2.3 Statistical analysis

Statistical analysis one-way analysis of variance (ANOVA) and Duncan's test ($p = 0.05$) were used to access whether heavy metals concentrations varied significantly. All statistical calculations were performed using the SPSS 12 statistical software (IBM, Armonk, NY, USA). The standard

Fig. 1 Sampling location in the Western Harbour
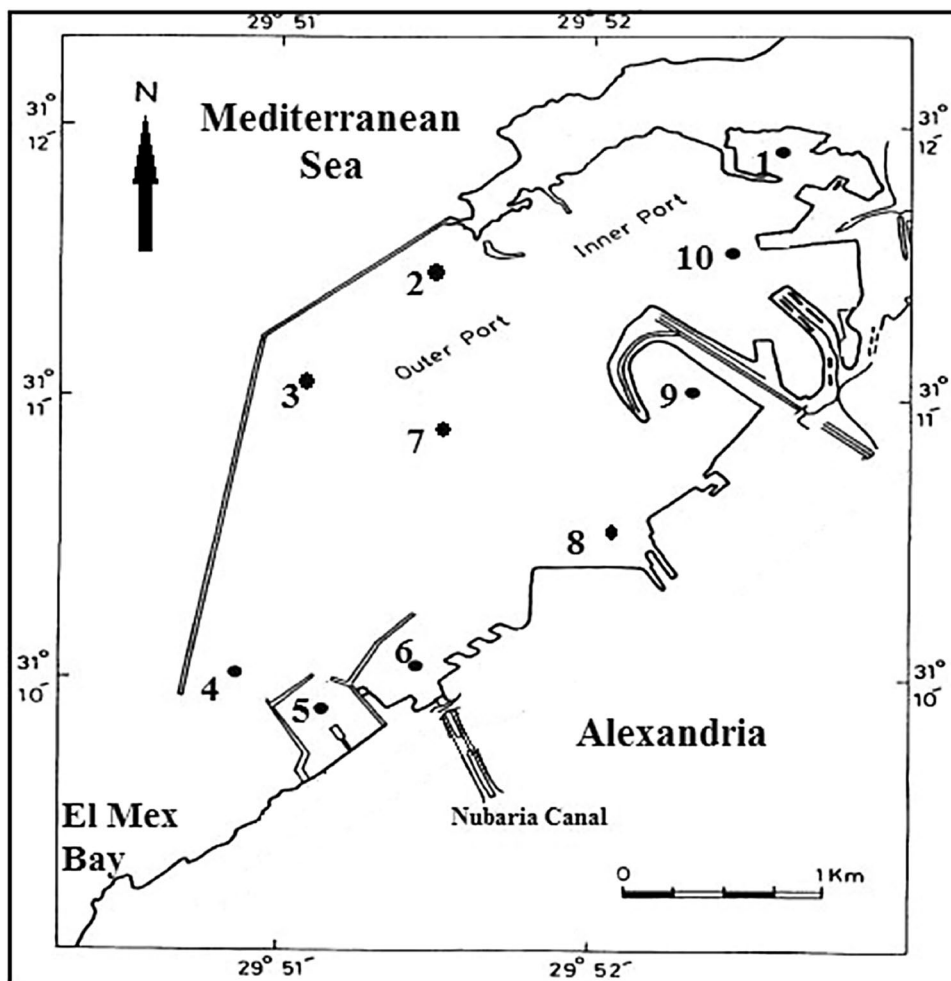
3 Results and discussion

Most of the harbour is between 5 and 20 m of depth. However, a deeper basin is located in the outer part of the harbour (the main part of the harbour), where water depths of up to 20 m are observed [3]. In the present study, the deepest station was station no. 7 (14.5 m) at the central part of the harbour (Table 1). On the other hand, the inner part is the less deep.

TOC plays an important role in controlling the availability of inorganic and organic contaminants and the toxicity of sediments [12].

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 [3]. TOC contents in the W.H ranged from 1.81 to 5.93%, the average TOC being

Table 1 Mean depth and total organic carbon (TOC) of studied metals in surface sediments from the W.H

Site	Depth (m)	%TOC
1	8.0	5.47
2	8.5	1.81
3	8.5	4.74
4	11.5	4.40
5	13.0	3.16
6	13.4	4.80
7	14.5	4.63
8	12.0	5.93
9	11.0	3.39
10	10.0	5.14
Mean	11.0	4.35

4.35% (Table 1). Total organic-carbon-rich sediments caver the entire harbour (inner part) basin (5.47 and 5.14%) were observed around the two sites (1 and 10) at the inner part of the harbour representing the Arsenal Quay (additional waste effluents from the shipyard situated on the W.H northern side) and the container Quay. In the same context, high TOC
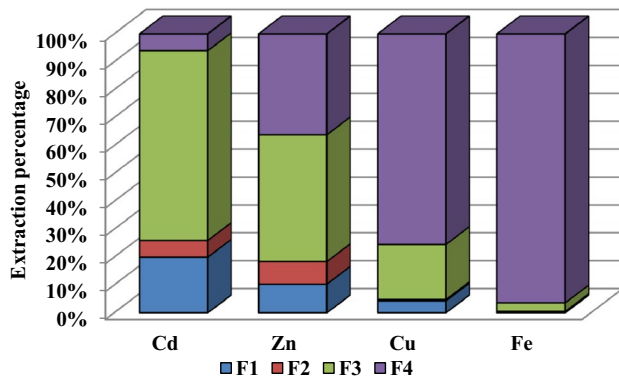
Fig. 2 Extraction percentage of Cd, Zn, Cu, and Fe in sampling sites in the Western Harbour sediments

value was observed at sampling site no.8, closed to the ships moorage area, due to anoxic conditions occurred in sediments. Whereas sediments of low organic-carbon content (range 1.81–4.8%) cover the harbour's surroundings.

3.1 Speciation and mobility of trace metals in the sediment fractions

The extractable contents and the percentages of the studied metals with respect to the sums of four fractions in the marine sediments from each extraction step are shown in Tables 2, 3, 4, and 5, and can be seen in Fig. 2, which illustrates the results as percentages of metal extracted in each fraction, for the ten sediment samples. Cd was present at higher percentages in the oxidizable-organic fraction (labile fraction) in the study area, and reflecting Cd more mobile and potentially more bioavailable in sediments from W.H. The non-residual fractions (exchangeable + acid-reducible + oxidizable) of Cd in sediments were great (94%) (Fig. 2). However, Cd was hardly detected in the reducible

fraction, inferring that Cd bound to Fe and Mn oxides in the study area was very low. The dominant proportion of Cd was found in the oxidizable fraction (68%) in the W.H sediment, likely due to the higher content of organic matter and sulfides which are substances that can be easily oxidized. These results are consistent with the findings from Barcelona, Spain [8] and from Kranji, Singapore [22]. Therefore, Cd was potentially more available for release into the marine environment.

In the same context, about 64% of the total Zn content from the W.H sediments was in the non-residual fractions, indicating that under changing environmental conditions, Zn is potentially more available. The highest value for Zn was observed in the oxidizable fraction (Fig. 2) and this may result from the input of organic matter from the anthropogenic discharges from land-based sources, also reflects the special environmental conditions in the Western Harbour, resulting from pollution effects and intense navigation. The variation in the concentration of metals may be due to differences in the sources and prevailing physico chemical conditions and complex reactions such as adsorption, flocculation, and redox condition taking place in the sediments.

Under varied reduction conditions, the release of Cd, Zn, and Cu from the sediment is expected. This is in contrast to Zn which precipitates with sulfide, absorbed on the organic matter, and appears to be stable under the anaerobic conditions.

On the other hand, about 24.5% of the total Cu content from the W.H sediments was in the non-residual fractions, indicating that Cu is potentially non-bioavailable. It was mainly found in the residual fraction (74.5%, Fig. 2). Significant correlation between Cu and organic carbon (0.81, $\rho \leq 0.05$) was recorded, and this means that residual Cu increases with the increase of detrital materials as the W.H receiving detrital materials from Mahmoudia and Noubaria canals, suggesting relatively low mobility of this element

Table 2 Distribution of cadmium in sediment fractions ($\mu g\ g^{-1}$)

Sample	Total Cd	Exchangeable F1		Acid-reducible F2		Oxidizable-organic F3		Residual F4		$\Sigma F1 + F2 + F3$ (%)
		Conc.	%	Conc.	%	Conc.	%	Conc.	%	
1	1.956	0.800	41	0.006	8	0.891	46	0.114	6	94.19
2	1.006	0.139	14	0.006	27	0.562	56	0.038	4	96.23
3	1.254	0.121	10	0.006	1	1.061	85	0.061	5	95.17
4	1.513	0.115	8	0.006	12	1.029	68	0.182	12	87.99
5	1.080	0.121	11	0.006	4	0.901	83	0.015	1	98.60
6	0.724	0.055	8	0.006	3	0.615	85	0.030	4	95.82
7	0.788	0.121	15	0.006	2	0.594	75	0.061	8	92.31
8	1.033	0.218	21	0.006	2	0.700	68	0.091	9	91.20
9	0.736	0.267	36	0.006	4	0.424	58	0.015	2	97.94
10	1.039	0.345	33	0.006	1	0.604	58	0.083	8	91.98
Mean	1.113	0.230		0.076		0.738		0.069		94.14

Table 3 Distribution of zinc in sediment fractions (µg g^{-1})

Sample	Total Zn	Exchangeable F1		Acid-reducible F2		Oxidizable-organic F3		Residual F4		ΣF1 + F2 + F3 (%)
		Conc.	%	Conc.	%	Conc.	%	Conc.	%	
1	168.04	22.03	13.1	15.64	9.3	74.57	44.4	55.80	33.2	66.8
2	62.66	7.45	11.9	5.71	9.1	28.62	45.7	20.88	33.3	66.7
3	107.48	8.51	7.9	6.31	5.9	52.99	49.3	39.67	36.9	63.1
4	115.72	9.51	8.2	7.27	6.3	54.03	46.7	44.91	38.8	61.2
5	96.80	6.99	7.2	8.85	9.1	48.05	49.6	32.91	34.0	66.0
6	140.48	12.75	9.1	10.62	7.6	64.24	45.7	52.87	37.6	62.4
7	132.41	11.74	8.9	10.00	7.6	57.61	43.5	53.06	40.1	59.9
8	154.24	13.89	9.0	11.91	7.7	67.29	43.6	61.15	39.6	60.4
9	106.30	12.33	11.6	9.53	9.0	43.47	40.9	40.97	38.5	61.5
10	160.92	26.63	16.5	15.64	9.7	71.91	44.7	46.74	29.0	71.0
Mean	124.51	13.18		10.15		56.28		44.90		64

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

Sample	Total Cu	Exchangeable F1		Acid-reducible F2		Oxidizable-organic F3		Residual F4		ΣF1 + F2 + F3 (%)
		Conc.	%	Conc.	%	Conc.	%	Conc.	%	
1	395.14	13.28	3.36	1.67	0.42	91.06	23.04	289.13	73.17	106.01
2	109.92	11.12	10.12	1.67	1.52	41.85	38.07	55.28	50.29	54.64
3	190.86	7.97	4.18	1.41	0.74	56.43	29.57	125.05	65.52	65.81
4	267.00	10.55	3.95	0.04	0.01	48.56	18.19	207.85	77.85	59.15
5	162.94	7.03	4.31	0.00	0.00	62.19	38.17	93.72	57.52	69.22
6	388.13	7.9	2.04	0.16	0.04	55.18	14.22	324.89	83.71	63.24
7	279.02	8.13	2.91	1.5	0.54	5.33	1.91	264.06	94.64	14.96
8	286.56	6.24	2.18	4.08	1.42	5.64	1.97	270.6	94.43	15.96
9	167.21	6.57	3.93	0.00	0.00	4.27	2.55	156.37	93.52	10.84
10	328.39	18.62	5.67	0.32	0.10	98.92	30.12	210.53	64.11	117.86
Mean	257.52	9.74	4.3	1.09	0.48	46.94	19.78	199.75	75.5	57.77

Table 5 Distribution of iron in sediment fractions (µg g^{-1})

Sample	Total Fe	Exchangeable F1		Acid-reducible F2		Oxidizable-organic F3		Residual F4		ΣF1 + F2 + F3 (%)
		Conc.	%	Conc.	%	Conc.	%	Conc.	%	
1	5483.05	0.08	0.001	26.43	0.482	121.73	2.22	5334.81	97.30	2.7
2	4571.48	0.11	0.002	24.00	0.525	89.95	1.97	4457.43	97.51	2.5
3	4899.95	0.12	0.002	28.70	0.586	161.17	3.29	4709.96	96.12	3.9
4	5222.48	0.11	0.002	21.40	0.410	111.80	2.14	5089.17	97.45	2.6
5	4778.57	0.14	0.003	27.89	0.584	154.07	3.22	4596.47	96.19	3.8
6	5569.89	0.06	0.001	25.78	0.463	116.62	2.09	5427.43	97.44	2.6
7	5486.29	0.12	0.002	27.89	0.508	242.03	4.41	5216.25	95.08	4.9
8	5755.73	0.12	0.002	27.73	0.482	320.92	5.58	5406.96	93.94	6.1
9	5260.45	0.14	0.003	21.73	0.413	229.27	4.36	5009.32	95.23	4.8
10	5209.90	0.09	0.002	5.67	0.109	77.46	1.49	5126.66	98.40	1.6
Mean	5223.78	0.11	0.002	23.72		162.50		5037.45		3.5

Table 6 Mobility of studied metals in different forms of the W.H sediments

Step	Fraction	Mobility
1	Ion exchange	Cd > Zn > Cu > Fe
2	Oxides (reducible)	Zn > Cd > Fe ≥ Cu
3	Organic/sulphidic	Cd > Zn > Cu > Fe
4	Acid soluble (residual)	Fe > Cu > Zn > Cd

in the sediment. Much fewer amounts of this metal were bound to organic matter, F3, in the sediments as far as Cu is concerned (20%) followed by the exchangeable fraction (4%) and the oxides' (reducible) fraction (0.5%) (Fig. 2). Copper shows a relatively presence in forms bound to organic matter and sulfides, because it is a chalcophilic element, and it is mainly bound to sulfides in nature. Cu geomobility in sediments of the considered systems is probably controlled by its initial forms in the land sources. In the W.H sediments, the distributions of copper forms among particular fractions were similar in sediments from Los Angeles harbour, Western Gulf of California and Marine sediments from the front of the Ob and Yenisei estuaries by Gupta and Chen [9], Shumilin et al. [19] and Demina et al. [6], respectively.

Negligible percentages of Fe were extracted as the exchangeable and acid-reducible fractions (less than 1% of the extracted Fe, also reported by Tüzen [23]). The highest percentage of Fe was found in the residual fraction (96% of the total Fe), indicating that Fe was strongly bound to sediments. Thence, most of the Fe is present in the residual fraction, followed by the oxidizable fraction, at values of 3.1%. Iron was mostly concentrated in the acid-soluble fraction, F4, in sediments, as crystalline Fe oxides are dissolved by acid (Fig. 2). Indicating that Fe originates from geochemical background rather than anthropogenic source, which means that it is less available to the aquatic fauna and has less chances of entering into the human food chain.

The spatial distribution of the total concentrations of studied metals in the W.H shows that station No. 1 was the most concentrated in all the studied elements. The distribution of cadmium represents the highest concentration in station No. 1 followed by station No. 4, which represents the entrance of the harbour water, and its load of polluted water from El Mex Bay. For zinc, stations Nos. 1 and 10 (inner part of the harbour), represents the highest concentration the same as the copper distribution. In addition, station No. 6 at the mouth of El Mahmoudia canal in the harbour (mainly agricultural wastes) recorded a high concentration of copper.

The mobility and immobility and thus toxicity of heavy metals in waste depend largely on their type of binding forms. It was noticed that Cd and Zn have the highest capability to be released from the sediment by the simple ion

exchange mechanism (Table 6). It is seen that the chloride content in the leachate can bind with Cd and Zn and enhance its mobility in the solid waste [11]. Under varied reduction conditions, the release of Cd and Zn from the sediment is expected. This is in contrast to Zn behavior which precipitates with sulfide, absorbed on the organic matter, and appears to be stable under the anaerobic conditions [13].

The calculated factors in W.H sediments show the highest ability of Cd and Zn to be released from the sediments, whereas Fe and Cu have the lowest. The residual concentration of any heavy metal is considered non-mobile fraction and is an important part influencing the mobility nature of the heavy metal. The combined effect of Cd and Zn in high concentration and with high mobility potential shows the increased possible risk of these metals to the W.H environment. In environmental studies, the determination of the different ways of binding gives more information on trace metal mobility, as well as on their availability or toxicity, in comparison with the total element content.

3.2 Identification of natural and anthropogenic sources

According to heavy anthropogenic inputs in normal regions, trace metals have been found in the first three extraction fractions (soluble in acid, associated with Fe and Mn oxides, and associated with organic matter and sulfides) [14], indicating that the sediments were polluted. The relative concentrations of trace metals in the different fractions are probably reflective of different origins of pollution, i.e., when the metals show an affinity for carbonate, they are weakly associated with sediments and have experienced more recent pollution. In regions, where metals are significantly associated with the oxidizable or reducible sediment, fractions are influenced by pollution that is less recent. Considering the percentage of metals extracted in the most labile fractions (F1 + F2 + F3),
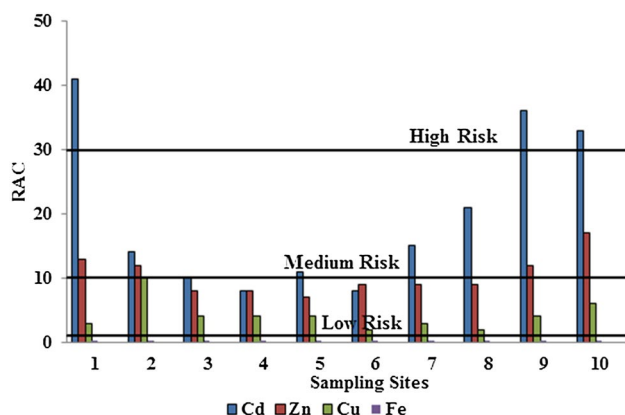
the order of mobility (from most to least bioavailable) was: Cd (94%) > Zn (64%) > Cu (22%) > Fe (3.5%) (Tables 2, 3, 4, 5). Cd showed the greatest amount in the bioavailable fractions, while Fe showed lower percentages in the labile fractions. Indicating that Fe originates from geochemical background rather than anthropogenic source.

3.3 Assessment of sediment contamination

According to the fractionation studies, the metals in the sediments are bound to different fractions with different strengths. The strength values can, therefore, give indication of sediment reactivity, which in turn assess the risk which connected with the presence of these metals in the aquatic environment. The risk assessment code (RAC), indicates that sediment which can release in exchangeable and carbonate fractions, less than 1% of the total metal will be considered safe for the benthic organisms. On the contrary,
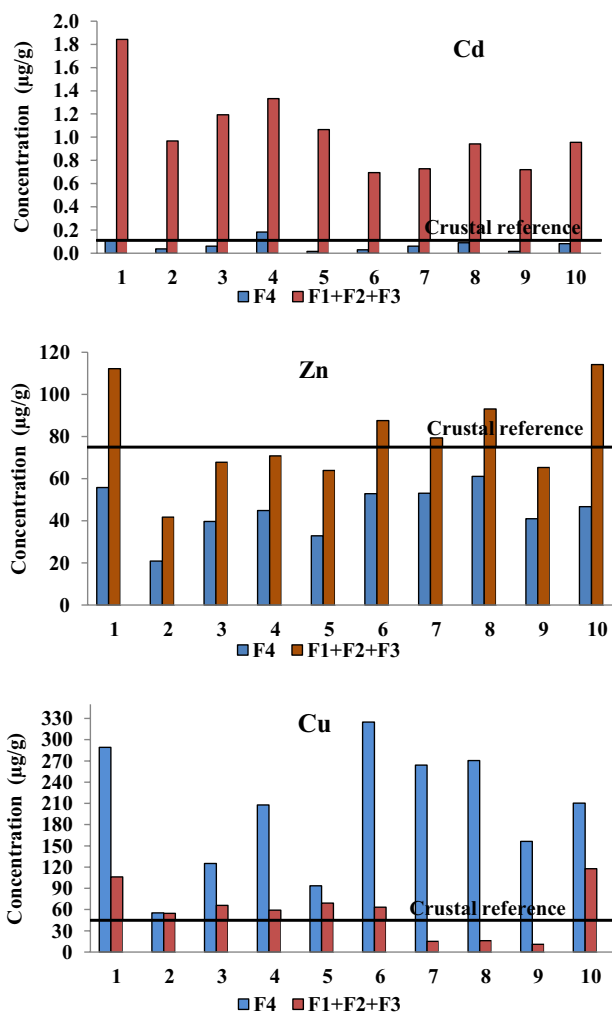
Fig. 4 Bioavailable fractions of Cd, Zn, and Cu in comparing with the background concentrations

Fig. 3 Risk assessment code (RAC) for the studied metals in W.H surface sediments

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, and this classification is described by Perin et al. [16]. Figure 3 illustrates the results of the risk factor analysis, with values given as percentages of the exchangeable and carbonate fraction (% F1) for the studied trace metals. In general, the sediments show no risk for Fe and a low risk for Cu and low-to-medium risks for Zn and medium-to-high risks for Cd with RAC values greater than 11% and 30%, respectively, indicating a substantial risk of metal mobilization from sediments across the entire study region. Zinc showed low-to-medium risk (RAC > 11%) in sediments from sites 1, 2, 9, and 10. While Cd shows high risk (RAC > 30%) in sediments from the same sites except stations 2 that showed medium risk. Therefore, Cd comes under the high-risk category and can easily enter the food chain because of the toxicity and availability of cadmium; it can pose serious problems to the ecosystem.

Average crustal abundance [20] is commonly used to provide elemental background concentration, in this study; Taylor's crustal abundance was used as reference baselines. The concentrations of Cd in the bioavailable or labile fractions, for all stations, were greater than the background concentrations, whereas the concentration of Cd in residual fraction for all stations except station no. 4 was below the reference level (Fig. 4). In the same context, the labile fractions of Zn, for most stations, were greater than the background concentrations, whereas the concentration of Zn in residual fraction for all stations was below the reference level (Fig. 4). Most of the bioavailable or labile fractions of Cu were above the reference level as well as all the residual fractions for all stations were above the reference level.

In general, the higher percentage of Cd and Zn in the nonresistant fractions (bioavailable) may be related to different types of organic matter discharged from direct influx of insufficiently treated industrial wastes directly or indirectly to the harbour, as has been reported in other studies [3, 7] stated that nonresistant steps are closely related to the anthropogenic origin.

4 Conclusion

The sequential extraction technique was applied to identify the amount of anthropogenic metals in contrast to natural origin and also to provide information on the mobility, bioavailability, and potential toxicity of trace metals in the environment. The chemical speciation of Cd, Zn, Cu, and Fe in majority of stations was in the order of oxidizable-organic > exchangeable > oxide-reducible > residual for Cd, oxidizable-organic > residual > exchangeable > acid-reducible for Zn, residual > oxidizable-organic > exchangeable > oxide-reducible for Cu, and residual > oxidizable-organic > oxide-reducible > exchangeable for Fe.

The calculated factors in W.H sediments show the highest ability of Cd and Zn to be released from the sediments, whereas Fe and Cu have the lowest. The residual concentration of any heavy metal is considered non-mobile fraction and is an important part influencing the mobility nature of the heavy metal. The combined effect of Cd and Zn in high concentration and with high mobility potential shows the increased possible risk of these metals to the W.H environment. It determined that Cd and Zn in W.H coastal surface sediments existed in the nonresistant fractions, while Cu and Fe existed in the resistant fractions (sedimentary matrix). It, therefore, showed that lithogenic discharge of Cd and Zn is greater than Cu and Fe. The mean bioavailable and mobile fraction (exchangeable and oxidizable-organic) concentrations of Cd and Zn were more than the rest of the fractions, since these fractions have adverse effect on the aquatic environment in contrast to other fractions. It, therefore, reflected the high and continuous discharge or sufficient time for redistribution of both Cd and Zn in the W.H surface sediments. Risk assessment code (RAC) values were reflective of average risks to the environment for the studied metals in most samples. In general, the sediments show no risk for Fe and a low risk for Cu and low-to-medium risks for Zn and medium-to-high risk for Cd with RAC values greater than 11% and 30%, respectively, indicating a substantial risk of metal mobilization from sediments across the entire study region. Therefore, Cd comes under the high-risk category and can easily enter the food chain because of the toxicity and availability of cadmium; it can pose serious problems to the ecosystem.

References

1. M.A.M. Abdallah, Trace metal behavior in Mediterranean-climate coastal bay: El-Mex Bay, Egypt and its coastal environment. Glob J Environ Res **2**(1), 23–29 (2008)
2. M.A.M. Abdallah, N.B. El Sayed, M.A. Saad, Distribution and enrichment evaluation of heavy metals in El-Mex Bay using normalization models. Fresenius Environ. Bull. **16**(7), 710–719 (2007)
3. M.A.M. Abdallah, Chromium geochemistry in coastal environment of the Western Harbor, Egypt: water column, suspended matter and sediments. J. Coast. Conserv. Plan. Manag. **18**, 1–10 (2014)
4. M.A.M. Abdallah, Speciation of trace metals in coastal sediments of El-Mex bay south Mediterranean Sea–West of Alexandria (Egypt). Environ Monit Assess **132**, 111–123 (2007)

5. G. Bortone, E. Arevalo, I. Deibel, Sediment and dredged material treatment. J Soil Sediments **4**, 225–232 (2004)

6. L.L. Demina, M.A. Levitan, N.,V. Politova, Speciation of some heavy metals in bottom sediments of the Ob and Yenisei estuarine zones. Geochem. Int. **44**, 182–195 (2006)

7. M.K. El-Sayed, S.K. El-Wakeel, A.E. Refaat, Factor analysis of sediments in the Alexandria western Harbor, Egypt. Oceanol. Acta **11**, 1–11 (1988)

8. A. Guevara-Riba, A. Sahuquillo, R. Rubio, G. Rauret, Assessment of metal mobility in dredged harbour sediments from Barcelona, Spain. Sci. Total Environ. **321**, 241–255 (2004)

9. S.K. Gupta, K.Y. Chen, Partitioning of trace metals in selective chemical fractions of nearshore sediments. Environ. Lett. **10**, 129–158 (1975)

10. C.A. Huh, B.P. Finney, J.K. Stull, Anthropogenic inputs of several heavy metals to nearshore basins off Los Angeles. Prog Oceanogr **30**, 335–351 (1992)

11. P. Kjeldsen, M.A. Barlaz, A.P. Rooker, A. Baun, A. Ledin, T.H. Christensen, Present and long-term composition, of MSW landfill leachate: a review. Crit. Rev. Environ. Sci. Technol. **32**, 297–336 (2002)

12. A. McGrath, P.R. Paquin, D.M. Di Toro, Use of the SEM and AVS approach in predicting metal toxicity in sediments. Fact Sheet Environ. Risk Assess. **10**, 1–6 (2002)

13. K. Nemati, N.K. Abu Bakar, M.R. Abas, Investigation of heavy metals mobility in shrimp aquaculture sludge—comparison of two sequential extraction procedures. Microchem. J. **91**, 227–231 (2009)

14. E.A. Passos, J.C. Alves, I.S. Dos Santos, J.H. Alves, C.B. Garcia, A.C.S. Costa, Assessment of trace metals contamination in estuarine sediments using a sequential extraction technique and principal component analysis. Microchem. J. **96**, 50 (2010)

15. P. Pazos-Capeáns, M.C. Barciela-Alonso, P. Herbello-Hermelo, P. Bermejo-Barrera, Estuarine increase of chromium surface sediments: distribution, transport and time evolution. Microchem. J. **96**, 362–370 (2010)

16. G. Perin, L. Craboledda, M. Lucchese, R. Cirillo, L. Dotta, M.L. Zanette, A.A. Orio, Heavy metal speciation in the sediments of Northern Adriatic sea—a new approach for environmental toxicity determination, in *Heavy Metal in the Environment*, vol 2, ed. by T.D. Lekkas (1985), pp. 454–466

17. E. Prohić, G. Kniewald, Heavy metal distribution in recent sediments of the Krka river estuary—an example of sequential extraction analysis. Mar. Chem. **22**, 279–297 (1987)

18. G. Rauret, Extraction procedures for the determination of heavy metals in contaminated soil and sediment. Talanta **46**, 449–455 (1998)

19. E. Shumilin, V. Gordeev, G. Rodr, G. Figueroa, L. Demina, K. Choumiline, Assessment of geochemical mobility of metals in surface sediments of the Santa Rosalia mining region, Western Gulf of California. Arch. Environ. Contam. Toxicol. **60**, 8–25 (2011)

20. S.R. Taylor, Abundance of chemical elements in the continental crust: a new table, Geochim. Cosmochim. Acta **28**, 1273–1285 (1972)

21. A. Tessier, P.G.C. Campbell, M. Bisson, Sequential extraction procedure for the speciation of particulate trace metals. Anal. Chem. **51**, 844–851 (1979)

22. D. The Cuong, J.P. Obbard, Metal speciation in coastal marine sediments from Singapore using a modified BCR-sequential extraction procedure. Appl. Geochem. **21**, 1335–1346 (2006)

23. M. Tüzen, Determination of trace metals in the River Yesilirmak sediments in Tokat, Turkey using sequential extraction procedure. Microchem. J. **74**, 105–110 (2003)

24. UN ESCAP, Commercial development of regional ports as logistics centres, transport and tourism division (TTD), in *ST/ESCAP/2194*, (United Nations, New York, 2002)

25. Z. Yang, Y. Wang, Z. Shen, J. Niu, Z. Tang, Distribution and speciation of heavy metals in sediments, from the mainstream, tributaries, and lakes of the Yangtze River catchment of Wuhan, China. J. Hazard. Mater. 166: 1186–1194 (2009)

26. C.K. Yap, A. Ismail, S.G. Tan, H. Omar, Correlation between speciation of Cd, Cu, Pb and Zn in sediments and their concentrations in total soft tissue of green-lipped mussel *Perna viridis* from the west coast of Peninsular Malaysia. Environ. Int. **28**, 117–126 (2002)

27. C. Yuan, J. Shi, B. He, J. Liu, L. Liang, G. Jiang, Speciation of heavy metals in marine sediments from the East China Sea by ICP-MS with sequential extraction. Environ. Int. **30**, 769–783 (2004)