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ORIGINAL RESEARCH ARTICLE

Geochemical fractionation of heavy metals in sediments of the Red Sea, Saudi Arabia

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Summary   The geochemical fractionation of heavy metals, including Mn, Fe, Cu, Pb, Zn, Cd and Ni, collected from the surface sediments of the Jeddah coastal zone of the Red Sea in Saudi Arabia was determined using a sequential extraction technique. The data obtained from the five fractions indicated that the concentration of metals varies among different locations in the study area. The total metal concentrations (%) in the exchangeable (F_1), carbonate (F_2), reducible (F_3) and organic-bound (F_4) fractions were measured to determine the mobility of each studied metal. The sum of the two fractions F_3 and F_4 represented 70% of the Cu, 72% of the Zn and 36% of the Pb. However, the sum of the three fractions F_2, F_3 and F_4 represented 76%, 74%, 68% and 58% of the Cd, Ni, Fe and Mn, respectively. Approximately 46% of the total copper was related to organics, which could reflect a high mobility of copper in these sediments. The maximum mobility of metals in the sediments was confirmed by the bioavailability factor (BF), which was within the ranges of 0.47—0.93, 0.34—0.92, 0.62—0.95, 0.69—0.95, 0.24—0.82, 0.54—0.98, and 0.60—0.95 for Fe, Mn, Cu, Zn, Pb, Cd, and Ni, respectively. Based on the BF, the metals exhibited the following order: $Cu \approx Zn > Cd \approx Ni \approx Fe > Mn > Pb$. The high levels of BF for the studied metals could reflect the potential for toxic metals to be easily released into the marine environment. The risk assessment code for Cd showed a medium risk in five sediment samples of the northern and southern regions and a high risk to the aquatic environment in the other sediment samples. However, the speciation of Fe, Mn, Cu, Zn, Pb and Ni in the studied sediments exhibited low to medium risks to the aquatic environment.

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1. Introduction

Sediments consist of organic and inorganic detrital grains with heterogeneous physical, chemical and biological characteristics (Hakanson, 1992). Sediments are rich in trace metals, which occur in various chemical forms with different mobilities, bioavailabilities, chemical interactions and potential toxicities (El Zokm et al., 2015; Masoud et al., 2010; Okbah et al., 2005). The presence of trace elements in sediments was studied by Tessier et al. (1979) to understand the chemical forms of metals present in the environment. Such research is performed because the chemical forms of metals play a certain role in the mobility of metals at the sediment/water interface and their subsequent transfer to the food chain (Rattan et al., 2005). Therefore, the fate of such trace metals should be investigated to understand their effects on surrounding organisms and what risks they could pose. Metals in sediments can occur in five categories: soluble and exchangeable; carbonates; reducible forms (Fe and Mn oxides); organics and sulfides; and silicates and detrital materials. This diversity is because metals can have different remobilization conditions under changing environments, consequently affecting their bioavailability and solubility. The determination of the total content of trace metals is not enough to evaluate their impact on the environment. Thus, the identification of geochemical forms of trace metals is necessary to understand the mobilization capacity of the metals and their impact on the surrounding environment (Li et al., 2000).

The catchment area of the Red Sea consists of sedimentary, granitic and metamorphic rocks that are weathered and eroded by the Red Sea (coastal) waters via wind and seasonal floods. These natural conditions have been altered due to increased human activities in Red Sea coastal areas (Moufaddal, 2002). These activities are the most frequent on Jeddah City's coast and include refilling, dredging, waste discharge, fishing, and oil spills. Some sites in Jeddah have been investigated over the last few years to study the anthropogenic impacts and effects of pollution on the environmental conditions of lagoons and shorelines (Abu-Zied et al., 2013, 2016; Abu-Zied and Hariri, 2016; Al-Mur et al., 2017; Youssef et al., 2015).

The main objective of this study is to investigate the speciation of trace metals, such as Fe, Mn, Cu, Zn, Pb, Cd and Ni, using sediments from the coast of Jeddah to provide a better understanding regarding their mobility and bioavailability and to conduct an environmental risk assessment.

2. Material and methods

2.1. Sample location

Samples were collected at point-source areas impacted by anthropogenic activities based on field surveys and observations. These impacted areas included the Salman Gulf, Downtown, and Al-Khumrah. The study area was divided into three zones: the north zone is represented by five stations (I, II, III, IV and V), the middle zone is represented by two stations (VI and VII) and the south zone is represented by stations VIII, IX, X, XI and XII (Fig. 1). Fine and coarse sand composed the major fraction of the studied sediments.
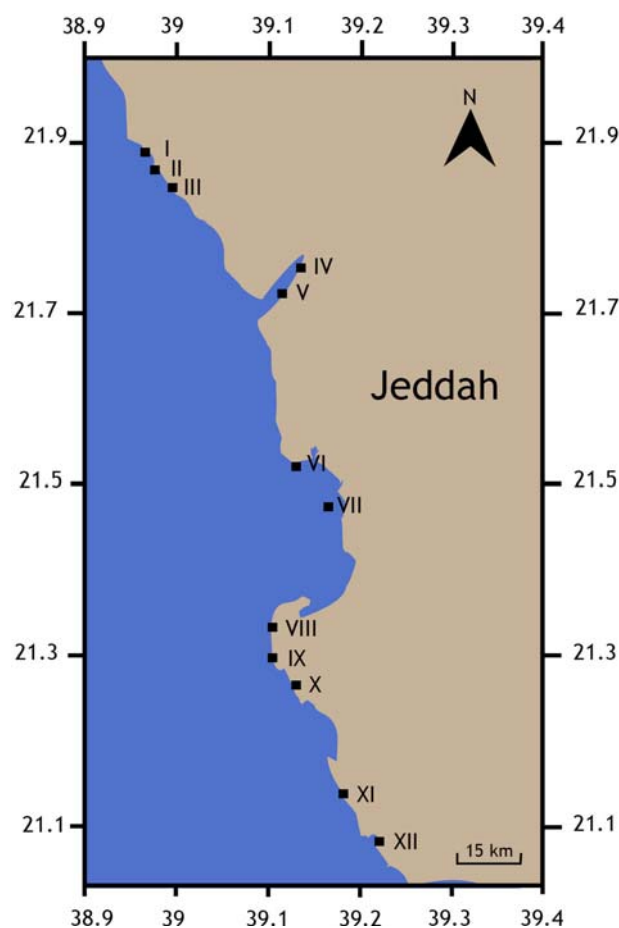

Figure 1   Location of sampling points of the coastal area of Jeddah, Red Sea.

2.2. Sample collection and preservation

Surface marine sediment samples (250 g, 7 cm from the surface) were collected using a plastic spatula to prevent any cross contamination. At each station, 3 sediment samples were collected using a grab sampler, immediately inserted into polyethylene bags and stored in an ice box until they could be transported to the lab. In the laboratory, all samples were kept cool at 4°C until analysis occurred. Before metal analysis, all sediment samples were homogenized and ground.

2.3. Geochemical analysis

Granulometric analysis of the sediment was performed by sieving techniques (Folk, 1974). The analysis was only performed on the finest sediments, which were separated using a sieving process. The majority of the sediment was the coarse sandy/gravel fraction, and we only focused on the fine fraction. In the first step, the foreign components and gravel were removed from the sediment samples through a 125 μm sieve. The remaining fraction was then ground and sieved through a 63 μm sieve. This fine fraction was then divided into four parts: 1. Part used for total organic carbon determination. 2. Part used to determine calcium carbonate (%).

3. Part used for the analysis of total metal concentration.
4. Part used to determine the different species of heavy metals (fractionation of heavy metals).

The TOC was measured using the procedure of Gaudette and Flight (1974). In this method, the powdered sediment sample was exothermically heated and oxidized with concentrated sulfuric acid (H_2SO_4) and potassium dichromate ($K_2Cr_2O_7$). The sample solution was titrated to remove excess dichromate using ferrous ammonium sulfate solution and the indicator diphenylamine. Then, the organic carbon values were converted to organic matter by multiplying the resulting values by 1.8.

Total carbonates were determined following the procedures described in Molina (1974). In the present study, $CaCO_3$ was determined by the dissolution of carbonate in an excess of 0.5 N HCl and titration of the remaining acid with 0.25 N NaOH (Rowell, 1994). This process involved two-phase analysis:

One gram (accurately weighed) of dried sediment sample was mixed with a known amount of hydrochloric acid (0.5 N HCl) in a conical flask and swirled slowly after the addition of the acid. The total $CaCO_3$ (%) was calculated by the following equation:

$$CaCO_3\% = 100 \times 0.05 \times [(N_{HCl} \times V_{HCl}) - (N_{NaOH} \times V_{NaOH})],$$

where N_{HCl} is the normality of standardized HCl, V_{HCl} the volume of standardized HCl, N_{NaOH} the normality of standardized NaOH and V_{NaOH} the volume of standardized NaOH.

The total concentration of heavy metals was determined according to Oregioni and Aston (1984). An accurately weighed 0.3 g sediment sample was completely digested in a cleaned and dried Teflon beaker at 80°C using a mixture of acids (in mL; HNO_3:$HClO_4$:HF; 3:2:1 v/v). The remaining supernatant for each sample was used to measure the total metal concentration using an inductively coupled plasma-optical emission spectrometer (Agilent ICP-OES 5100 VDV). The absorption wavelengths (in nm) were 259.943, 257.610, 213.857, 324.757, 220.356, 226.502 and 231.604. The operating parameters of the system were as follows: power 1.2 kW, plasma gas flow 12 L/min, auxiliary gas flow 1.0 L/min, nebulizer flow 0.7 L/min, and pump rate 15 rpm.

Working standard solutions of heavy metals were prepared with standards obtained from Fluka Analytical, St. Galen, Switzerland, with 1% HNO_3. Seven calibration standards, including a blank and concentrations ranging from 5—100 μg L^{-1}, were measured three times. HNO_3 was used as a blank, and all the analyses were performed in triplicate. The total metal concentration was calculated by the following formula:

$$C = Cs \times \left(\frac{V}{Wt}\right),$$

where C is the concentration of sediment sample in μg g^{-1}, Cs is the liquid supernatant concentration (ICP reported) in μg L^{-1}, V is the volume (mL) of acid used to dissolve the sediment sample and Wt is the weight (g) of the sediment sample. For each individual sample, triplicate measurements were recorded by the ICP-OES.

2.4. Sequential extraction procedure

Sequential extraction of the metals Fe, Mn, Cu, Zn, Pb, Cd and Ni was carried out based on the methodology of Tessier et al. (1979). This method was used because such metals can be remobilized into/out of sediments based on the surrounding solution characteristics, such as the formation of complexes, ionic strength, acidity and redox potential. In this study, the methodology used to obtain the five metal fractions was as follows:

The exchangeable and acid-soluble fraction (F_1) was obtained by adding 10 mL of 1 M sodium acetate solution (pH 8.2) into one gram of sediment sample and shaking the mixture in a mechanical shaker at 250 rpm at room temperature for 1 h. Then, after centrifugation at 7000 rpm for 20 min, the extract was placed in a polyethylene bottle and stored at 4°C until further analysis. After that, the residue was shaken for 20 min in 10 mL of deionized water, and then the supernatant was discarded.

The carbonate-bound fraction (F_2) was extracted by adding a sodium acetate solution (pH 5.0) to the residual from the first step. At room temperature, the mixture was shaken (250 rpm) for 1 h.

The reducible fraction (F_3), which was bound to iron-manganese oxides, was obtained by adding 0.05 M hydroxylamine HCl in 25% (v/v) acetic acid to the residue from the 2nd step. The mixture was agitated for 6 h at 70°C. The F_3 fraction was separated, and the residue was washed after completion of the first step.

The sulfide and organic-bound fraction (F_4) were obtained from the residual of the F_3 fraction. In this step, 3 mL of 0.02 M HNO_3 and 5 mL of 30% H_2O_2 were added to the residue, the pH was adjusted to 2 by HNO_3, and the mixture was heated at 85°C for 2 h. After that, 3 mL of 30% H_2O_2 was added, and heating continued for 3 h. The solution was then cooled, and 5 mL of NH_4OAC was added. Then, the extraction of F_4 and residue washing were carried out as performed in the first step.

The residual fraction (F_5) was obtained by complete digestion of 0.2 g of the residue left from step F_4 in a mixture of HNO_3, $HClO_4$ and HF (3:2:1 v/v). Then, the metal concentrations (μg g^{-1}) in this solution and in all other extracts and the total metal concentration were measured using inductively coupled plasma spectrophotometry.

The % recovery of trace metals in the five extracts/fractions, including the residual fraction, was determined using the following equation from Ahmadipour et al. (2014):

$$Recovery \% = \left\{\sum \frac{(Exch. + Carb. + Red. + Org. + Resi.)}{TM}\right\} \times 100,$$

where Exch. = exchangeable, Carb. = carbonate, Red. = reducible, Org. = oxidizable organic, Resi. = residual and TM = total metal.

2.5. Quality control

All the chemicals were of analytical grade quality and purchased from Sigma-Aldrich, USA. Ultrapure, deionized water was used throughout the procedure, and glassware and plastics were soaked in 10% HNO_3 for 24 h. All analytical solutions were prepared using ultrapure water (resistivity $\geq$ 18.3 MΩ cm) obtained from a Milli-Q device (Millipore, Bedford, MA, USA). A quality control standard of 10 μg L^{-1} was used to check the calibration and had to pass with 90% confidence before any samples were run.

Table 1 Comparison of the analytical results of the certified reference materials (HISS-1, National Research Council of Canada in $\mu g\, g^{-1}$) with the measured data.

Metal	Measured value	Certified value	Recovery %
Fe	0.24 ± 0.09	0.236 ± 0.017	101.7
Mn	60.85 ± 4.20	61.24 ± 2.30	99.4
Zn	4.74 ± 0.79	4.60 ± 1.21	103.0
Cu	2.10 ± 0.37	2.08 ± 0.08	101
Pb	2.75 ± 0.40	2.83 ± 0.74	97.2
Cd	0.020 ± 0.09	0.022 ± 0.028	91.0
Ni	2.16 ± 0.29	1.99 ± 0.55	92.1

To validate the method in this work, QA/QC concerns were addressed through the use of certified reference materials (CRM), blank reagents and triplicate samples. Quality control for the total metal concentrations was performed using a certified reference material, and the indicated heavy metals in marine sediments (HISS-1, National Research of Council of Canada, in $\mu g\, g^{-1}$) were analyzed (Table 1). Six batches were analyzed in duplicate, and the accuracy of the results ranged from 90—110%; the precision of the analytical process was determined as the relative standard deviation (RSD). The precision for the analysis of the standard solution was within 10%. The coefficients of variation were 8.0% for Fe, 8.5% for Mn, 7.4% for Zn, 4.2% for Cu, 6.5% for Pb, 5.9% for Cd and 6.2% for Ni. Sequential extraction reagent blanks showed no detectable contamination. The detection limit (LOD) was 2.5 $\mu g\, L^{-1}$ for Fe, Mn, Zn, Cu, and Cd and 5.0 $\mu g\, L^{-1}$ for Pb.

3. Results and discussion

3.1. Carbonates, total organic matter (TOM) and grain size distribution

The percentages of carbonates ($CaCO_3$) and TOM in the sediments of the studied stations are shown in Table 2. The carbonate percentages exhibited the highest levels at four stations (V, VIII, IX and XII), with values of approximately 40—60%, indicating that biogenic materials constitute an important part of the nearshore sediments in the study area. $CaCO_3$ decreased at stations I, III, IV, VI, X, and XI, with values of approximately 20—30%, and at stations II and VII, it decreased to less than 20%.

The distribution of TOC (Table 2) in the studied sediments showed that the highest value of 1.44% occurred at station X and the lowest value of 0.26% was recorded at station II. However, the average value was $0.95 \pm 0.4\%$. The organic carbon from stations VI to XII fluctuated between 1.03% and 1.44% with a mean value of 1.0%. In general, the variations in total TOC in the bottom sediments of the study area could be related to algal and seagrass cover, terrigenous and domestic wastewater input, and local hydrodynamics (El-Metwally et al., 2017; Mansour et al., 2013).

The grain size distribution revealed that the sand fraction was the dominant component of the studied sediments (Table 2). The sand fraction was high, ranging from 95 to 100%, except at stations II and X, where it displayed values of 61% and 85.5%, respectively. The clay and silt fractions fluctuated from 0—39%. Additionally, the sediments in the study area contained a considerable amount of shell fragments.

3.2. Distribution of total heavy metals

Sediment particles consist mainly of biogenic and nonbiogenic (lithogenous) components, which are considered the final sinks for heavy metals delivered to the marine environment. Sediments are able to absorb a higher level of both toxic and persistent chemicals than water (Rodríguez-Barroso et al., 2009; Yuan et al., 2004). The total metal concentrations of Fe, Mn, Zn, Cu, Pb, Cd and Ni in the marine sediments of the coastal zone of Jeddah are presented in Table 2. The concentrations of these metals showed average values (in units of $\mu g\, g^{-1}$) of 3433—5883 (4472 ± 838), 483—1200 (784 ± 253), 241—532 (390 ± 109), 43—92 (67 ± 16),

Table 2 Sediments characterization and total metals concentrations, Jeddah coastal zone (Saudi Arabia).

St.	Latitude (N)	Longitude (E)	Sand %	Silt clay %	TOC %	CaCO₃ %	Fe	Mn	Zn	Cu	Pb	Cd	Ni
	Locations		Grain size				Total concentrations ($\mu g\, g^{-1}$)						
I	21.876617	38.972557	98.0	2.0	0.35	25.80	3800	550	241	58	121	2.04	110
II	21.866340	38.975300	61.0	39.0	0.26	5.03	3683	567	257	60	170	1.58	134
III	21.845668	38.993319	95.8	4.2	0.70	21.44	3950	1083	314	83	206	1.08	117
IV	21.751210	39.132770	96.2	3.8	0.66	29.36	3433	783	326	65	226	1.22	153
V	21.720934	39.113549	100.	0.0	0.63	53.34	4433	483	309	63	138	1.37	167
VI	21.520035	39.130082	96.0	4.0	1.03	31.45	5883	1200	410	43	155	2.32	147
VII	21.473369	39.163543	100.	0.0	1.09	16.59	4467	700	511	87	225	1.75	150
VIII	21.332450	39.119300	100.	0.0	1.09	42.60	4233	650	485	68	186	2.55	142
IX	21.320480	39.104820	98.5	1.5	1.18	46.47	4133	633	519	92	240	1.74	172
X	21.265594	39.128387	85.5	14.5	1.44	29.50	5683	1083	462	77	76	1.69	136
XI	21.136170	39.178060	97.3	2.7	1.37	30.05	4300	633	532	55	68	1.65	106
XII	21.082930	39.219490	94.9	5.1	1.30	61.37	5300	933	334	57	85	1.47	162
Min			61.0	0.00	0.26	5.03	3433	483	241	43	68	1.08	106
Max			100.	39.0	1.44	61.37	5883	1200	532	92	240	2.55	172
Avg.			93.3	6.8	0.95	35.06	4472	784	390	67	157	1.72	141
±SD			13.1	13.0	0.4	17.6	838	253	109	16	63	0.47	23

68—240 (157 ± 63), 1.08—2.55 (1.72 ± 0.47) and 106—172 (141 ± 23), respectively.

The lowest Fe concentrations were recorded at station IV, while the highest concentrations occurred at station VI (Table 2). The lowest concentrations of Mn were recorded at station V, while the highest values occurred at station VI. The minimum value of Zn (241 μg g^{-1}) was recorded at station I, whereas its maximum value (532 μg g^{-1}) was recorded at station XI. When comparing the Zn concentrations in this study with those obtained for the Red Sea, the studied sediments yielded an average concentration of Zn (390 ± 109 μg g^{-1}) 8 times higher than that previously reported in the sediment of the Red Sea (51 ± 14 μg g^{-1}) (Okbah et al., 2005). This may be related to the effect of industrial activities along the study area.

Cu ranged from 43 to 92 μg g^{-1} (average value 67 ± 16 μg g^{-1}), exhibiting the lowest values at station VI, while the highest levels were recorded at station IX (Table 2). Cu was introduced into the sediments in lithogenic and biogenic forms. Clay minerals represent the main source of lithogenic Cu. However, the decomposition of organic matter releases Cu that can be adsorbed to the surface of clay minerals. Additionally, anthropogenic Cu and metal pollutants can enter the environment via the effluents of mining and industrial activities, fuel burning, sewage discharge and agriculture activity (fertilizers and pesticides).

The total Pb, Cd and Ni concentrations in the sediments of the coastal zone of Jeddah are shown in Tables 2 and 3. Their values varied from 68—240, 1.08—2.55 and 106—172 μg g^{-1}, respectively. The lowest concentrations of Pb and Ni were recorded at station XI, while their highest values occurred at station IX. Their average values were 157 ± 63 μg g^{-1} and 141 ± 23 μg g^{-1}, respectively. The highest concentration of Cd (2.55 μg g^{-1}) was recorded at station VIII, with an average value of 1.72 ± 47 μg g^{-1} (Table 2).

Comparisons of the heavy metal concentrations in the current study with other works in the same area and other areas of the world, such as the Red Sea coast (Hurghada area, Red Sea), Caspian Sea (Iran), Black Sea (Turkey), and Al-Hodeidah coast (Yemen) (Table 3) indicated that Fe, Mn, Zn, Cu, Pb and Ni revealed values higher than those demonstrated by Badr et al. (2009), Salem et al. (2014), El-Moselhy and Gabal (2004), Heba et al. (2004), Mora and Sheikholeslami (2002), Topcuoglu et al. (2002), while Cd presented lower concentrations than those reported by El-Moselhy and Gabal (2004). The sediments of Jeddah (Red Sea) studied by Al-Mur et al. (2017) showed higher levels of Fe, Mn, Zn, Cu and Pb than those reported in the present study.

3.3. Fractionation of heavy metals

The heavy metals in the studied sediments were fractionated into five categories according to binding, including exchangeable, carbonate, Fe-Mn oxide, organic matter (oxidizable) and residual fractions. This is because each of these categories has a different remobilization regime under changing environments. Thus, the speciation of heavy metals is important for measuring their bioavailability in the environment and for evaluating their potential risks to living organisms (Sadhana Pradhanang, 2014). In the present study, the investigated

Table 3 Heavy metal concentrations (μg g^{-1} dry weight) from Jeddah coast, Red Sea during 2017 in comparison with other studies in the same area and other areas of the world.

Location	Fe	Mn	Zn	Cu	Pb	Cd	Ni	References
Jeddah, Red Sea	3433–5883	483–1200	241–532	43–92	68–240	1.08–2.55	106–172	Present study
Jeddah, Red Sea	8506.13	478.45	623.09	251.82	362.75	–	67–90	Al-Mur et al. (2017)
Jeddah, Rabigh, Yanbu, Red Sea	2.0–2671	34–205	52–76	17–24	80–99	1.8–3.95	11.41	Badr et al. (2009)
Egyptian Red Sea coast	3490	127.09	22.64	1.94	3.26	0.102	1.91	Salem et al. (2014)
Hurghada area, Red Sea	2000	177	4.66	0.67	12.89	2.30		
Caspian Sea, Iran	–	–	–	–	11–24	0.10–0.24	29–67	Mora and Sheikholeslami (2002)
Black Sea, Turkey	5000	206–870	34–267	4–95	0.05–31	0.02–0.93	13.65	Topcuoglu et al. (2002)
Al-Hodeidah, coast, Yemen	100–200	9–24	4.18	36–80	5–6	–	7–116	Heba et al. (2004)
North of Suez Gulf	–	–	4.26–23.68	1.84–10.25	13.9–28.34	2.26–4.4	–	El-Moselhy and Gabal (2004)

Table 4   Minimum, maximum and average content $\pm$ SD, and its relative percentage of trace metals in the five fractions extracted.

		Exchangeable		Carbonate		Reducible		Oxidizable		Residual		Total conc.
		Conc.	%	Conc.	%	Conc.	%	Conc.	%	Conc.	%	
Fe	Min	85	2	420	10	820	21	460	12	321	7	343
	Max	156	4	770	15	2320	52	1660	34	2010	53	5883
	Avg.	116	3	600	13	1530	34	1009	23	1230	29	4472
	SD	20	1	102	2	572	11	373	7	588	15	839
Mn	Min	6	1	5	0.4	20	3	40	4	52	8	483
	Max	23	4	105	12	300	47	380	50	726	67	1200
	Avg.	14	2	53	7	176	24	196	27	344	40	784
	SD	5	1	31	4	98	15	108	15	250	22	254
Zn	Min	2	1	10	3	84	24	52	17	20	5	241
	Max	21	6	70	21	227	66	237	50	117	31	532
	Avg.	10	3	36	10	147	39	137	33	66	17	391
	SD	6	2	22	7	47	12	74	13	34	9	110
Cu	Min	1	1	5	6	11	16	20	33	2	5	43
	Max	3	6	12	22	29	34	45	58	21	38	92
	Avg.	2	3	5	12	17	25	31	46	12	16	67
	SD	1	2	3	5	6	6	8	8	9	10	16
Pb	Min	2	1	10	5	11	5	14	12	15	18	68
	Max	8	10	24	28	32	32	46	39	165	73	240
	Avg.	5	4	14	11	19	15	30	21	90	50	158
	SD	2	3	5	8	8	9	10	8	57	20	63
Cd	Min	0.02	0.78	0.18	21	0.14	13	0.24	12	0.04	2	1
	Max	0.05	2.78	0.55	47	0.54	32	1.08	28	0.69	44	3
	Avg.	0.03	1.58	0.37	34	0.37	22	0.60	21	0.35	21	2
	SD	0.01	1	0.13	10	0.1	7	0.28	5	0.22	14	0.5
Ni	Min	1	1	11	6	32	20	26	22	6	6	106
	Max	7	5	27	21	65	47	61	43	63	38	172
	Avg.	3	2	20	14	42	30	43	30	34	23	141
	SD	2	1	6	4	11	9	13	8	19	1	23

metals revealed differences in the concentrations that were recorded at each step of the extraction. The results of the sequential extraction of Fe, Mn, Zn, Cu, Pb, Cd and Ni in the studied sediments are presented in Table 4 and Figs. 2—4 and discussed in the following text.

3.3.1. Exchangeable fraction (F_1)
Fraction F_1 includes the weakly sorbed metal forms held on the surfaces of soil and sediment grains by weak electrostatic interactions and ion-exchange processes. The metals of fraction F_1 can be released into the environment when conditions become more acidic, promoting a dangerous effect on the environment (Bakircioglu et al., 2011; Nemati et al., 2009). The range and mean content of the exchangeable metals of this study and the relative percentage of their equivalents are presented in Table 4 and Figs. 2—4. The range and average ($\mu g\ g^{-1}$) of released heavy metals in F_1 varied as follows: 85—156 (116 $\pm$ 20) for Fe, 6—23 (14 $\pm$ 5) for Mn, 2—21 (10 $\pm$ 6) for Zn, 1—3 (2 $\pm$ 1) for Cu, 2—8 (5 $\pm$ 2) for Pb, 0.02—0.05 (0.03 $\pm$ 0.01) for Cd and 1—7 (3 $\pm$ 2) for Ni (Table 4). It is evident that the metal concentrations of F_1 were lower than those of the other fractions in the present study (or negligible).

The relative percentage of total metals in this fraction corresponded to an average of 2—3% for Fe, Mn, Zn, Cu, and Ni, decreased to 1.58% for Cd and increased to 4% of the total for Pb (Figs. 2—4). The lower percentages of these metals might be explained by the decrease in metal sorption with increasing sediment pH, whereas the metal cations in sediments increase with increasing pH, likely due to an increase in surface negative charges. Additionally, the lower concentrations of the exchangeable fractions of Fe, Mn, Zn, Cu, Ni, Cd and Pb in the studied sediments might indicate the potential mobility of these metals. However, the percentages of Cd and Pb in this fraction were low, indicating that their potential environmental and ecological risks cannot be ignored. As shown in Figs. 2—4, the mobility order of heavy metals for the first fraction (F_1) was Fe > Mn > Zn > Pb > Ni > Cu > Cd.

3.3.2. Carbonate-bound metals fraction (F_2)
The fractionation results (minimum, maximum and mean concentrations) of the presently studied metals bound to carbonate are shown in Table 4. The ranges and the average concentrations were as follows: Fe had the highest value (420—770; 600 $\pm$ 102 $\mu g\ g^{-1}$), followed by Mn (5—105; 53 $\pm$ 31 $\mu g\ g^{-1}$), Zn (10—70; 36 $\pm$ 22 $\mu g\ g^{-1}$), Ni (11—27; 20 $\pm$ 6 $\mu g\ g^{-1}$), Pb (10—24; 14 $\pm$ 5 $\mu g\ g^{-1}$), Cu (5—12; 5 $\pm$ 3 $\mu g\ g^{-1}$) and Cd (0.18—0.55; 0.37 $\pm$ 0.13 $\mu g\ g^{-1}$). As
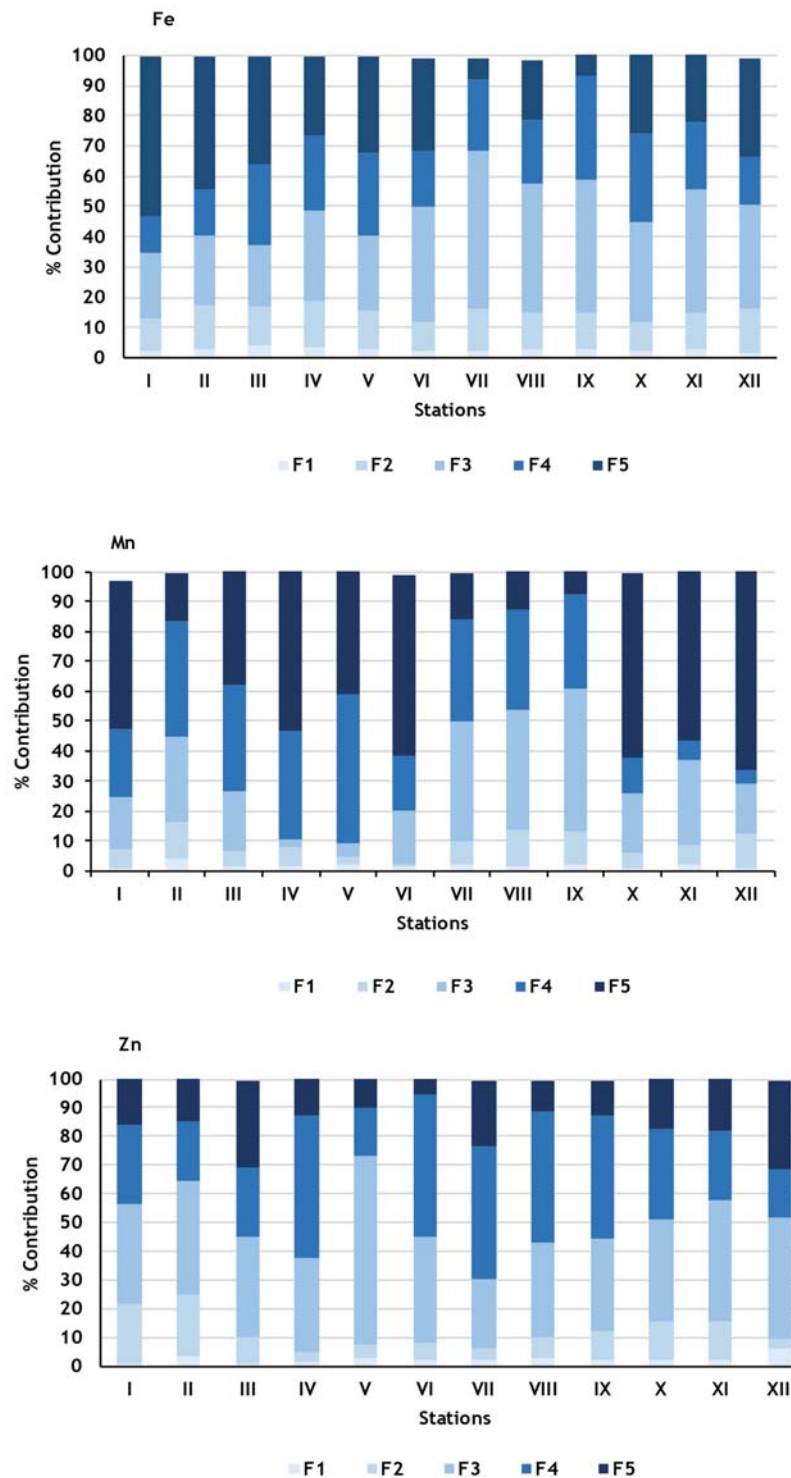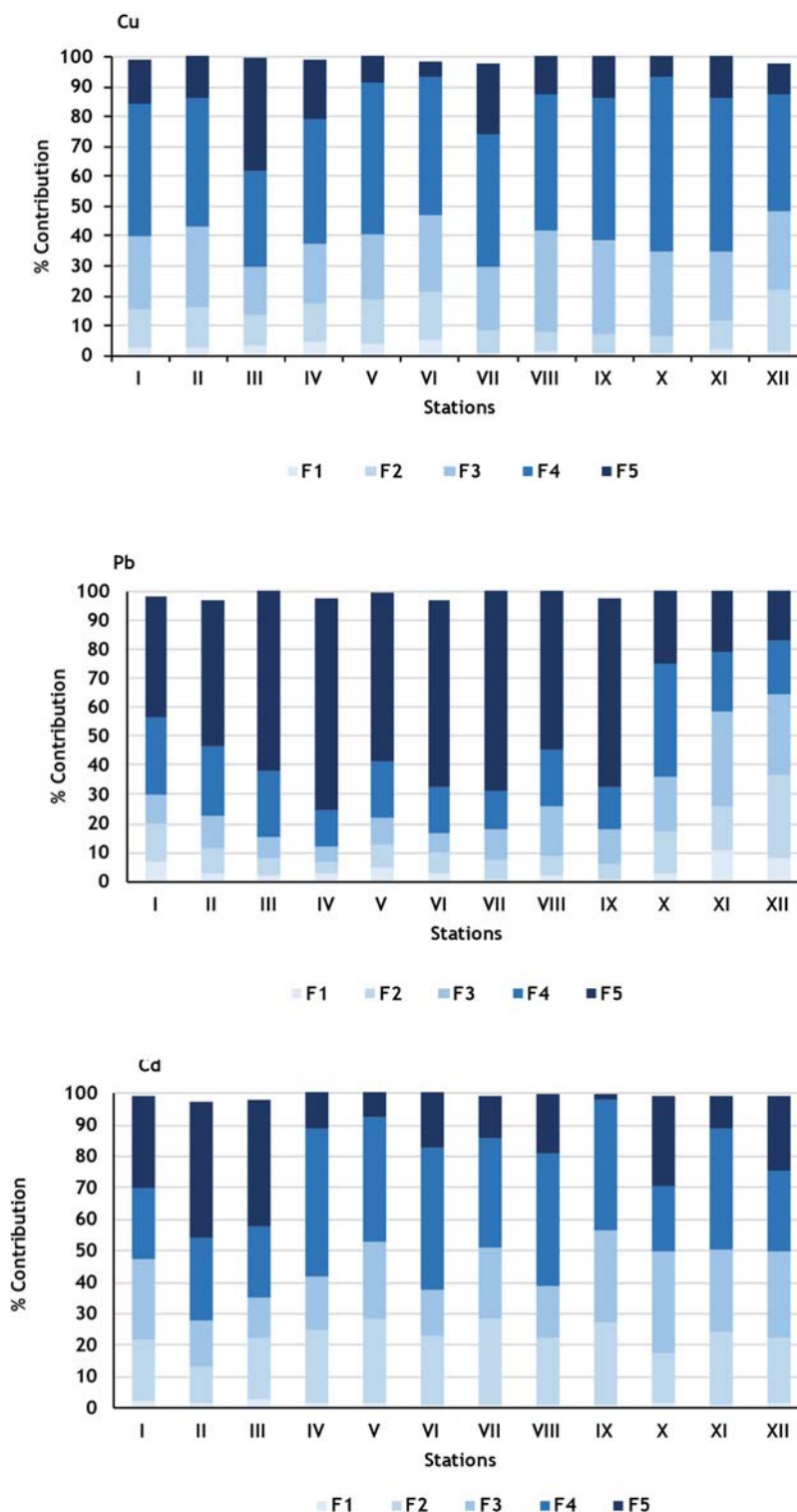
Figure 2 The relative percentage of Fe, Mn, and Zn from the total concentration in each fraction of the studied sediments.

shown in Table 4, the metals in the carbonate fraction (average value) in the study area were arranged in the following order: Cd (34%) > Ni (14%) > Fe (13%) > Cu (12%) > Pb (11%) > Zn (10%) > Mn (7%). This trend in the levels of metal concentrations differs partially from those of Egyptian Red Sea coastal sediments, which had metal concentrations following this order: Mn > Cu > Ni > Pb > Co > Cd (El-Said and Youssef, 2013).

3.3.3. Reducible fraction (F_3)

The metals in fraction F_3 are those bound to the hydrous oxides of Mn and Fe; they are released into the environment when a reducing condition develops. Thus, a reducing solution was used as the extractant (Gleyzes et al., 2002). The concentrations of heavy metals in this fraction, associated with Mn-Fe hydrous oxides (range and average; in $\mu g\,g^{-1}$), were 820—2320 (1530 ± 572) for Fe, 20—300 (176 ± 98) for
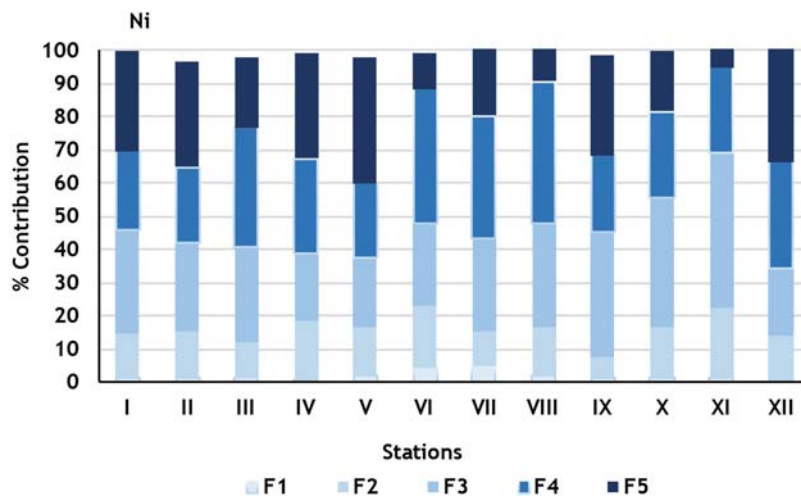
Figure 3 The relative percentage of Cu, Pb, and Cd from the total concentration in each fraction of the studied sediments.

Mn, 84—227 (147 ± 47) for Zn, 11—29 (17 ± 6) for Cu, 11—32 (19 ± 8) for Pb, 0.14—0.54 (0.37 ± 0.14) for Cd and 32—65 (42 ± 11) for Ni (Table 4). The relative percentages of Fe, Mn, Zn, Cu, Pb, Cd and Ni in the reducible fraction were 34%, 24%, 39%, 25%, 15%, 22% and 30%, respectively (Table 4 and Figs. 2—4). As shown in Figs. 2—4, the mobility of the metals in F_3 followed this order: Fe > Mn > Zn > Ni > Pb > Cu > Cd.

3.3.4. Oxidizable fraction (F_4)

The metals of fraction F_4 are known to bind with organic matter and sulfide compounds that can be released into the environment when oxidizing conditions develop. The heavy metals associated with organic and sulfide compounds can remain in the sediments and soils for a long time until they are released by decomposition processes or oxidizing agents,

Figure 4   The relative percentage of Ni from the total concentration in each fraction of the studied sediments.

leading to their complexation and bioaccumulation (Kennedy et al., 1997). This fraction may be linked to humic substances with high molecular weights and is therefore considered to be of low mobility, releasing small amounts of metals into the environment (Filgueiras et al., 2002).

F_4 showed wide variations in the concentrations of certain metals in the studied sediments. The range and mean values (in $\mu g\,g^{-1}$) of F_4 were 460—1600 (1009 ± 373) for Fe, 40—380 (196 ± 108) for Mn, 52—237 (137 ± 74) for Zn, 20—45 (31 ± 8) for Cu, 14—46 (30 ± 10) for Pb, 0.24—1.08 (0.60 ± 0.28) for Cd and 26—61 (43 ± 13) for Ni (Table 4). The relative percentages of the studied metals (Fe, Mn, Zn, Cu, Pb, Cd and Ni) in F_4 were 23 ± 7%, 27 ± 15%, 33 ± 13%, 46 ± 8%, 21 ± 8%, 21 ± 5% and 30 ± 8%, respectively (Table 4 and Figs. 2—4).

The present data revealed that more than 46% of the total Cu is related to the organic carbon in the studied sediments, whereas Cu could be transported to surface sediments in association with a biogenic carrier phase or via anthropogenic waste (Abu-Zied et al., 2013). Additionally, Chester et al. (1988) noted that approximately 50% of the Cu in surface water particulates was associated with organics.

3.3.5. Residual fraction (F_5)

F_5 includes the rest of the metals and is associated with minerals that are bound via their crystalline structure, immobilized, and that will not constitute a threat to the ecosystem. The residual fraction contains metals that are chemically stable, immobile, and biologically inert. The relative percentage of metals in this fraction was at a level of approximately 7—53% for Fe, 8—67% for Mn, 5—31% for Zn, 5—38% for Cu, 18—73% for Pb, 2—44% for Cd and 6—38% for Ni (Table 4).

The Fe content in the residual fraction of the sediments ranged between 321 $\mu g\,g^{-1}$ at station IX and 2010 $\mu g\,g^{-1}$ at station II, with an average of 1230 ± 588 $\mu g\,g^{-1}$ (Table 4). A high relative percentage of Fe was found in the residual fraction, but Fe presented low concentrations in the other fractions of this study. The value ranged between 7% at station XI and 53% at station I, with some exceptions, such as stations VII, VIII and IX, where it ranged from 7 to 20%. This may also indicate that Fe tends to be incorporated into the

lattice structure of the sediment. Mn showed a similar tendency to that of Fe, bound to the residual form with a relative percentage from 35 to 67% of the total concentration for all the sediment samples, except for the sediment samples of stations II, VII, VIII and IX, where the percentage ranged from 8—15% of the total concentration (Figs. 2—4). The data observed in Table 4 show that the range and mean value of Mn are between 52 and 726 $\mu g\,g^{-1}$ (344 ± 250 $\mu g\,g^{-1}$). These results may indicate that Fe and Mn have a greater affinity for the nonresidual fraction, which may increase the potential bioavailability and mobility of Fe and Mn in the environment.

The range and mean concentration of Zn in the residual fraction are presented in Table 4 and Fig. 2. The concentrations ranged between 20 $\mu g\,g^{-1}$ at station VI and 117 $\mu g\,g^{-1}$ at station VII, with an average of 66 ± 34 $\mu g\,g^{-1}$. The relative percentage of Zn ranged from 4.9—31% at stations III (95 $\mu g\,g^{-1}$, 30%) and XII (103 $\mu g\,g^{-1}$, 31%), whereas at the remaining stations, the relative percentages of Zn ranged from 5—23%. The residual form of Cu was relatively high at station III (31 $\mu g\,g^{-1}$, 38% of the total Cu) and decreased to its lowest level (2 $\mu g\,g^{-1}$, 5% of the total Cu) at station VI. These results showed that low concentrations of Cu were recorded in the residual fraction, while high Cu concentrations were dominant in the other extracts in the present study, indicating that Cu could be more bioavailable in the studied sediments (Fig. 3).

Pb was dominant in the residual extract of the studied sediment samples at nine stations, ranging between 15 and 165 $\mu g\,g^{-1}$ (from station XI to station IV) and representing 41 to 73% of the total Pb (Fig. 3), and decreased to its lowest level at station XII (16 $\mu g\,g^{-1}$, 18% of the total Pb). The Pb at the sampling sites showed remarkable variations within the study area, likely due to variations in the mineralogical composition of the sediments, which are the main carrier of Pb. The distribution of Cd content in various chemical forms reflects the extent of Cd contamination in Jeddah coastal area sediments. The residual form ranged between 0.04 and 0.69 $\mu g\,g^{-1}$ (24% to 44% of the total content) for stations I, II, III, X, and XII and from 0.04 to 0.69 $\mu g\,g^{-1}$ (2% to 44% of the total content) for the other stations. The Ni in the residual

fraction ranged between 6 and 63 $\mu g\,g^{-1}$, with a mean value of $34 \pm 20\,\mu g\,g^{-1}$; its relative percentage ranged between 9 and 38% of the total content. Three sediment samples exhibited low levels in this fraction and were from stations VI (15 $\mu g\,g^{-1}$, 10%), VIII (14 $\mu g\,g^{-1}$, 10%) and XI (6 $\mu g\,g^{-1}$, 6%).

A comparison of the five sequential extracts showed that a large proportion of metals in this study were found in three phases (the carbonate, reducible and oxidizable fractions). This is likely due to the occurrence of low pH values, which prevented reabsorption and caused the metals to be more soluble in the extracting solution.

3.4. Bioavailability factor (BF)

The BF was described by Bielicka-Giełdoń et al. (2013). The BF was computed from the total concentration of heavy metals and the content of bioavailable forms according to the following formula:

$$BF = \frac{C_{bio}}{C_{total}},$$

where C_{bio} and C_{total} are the concentration of bioavailable metals and the total concentration of metals in the studied sediments, respectively. The bioavailable metals are those in fractions F_1, F_2, F_3 and F_4, according to the protocol described in Tessier et al. (1979), and may be analogous to changes in environmental marine conditions and affect heavy metal binding in sediments. The bioavailability factor allows for the determination of possibly toxic elements in marine sediments.

The largest amount of Fe was extracted from the non-residual fractions (F_1, F_2, F_3 and F_4) and was in ranges of 2—4%, 10—15%, 21—52% and 12—34% of the total Fe for the exchangeable, carbonate, oxidizable and organic fractions, respectively. The smallest concentrations of Fe were found in the exchangeable and carbonate fractions. The BF ranged from 0.47 to 0.93, indicating the mobilization of more than 50% of the Fe in the studied sediment samples.

The largest contents of Mn were recorded in the reducible and organic forms, with nearly 50% of the total Mn content in the studied sediments. The smallest amounts of this metal were present in the exchangeable and carbonate fractions in the ranges of 1—4% and 0.4—12%, respectively. The bioavailability factor was in the range of 0.34 to 0.47 for six stations: I, IV, VI, X, XI and XII. The largest bioavailability factor was in the range of 0.60 to 1 for six stations: II, III, V, VII, VIII and IX. This reflects the considerably higher mobility of Mn in the sediments of these sampling sites.

The concentrations of Zn in the most mobile fractions of the present study, the reducible and oxidizable fractions (F_3 and F_4), represented an average of approximately 72% of the total content. The lowest content of Zn was obtained in the exchangeable fraction (F_1; approximately 0.6—6% of the total Zn). The bioavailability factor of the study area was in the range of 0.70 to 1%. Generally, the BF value of Zn in sediments was more than 1 for all of the sediment samples, except for those of stations III and XII (approximately 0.70%). This result illustrated the high Zn bioavailability and demonstrates a potential risk to aquatic life.

The highest levels of Cu concentration were observed in the reducible fraction (F_3, ranging from 16—34%) and in the oxidizable fraction (F_4, ranging from 33—58%). Approximately 46% of the total Cu was linked to the organic fraction. The smallest amounts of Cu, ranging from 0.7—6% of the total Cu, were present in the exchangeable fraction (F_1) and the carbonate fraction (F_2, ranging from 6—22%). The maximum mobility of Cu in the sediments was confirmed by its BF, which was in the range of 0.60 to 1%. This reflects the high mobility of Cu in the studied sediments.

High concentrations of Pb were recorded in the organic extract (F_4) and ranged from 12.4—39.1% of the total Pb, followed by the reducible fraction (F_3, 5—32% of the total Pb) and the carbonate fraction (F_2, 5—28% of the total Pb), while the smallest amounts of Pb occurred in the exchangeable fraction (F_1), ranging from 1% to 10% of the total Pb. In general, a high Pb bioavailability factor of greater than 0.70% was reported at three stations (stations X, XI and XII).

Table 5 Risk assessment code (RAC).

Criteria (%), Singh et al. (2005)	Sites	Mn	Zn	Cu	Pb	Cd	Ni
		Percentage of Exchangeable + Carbonate					
No risk <1	I	7.45	21.58	15.50	20.05	25.00	14.70
Low risk 1—10	II	16.41	24.90	16.39	11.65	27.85	15.50
Medium risk 11—30	III	6.56	10.19	13.94	8.37	25.00	12.10
High risk 31—50	IV	8.18	4.60	17.65	7.02	48.36	18.10
Very high risk >50	V	4.55	7.44	18.49	12.95	41.61	16.70
	VI	2.00	8.05	21.32	10.00	46.12	22.80
	VII	10.15	5.87	8.79	7.38	36.00	15.20
	VIII	13.69	10.11	8.00	8.85	43.13	16.40
	IX	13.27	11.94	7.01	6.17	42.53	7.70
	X	6.10	15.37	6.57	17.21	22.49	16.40
	XI	8.85	15.23	11.51	25.77	40.00	22.20
	XII	12.43	9.28	23.03	36.01	27.21	14.20
	Min	2.00	4.60	6.57	6.17	22.49	7.70
	Max	16.41	24.90	23.03	36.01	48.36	22.80
	Avg.	9.15	12.43	14.13	15.26	35.44	15.89
	±SD	4.61	6.77	5.89	10.10	9.62	4.59

However, the lowest BF values were found at the other stations (ranging from 0.20 to 0.40%), except for station I.

The Cd concentration in the most mobile fractions relative to the total content of the study area sediments was in the range of 21—47% (average of 34%) for the carbonate fraction, followed by the reducible fraction (13—32%; average of 22%). Another 12—27% (average of 21%) of Cd was associated with organic matter (F_4). The exchangeable form represented low amounts of the total Cd, ranging from 1 to 3%, with an average of 1%. The BF of Cd was in the range of 0.5% (station II) to 1% (station IX). Generally, the BF values of Cd in the sediments were greater than 1 for all of the sediment samples, except for stations II and III (which were approximately 0.60). This confirms the high bioavailability of Cd and demonstrates a potential risk to aquatic life.

As shown in Table 4 and Fig. 4, the highest Ni content was determined in the nonresidual extracts (F_1, F_2, F_3 and F_4), ranging from 1—5%, 6—21%, 20—47% and 22—43% of the total Ni for the exchangeable, carbonate, oxidizable and organic fractions, respectively. Much of this metal was also linked to the reducible and organic carbon extracts (F_3 and F_4), approximately 43—89% of the total content. The smallest levels of Ni were present in the exchangeable and carbonate/acid-soluble fractions. The bioavailability factor was less than 1% for sediments from stations II, IV, V, IX and XII and ranged from 0.70 to 0.95 for the other stations. The results obtained may reflect a high loading of contaminants due to enhanced anthropogenic activity in urbanized areas.

The sequential leaching procedure for the studied sediments showed potentially toxic metals, as indicated by the mobility and bioavailability characteristics (BF). The maximum mobility of the metals in the sediments (the metal species in the bioavailable fraction) (range; average) was (0.47 to 0.93; 0.71), (0.34 to 0.92; 0.60), (0.69 to 0.95; 0.83), (0.62 to 0.95; 0.84), (0.24 to 0.82; 0.49), (0.54 to 0.98; 0.78) and (0.60 to 0.95; 0.76) for Fe, Mn, Zn, Cu, Pb, Cd and Ni, respectively. In general, the high levels of BF for the studied metals could reflect their potential toxicity and that they could be easily released into the marine environment and ingested by marine organisms, thereby entering the food chain (Oyeyiola et al., 2011).

3.5. Risk assessment code (RAC)

The RAC was applied in this study based on the values of the exchangeable and carbonate fractions (Table 5) to measure the availability of the metals in solution, such as in an aquatic system. According to the RAC calculations, the concentration of metals in the fractionated sediments varied from fraction to another, showing different strengths (Singh et al., 2005). In the RAC (Table 5), when the percentage of metals in the exchangeable and carbonate fractions is less than 1%, the release of metals into solution is undetectable and safe to the environment. However, if the percentages in the same fractions are >50%, the metals are considered highly dangerous and can easily enter the food chain (Jain, 2004). The RAC of Cd displayed a medium risk at five sediment sample stations (I, II, III, X and XII) and a high risk to the aquatic environment for the other sediment samples. The other metals (Fe, Mn, Zn, Cu, Pb and Ni) exhibited low to medium risks. This elevated risk in the studied environment is

Table 6 Principal component analysis with Varimax rotation.

	OC	CaCO$_3$	T-Fe	NR-Fe	T-Mn	NR-Mn	T-Zn	NR-Zn	T-Cu	NR-Cu	T-Pb	NR-Pb	T-Cd	NR-Cd	T-Ni	NR-Ni	% of Variance	% Cumulative
PC1	0.817	0.353	0.93	0.941	0.589	0.102	0.710	0.778	0.711	0.736	−0.293	−0.342	0.311	0.425	0.346	0.749	83.106	83.106

Extraction Method: Principal Component Analysis; Rotation Method: Varimax with Kaiser Normalization.

Table 7 Correlation matrix for the different studied components in Jeddah sediments, Red Sea.

	OC	CaCO3	T-Fe	NR-Fe	T-Mn	NR-Mn	T-Zn	NR-Zn	T-Cu	NR-Cu	T-Pb	NR-Pb	T-Cd	NR-Cd	T-Ni	NR-Ni
OC	1.000															
CaCO3	0.435	1.000														
T-Fe	**0.644***	0.341	1.000													
NR-Fe	**0.873****	0.336	**0.753****	1.000												
T-Mn	0.395	−0.019	**0.658***	0.425	1.000											
NR-Mn	0.071	−0.300	−0.085	0.239	0.279	1.000										
T-Zn	**0.823****	0.141	0.318	**0.802****	0.083	0.319	1.000									
NR-Zn	**0.715****	0.155	0.309	**0.755****	0.028	0.262	**0.951****	1.000								
T-Cu	**0.878****	−0.088	−0.248	0.240	−0.067	**0.655***	0.369	0.236	1.000							
NR-Cu	**0.747****	0.150	−0.005	0.436	−0.185	0.379	0.491	0.452	**0.831****	1.000						
T-Pb	−0.313	−0.237	−0.499	−0.079	−0.114	**0.716****	0.059	0.098	0.554	0.298	1.000					
NR-Pb	−0.197	−0.084	−0.415	−0.236	−0.267	**0.615***	−0.043	−0.124	0.504	0.343	0.445	1.000				
T-Cd	0.193	0.050	0.316	0.275	−0.030	0.081	0.356	0.497	−0.277	−0.024	−0.067	0.112	1.000			
NR-Cd	0.396	0.312	0.306	0.492	−0.115	0.046	**0.601***	**0.742****	−0.145	0.132	0.059	−0.059	**0.871****	1.000		
T-Ni	**0.680***	0.573	0.217	0.435	−0.041	0.127	0.129	0.187	0.226	0.432	0.370	0.039	−0.058	0.213	1.000	
NR-Ni	**0.665***	0.334	0.551	**0.837****	0.329	0.387	**0.727****	**0.776****	0.110	0.282	0.224	-0.064	0.525	**0.717****	0.531	1

* Correlation is significant at the 0.05 level.
** Correlation is significant at the 0.01 level.
No. of samples = 12. T: total metal concentration; NR: non-residual of heavy metal represents the sum of the four fractions (exchangeable + carbonate + reducible + oxidizable).

probably a result of the usage of gasoline and the discharge of uncontrolled industrial and sewage wastes (Abu-Zied et al., 2013, 2016; Al-Mur et al., 2017; Badr et al., 2009), which began in the early 1970s; however, as of recently, there has been a decrease in these activities due to the implementation of environmental laws.

3.6. Statistical analyses

Primary component analysis was applied to the present data obtained from the heavy metal fractionation of Jeddah surface sediments (Table 6). One component (PC), with a variance of 83.11%, is highly correlated with organic carbon, total heavy metals (Fe, Zn, Cu, and Ni) and the nonresidual fraction of the same metals (the nonresidual fraction represents the sum of the four fractions F_1, F_2, F_3 and F_4); the high loadings among this group exceed 0.7 (0.817, 0.930, 0.941, 0.710, 0.778, 0.711, 0.346, 0.746 and 0.749, respectively).

The correlation matrix between the total metals, nonresidual fractions of heavy metals and organic carbon can also be used to assess the degree of contribution of human sources to the examined metals (Table 7). The total organic carbon content is significantly positively correlated with total Fe, total Zn, total Cu, total Ni, nonresidual Fe, nonresidual Zn, nonresidual Cu and nonresidual Ni ($r = 0.644$, 0.873, 0.823, 0.715, 0.878, 0.747, 0.680 and 0.665, respectively). This reflects that the strong affinity of organic matter for Fe, Zn, Cu and Ni was mostly due to anthropogenic sources. The relationships between organic matter and the total concentrations of Mn, Pb and Cd were poor ($r = 0.395$, -0.313 and 0.193, respectively). On the other hand, no association was observed between the same elements in the nonresidual fractions and organic matter content.

4. Conclusion

One important environmental issue that is investigated in this study area is the concentration of heavy metals in sediments linked to different geochemical fractions. The heavy metals present in the marine sediments revealed variations in the type of different chemical phases in the study area. Cu showed a strong affinity with the organic fraction in all sediments of this study area. Cu, Zn and Pb were present in the reducible and oxidizable forms. Some metals, such as Cd, Ni, Fe and Mn, tend to accumulate in the carbonate, reducible and organic fractions.

Acknowledgments

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