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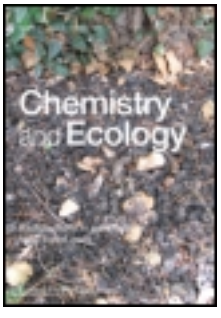

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Fractionation analysis of some heavy metals in sediments of the north-western part of the Red Sea, Egypt

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Fractionation analysis of some heavy metals in sediments of the north-western part of the Red Sea, Egypt

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Sequential extraction was used to study operationally determined chemical forms (exchangeable, carbonate, reducible metal, oxidisable metal and the residual fractions) of the metals Cd, Cu, Zn and Pb in sediments from 12 sample sites collected from the north-western part of the Red Sea, where improper recreational facilities have resulted in diverse impacts on the coastal environments fronting some of the recreation projects. The results showed that the average percentage of each phase was different among metal types; the residual binding fraction was the most important phase for binding Zn and to a lesser degree Cu. The reducible fraction was the second most important phase for Zn and Cu. For Pb, the fractions bounded to the residual fractions and the reducible phases are equal and exhibited the highest percentages. By contrast, the carbonate fraction was predominant for Cd. The percentages of Cd, Cu, Zn and Pb associated with the carbonate and exchangeable fractions, which are potentially the most harmful to the environment, were calculated and assessed at different sampling sites of the studied sediments. According to the Risk Assessment Code (RAC), the results reveal that Cd is the only metal that poses a high risk to the environment.

Keywords: Egypt; fractionation analysis; heavy metals; Red Sea sediment; risk assessment code

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1. Introduction

The widespread use of heavy metals in industries ranging from large-scale mining to intensive agriculture has resulted in a variety of heavy metals being released into the environment with concentrations in excess of natural background levels [1]. One of the major problems of heavy metals, with respect to their effects on aquatic organisms, is their long biological half-life. They are, therefore, among the most frequently monitored micropollutants [2]. Because sediments become large repositories of toxic heavy metals, potential environmental damage might be comparatively small if heavy metals are ultimately fixed in sediments [3]. However, sediment-associated pollutants can influence the concentrations of trace metals in both the water column and biota if they are desorbed or become available to benthic organisms [4]. Information on the total concentrations of metals alone is not sufficient to assess the environmental impact of polluted sediments because heavy metals are present as easily exchangeable metal carbonates, oxides, sulfides, organometallic compounds, ions in the crystal lattice of minerals, etc. which determine their mobilisation

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capacity and bioavailability [4]. It is necessary to identify and quantify the forms in which a metal is present in sediments to gain a more precise understanding of the potential and actual impacts of elevated concentrations, and to evaluate processes of downstream transport, deposition and release under changing environmental conditions. The dominant geochemical processes responsible for the exchange of metals at the water–sediment interface are adsorption and precipitation [5].

Binding fractions of heavy metals in sediments can be divided into five groups: exchangeable, carbonates, hydroxides, organic and residuals. It is intended that at each step of the analytical scheme, samples be exposed to the action of an extractant, which solubilises a specific component and its associated metals. The procedures assume that one reagent attacks a well-defined component only, without affecting the remaining fractions (i.e. it is selective) and that there are no problems with re-adsorption of the already solubilised elements [6].

In recent years, immense and increasing international scientific effort has dealt with the fractionation of heavy metals in different types of sediments. Much work has focused on marine sediments including estuaries [6]. A number of studies on sediment fractionation in different rivers have also been performed [7]. Other studies have been carried out in lake sediments [8]. The fractionation of heavy metals in mangrove sediments has also been taken into consideration [9].

The Egyptian coast of the Red Sea has become an emerging research issue, because it has been the site of intensive tourism developments over the last 20 years. Improper designs and non-environmentally friendly seashore recreation facilities have been constructed by some developers. Frihy *et al.* [10] reviewed the methods for constructing coastal recreational facilities in the Egyptian Red Sea and recommended that field surveys are essential to study the coast and marine components, as well as processes at a particular site, Accordingly, this study was undertaken to assess the fractionation analysis of cadmium, copper, lead and zinc in sediments from 12 sample sites collected from the north-western part of the Red Sea. The assessment was made based on a sequential extraction procedure to understand the binding fractions and mobility of metals in the surrounding environment. The current research deals with two toxic heavy metals (lead and cadmium) and two trace metals (copper and zinc) that are widely affected by anthropogenic inputs [11].

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2. Materials and methods

2.1. *Study area and sampling*

Most of the Red Sea shoreline is fronted by a discontinuous series of extensive fringed coral reefs up to a maximum of 700 m wide. In some areas, such as Hurghada, these reefs are fronted by a group of barrier islands made up of igneous and metamorphic rocks [10]. Examples of these islands are El-Fanadir, Gifftun El Kabier, Giftftun El Saghier, Abou Minqar and Umm Gawish [12]. The Red Sea coasts are known for their water sports, nightlife and warm weather. The classical beach–nearshore profile along most of the Red Sea coast is simply composed of the beach, intertidal flat (reef flat), reef crest and reef slope. Generally, the reef flat area is occasionally exposed during low tide and partially or totally submerged at high tide [10].

Because of an unawareness of the importance and delicacy of Red Sea ecosystems, many recreation facilities have been implemented based on improper designs that failed to consider environmental dimensions. Such developments have had diverse impacts on the coastal environments fronting some of the recreation projects. These impacts, including 'infringements' by the recreation facilities along parts of the Red Sea, have been discussed by Moufaddal [13]. As an example human impact, due to the need for construction space, the reef surface has been landfilled and reclaimed to a distance of 700 m out to sea (Figure 1B). Other illegal perpetuations include excavations to create artificial swimming pools (Figure 1A,C), dumping large amounts of

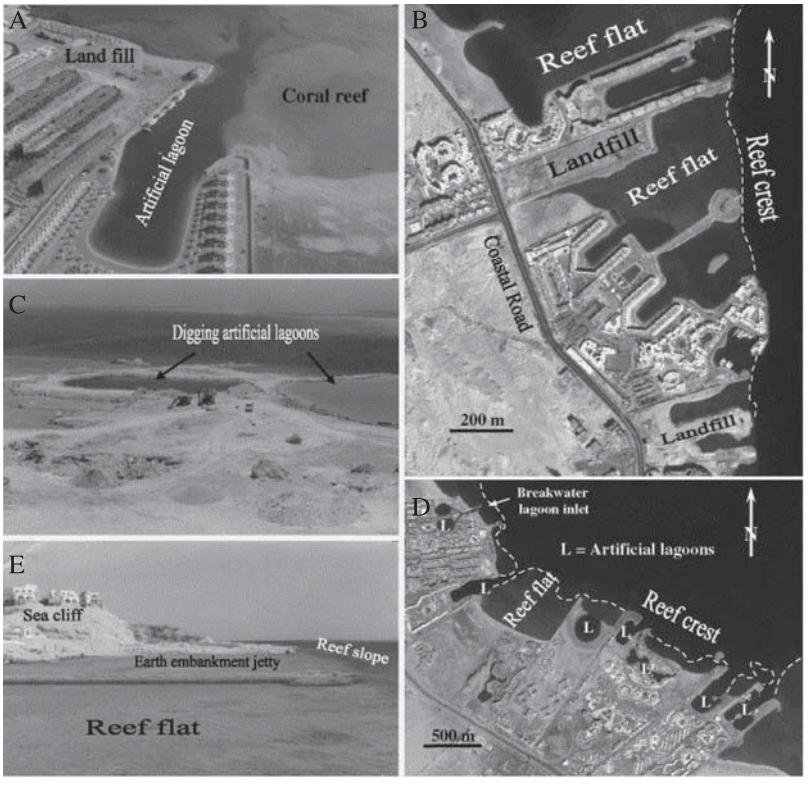

Figure 1. Red Sea development photos. (A) Earth development, (B) *IKNOS* satellite image, documenting coastal development, (C) artificial lagoon construction, (D) *IKNOS* satellite image documenting lagoons, breakwater inlet, and (E) building atop an escarpment and a built-up jetty.

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filling onto the reef flat to create extra space (Figure 1B), as well as building solid embankments to be used as jetties and moorings (Figure 1E). Subsequently, the reef ecosystem has suffered dramatic and irreversible damage. The depositional–hydrodynamic pattern has been affected as a result of blocking littoral currents with protruded constructions (Figure 1B,D). As a result, some coastal segments have been subjected to local down drift erosion. These consequences are also associated with changes in water quality and a deterioration in the marine ecosystem. Economic consequences in the form of penalties and environmental restoration are also expected [10].

The area of study (Figure 2) covers the north-western part of the Egyptian coast of the Red Sea around Hurghada, between latitude 27°5′ N and 27°30′ N and longitude 33°37′ E and 34°0′ E. It is situated near the southern end of a remarkable maze of reefs and islands, where all forms of reefs can be found. There is a higher rate of evaporation, daily temperature hovers around 30°C most of the year and rainfall is scarce. Water movements are due to three causes; tides, winds and changes of density. Salinity is $\sim$ 40.41 parts per thousand and the water is well oxygenated (5.81 mg·L^{-1}). The pH is on the alkaline side (8.24). The sediments are mainly sand [14]. Four sections (a, b, c and d) perpendicular to the coast were selected to cover the study area. Sections a, b and d face tourist villages (Magawish, Fanadir and Abu-Shar, respectively), where tourism activity is present. However, section c is in front of the marine biological station. Each section included three stations of various depths (Table 1) and the sampling location was detected using GPS. At each station, three replicates of sediment samples were collected at the surface layer (0–5 cm depth) by scuba-diving. The three replicate samples were placed in self-sealed acid pre-cleaned plastic bags. All samples were immediately stored in an ice-cooled box and transferred to the laboratory.

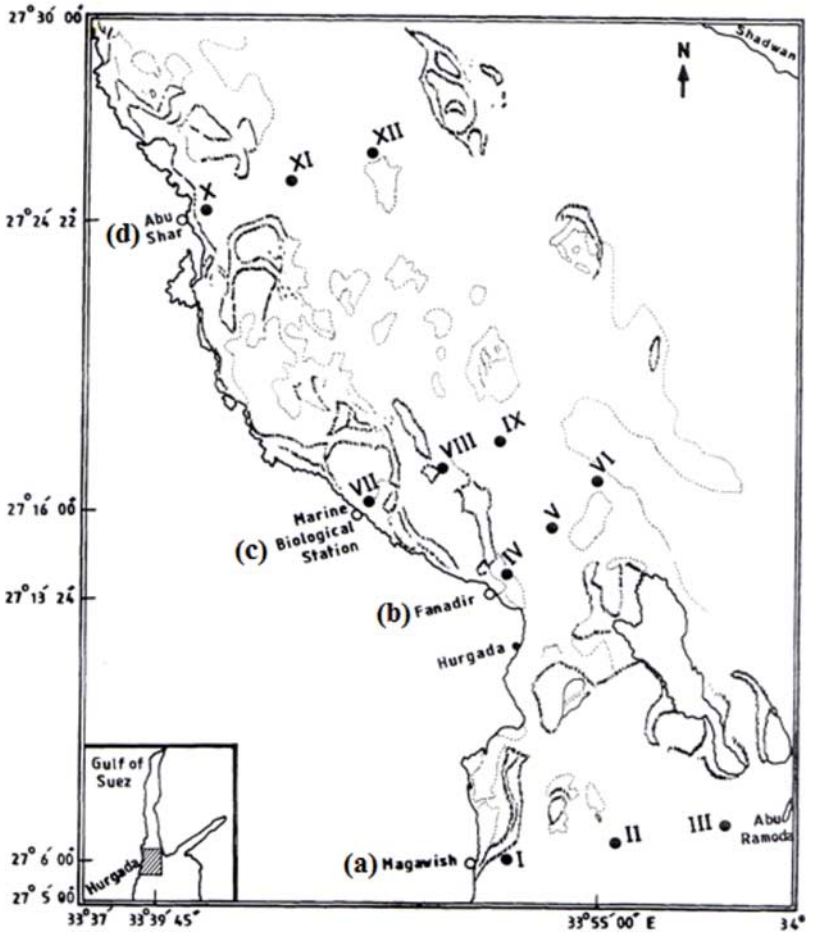

Figure 2. Study area.

2.2. *Sample pretreatment and chemical analysis*

In the laboratory, the samples were air dried, then oven dried at 40 °C to constant weight, sieved using 0.75 mm plastic sieve and finely powdered in an agate mortar. Dried samples were stored in desiccators until analysis.

A selective sequential extraction procedure (SEP) was followed to determine heavy metal retention profiles [15]. Details of the SEP are described as follows: (1) exchangeable fraction; 1 g of the dried sediment sample is extracted with 10 mL of 1 M $MgCl_2$ (pH 7.0) for 1 h at room temperature (25–30 °C) with continuous shaking. (2) Carbonate bound fraction; the residue from the exchangeable fraction is extracted with 10 mL of 1 M NaOAc (adjusted to a pH of 5.0 with HOAc) for 5 h at room temperature with continuous agitation. (3) Fe–Mn oxide-bound fraction; the residue from carbonates fraction is extracted with 20 mL of 0.04 m $NH_2OH.HCl$ in 25% (v/v) acetic acid for 6 h in a water bath (96 °C) and with occasional agitation. (4) Organic matter/sulfide-bound fraction; the residue from Fe–Mn oxides is extracted with 5 mL of 0.1 N HNO_3 and 10 mL of 30% H_2O_2 for 5 h in a water bath (85 °C) and with occasional agitation. After cooling, the extracted solution is added to 15 mL of 3.2 M NH_4OAc in 20% HNO_3 and shaken continuously for 30 min at room temperature. (5) The residual fraction; the residue from the organic matter/sulfide-bound fraction is digested for 3 h in a water bath by a mixture of acids (HNO_3/HF/ $HClO_4$/HCl). All

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Table 1. Sampling stations and their depths.

Sampling site	Station number	Station depth	
Magawish	Section (a)	I	7
		II	16
		III	28
Fanadir	Section (b)	IV	6
		V	16
		VI	29
Marine biological station	Section (c)	VII	6
		VIII	17
		IX	28
Abu-Shar	Section (d)	X	6
		XI	17
		XII	27

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extractions, except the final digestion, were conducted in 50-mL polypropylene centrifuge vials to minimise losses of solid material. Between each successive extraction, separation was achieved by centrifuging at 3000 rpm for 5 min. The supernatant was then removed with a pipette, filtered through a 0.45 μm filter and stored for analysis. Preparation/reagent blank samples were prepared for each fraction using the same procedure. Analysis of total metals was performed through digestion of 0.5 g dry sediment using a Suprapur-quality mixture of acids ($HNO_3/HF/HClO_4/HCl$). Determination of Cd, Cu, Pb and Zn was performed using flame atomic absorption spectrometry (AAS) with an air/acetylene flame (Model: Perkin–Elmer AAS 3100). Working standards of studied metals were prepared by diluting concentrated stock solutions (Merck, Germany) of 1000 $mg \cdot L^{-1}$ in metal-free distilled water. For metal analysis at each step of the sequential extraction, standards were prepared for the corresponding extract to minimise matrix effects. Each metal concentration was estimated quantitatively according to the standard conditions described in the instrument manual.

2.3. *Quality assurance*

IAEASL1 reference material was used as quality control material for the total metal amount, not for individual steps of a sequential extraction analysis. Cd, Cu, Pb and Zn data from the IAEASL1 are assigned as information or recommended values. All the data are based on dry weight. The recovery rates for heavy metals in the standard reference material were around 98.67–103.84% (Table 2). Throughout the study, all reagents used were of analytical grade.

An internal check was performed on the results of the sequential extraction by comparing the total amount of metals extracted using different reagents during the sequential extraction procedure with the results of the total digestion. The recovery of the sequential extraction was calculated as follows:

$$\text{Recovery} = [(C_{\text{Exchangeable}} + C_{\text{Carbonate}} + C_{\text{Reducible}} + C_{\text{Oxidisable}} + C_{\text{Residual}})/C_{\text{totaldigestion}}] \times 100$$

The results shown in Table 2 indicate that the sums of the five fractions are in good agreement with the total digestion results with the satisfactory recoveries (75.07–120.70%) and the method used is reliable and repeatable.

2.4. *Detection limit*

Detection limits (DLs) were determined for the four studied metals in each fraction, following the procedure of Miller and Miller [16]. Ten analytical blanks were analysed for each step of

Table 2. Recovery % for the selected metals from the standard reference material and the internal check.

Element	IAEA-SL-1 (measured values)*		IAEA-SL-1 (certified value)	**Recovery %	Concentration (mg·kg^{-1}) Sum***	Total	****Recovery %
Cd	0.24–0.31	(0.27 ± 0.03)	0.26	103.84	0.07–2.95	0.07–2.75	79.20–110.53
Cu	28.2–33.9	(31.14 ± 2.50)	30	103.8	0.15–5.47	0.20–5.75	75.07–120.70
Pb	34.1–41.2	(37.18 ± 3.43)	37.7	98.67	31.83–831.56	38.04–865.00	75.60–118.87
Zn	220–235	(227.8 ± 5.72)	223	102.15	9.41–469.36	10.65–515.23	76.38–105.97

Notes: *Ranges and average values. **Recovery = measured/certified × 100. ***Ranges of concentrations of the fractions studied. ****Recovery = Sum/Total × 100.

Table 3. Risk Assessment Code (Perin *et al*. [17]).

Risk	Metal in carbonate and exchangeable fractions (%)
No risk	<1
Low risk	1-10
Medium risk	11-30
High risk	31-50
Very high risk	>50

the extraction process. The DLs were calculated as $3\sigma/a$, where a is the slope of the calibration curve, and σ is the standard deviation (in absorbance units) calculated from 10 readings of the sample blank. DL values took into account the use of 1 g portions of sample in extractions, and any necessary dilutions. Detection limits were determined for the metals, for each extraction step. DL values in $\mu g \cdot g^{-1}$ varied from 0.007 (carbonate fraction) to 0.009 (reducible and residual fractions) for Cd; from 0.009 (exchangeable fraction) to 0.020 (residual fraction) for Cu; from 0.020 (exchangeable fraction) to 0.090 (oxidisable and residual fractions) for Pb; and from 0.008 (exchangeable fraction) to 0.267 (residual fraction) for Zn.

2.5. *Statistical analysis*

All statistical aspects (Pearson's correlation coefficients matrix and principal component analysis) were calculated, using the MINTAB program v. 13.1.

2.6. *Risk Assessment Code*

The potential mobility of heavy metals from the studied sediments within the four sampling sections (sections a, b, c and d) was assessed using the Risk Assessment Code (RAC). The RAC assesses the availability of metals in solution by applying a scale to the percentage of sediments that can reduce metals in the exchangeable and carbonate fractions. This classification is shown in Table 3 [17].

3. Results and discussion

Total metal concentrations and the fractionation data for the studied sediments are given in Tables 4-7. The data reported are calculated as dry weight.

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Table 4. Cadmium concentrations ($mg \cdot kg^{-1}$) and percentages in each fraction of studied sediments.

Stations		Exchangeable fraction		Carbonate fraction		Reducible fraction		Oxidizable fraction		Residual fraction		Total Conc
		Conc	%	Conc	%	Conc	%	Conc	%	Conc	%	
Section (a)	I	N.D.	0.00	0.02	34.78	0.02	28.99	N.D.	0.00	0.03	36.23	0.07
	II	0.02	2.90	0.40	48.25	0.08	9.65	0.10	12.06	0.23	27.14	0.75
	III	0.02	1.36	0.58	48.94	0.18	15.29	0.28	23.79	0.13	10.62	1.25
Section (b)	IV	N.D.	0.00	0.69	*32.72*	0.38	18.07	0.46	21.87	0.58	27.34	2.00
	V	N.D.	0.00	0.73	*51.16*	0.22	15.46	0.20	14.05	0.28	19.33	1.50
	VI	0.01	0.81	0.38	39.10	0.22	22.40	0.12	12.22	0.25	25.46	1.00
Section (c)	VII	N.D.	0.00	0.09	44.44	0.02	10.10	0.04	20.20	0.05	25.25	0.25
	VIII	0.03	1.81	0.62	35.33	0.30	16.99	0.26	14.72	0.55	31.14	1.75
	IX	N.D.	0.00	1.45	49.03	0.50	16.93	0.48	16.25	0.53	17.78	2.75
Section (d)	X	N.D.	0.00	0.37	48.55	0.06	7.92	0.18	23.75	0.15	19.79	0.75
	XI	0.02	0.98	0.68	41.82	0.04	2.46	0.44	27.06	0.45	27.68	1.50
	XII	0.02	1.14	1.07	50.78	0.08	3.79	0.46	21.79	0.48	22.50	2.00
Range		N.D.–0.03	0.00–2.90	0.02–1.45	32.72–51.16	0.02–0.50	2.46–28.99	N.D.–0.48	0.00–27.06	0.03–0.58	10.62–36.23	0.07–2.75
Average		0.01	0.75	0.59	43.74	0.18	14.00	0.27	17.31	0.31	24.19	1.30
SD		0.01	0.94	0.39	6.75	0.16	7.64	0.16	7.38	0.20	6.73	0.78

Note: ND, not detected (below the detection limit).

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Table 5. Copper concentrations ($mg \cdot kg^{-1}$) and percentages in each fraction of studied sediments.

Stations		Exchangeable fraction		Carbonate fraction		Reducible fraction		Oxidizable fraction		Residual fraction		Total Conc
		Conc	%	Conc	%	Conc	%	Conc	%	Conc	%	
Section (a)	I	0.13	3.52	0.34	9.25	0.46	12.66	1.06	29.17	1.65	45.40	4.00
	II	N.D.	0.00	0.06	5.04	0.26	20.49	0.12	9.46	0.83	65.01	1.62
	III	N.D.	0.00	0.03	4.26	0.10	13.30	0.12	15.96	0.50	66.49	0.75
Section (b)	IV	0.04	0.73	0.64	11.70	1.90	34.73	1.04	19.01	1.85	33.82	5.75
	V	N.D.	0.00	0.30	11.50	0.62	23.45	0.42	15.89	1.30	49.17	2.75
	VI	N.D.	0.00	0.02	13.41	0.04	22.35	0.04	22.35	0.08	41.90	0.23
Section (c)	VII	0.09	7.82	0.17	14.92	0.20	17.76	0.12	10.66	0.55	48.85	1.50
	VIII	0.02	2.78	0.08	13.89	0.18	31.25	0.10	17.36	0.20	34.72	0.75
	IX	N.D.	0.00	0.02	6.98	0.06	17.44	0.06	17.44	0.20	58.14	0.29
Section (d)	X	0.05	3.98	0.22	18.56	0.56	46.40	0.10	8.29	0.28	22.78	1.00
	XI	0.01	1.81	0.05	10.88	0.24	54.42	0.02	4.54	0.13	28.34	0.50
	XII	0.01	5.30	0.01	5.30	0.04	26.49	0.02	13.25	0.08	49.67	0.20
Range		N.D.–0.13	0.00–7.82	0.01–0.64	4.26–18.56	0.04–1.90	12.66–54.42	0.02–1.06	4.54–29.17	0.08–1.85	22.78–66.49	0.20–5.75
Average		0.03	2.16	0.16	10.47	0.39	26.73	0.27	15.28	0.64	45.36	1.61
SD		0.04	2.57	0.19	4.44	0.52	12.98	0.38	6.68	0.63	13.81	1.73

Note: ND, not detected(below the detection limit).

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Table 6. Zinc concentrations ($mg \cdot kg^{-1}$) and percentages in each fraction of studied sediments.

Stations		Exchangeable fraction		Carbonate fraction		Reducible fraction		Oxidizable fraction		Residual fraction		Total Conc
		Conc	%	Conc	%	Conc	%	Conc	%	Conc	%	
Section (a)	I	1.02	0.22	2.06	0.44	40.22	8.57	168.08	35.81	257.98	54.96	515.23
	II	0.95	0.66	N.D.	0.00	27.16	18.75	2.00	1.38	114.75	79.21	189.65
	III	0.02	0.17	0.03	0.34	0.82	8.72	1.24	13.18	7.30	77.59	10.65
Section (b)	IV	0.52	0.14	2.67	0.74	83.26	22.93	47.48	13.08	229.10	63.11	455.54
	V	0.39	0.16	1.10	0.44	20.56	8.26	17.42	6.99	209.58	84.15	245.32
	VI	0.06	0.12	0.30	0.59	4.38	8.55	3.44	6.72	43.03	84.01	50.65
Section (c)	VII	0.47	0.18	0.87	0.33	33.10	12.46	13.76	5.18	217.40	81.85	250.65
	VIII	0.18	0.18	0.48	0.50	23.42	24.40	7.74	8.06	64.18	66.86	105.68
	IX	0.01	0.05	0.13	0.86	0.48	3.24	0.52	3.50	13.70	92.34	15.77
Section (d)	X	0.72	0.29	0.74	0.30	58.58	23.65	4.24	1.71	183.38	74.05	234.43
	XI	0.07	0.06	1.07	0.89	34.28	28.48	36.78	30.56	48.15	40.01	125.65
	XII	0.14	0.28	0.72	1.41	14.90	29.11	1.04	2.03	34.38	67.17	60.52
Range		0.01–1.02	0.05–0.66	N.D.–2.67	0.00–1.41	0.48–83.26	3.24–29.11	0.52–168.08	1.38–35.81	7.30–257.98	40.01–92.34	10.65–515.23
Average		0.38	0.21	0.85	0.57	28.43	16.43	25.31	10.68	118.58	72.11	188.31
SD		0.36	0.16	0.81	0.36	24.32	9.09	47.44	11.27	94.39	14.56	163.74

Note: ND, not detected (below the detection limit).

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Table 7. Lead concentrations ($mg \cdot kg^{-1}$) and percentages in each fraction of studied sediments.

Stations		Exchangeable fraction		Carbonate fraction		Reducible fraction		Oxidizable fraction		Residual fraction		Total Conc
		Conc	%	Conc	%	Conc	%	Conc	%	Conc	%	
Section (a)	I	4.54	1.17	4.38	1.13	56.88	14.70	N.D.	0.00	321.13	83.00	370.00
	II	0.32	0.40	5.10	6.32	24.78	30.72	3.74	4.64	46.73	57.93	106.69
	III	0.18	0.41	1.07	2.37	14.22	31.45	5.22	11.54	24.53	54.23	38.04
Section (b)	IV	4.88	0.74	20.33	3.09	402.28	61.16	18.04	2.74	212.28	32.27	865.00
	V	7.10	0.85	30.02	3.61	339.96	40.88	76.10	9.15	378.38	45.50	745.00
	VI	3.50	0.67	49.78	9.57	277.80	53.38	60.30	11.59	129.03	24.79	450.00
Section (c)	VII	7.29	1.13	24.50	3.78	266.14	41.10	61.38	9.48	288.28	44.52	549.97
	VIII	3.52	1.19	9.34	3.15	158.18	53.28	22.08	7.44	103.78	34.95	250.00
	IX	0.33	0.21	0.83	0.53	29.58	18.87	10.02	6.39	116.00	74.00	185.00
Section (d)	X	2.54	0.54	28.26	6.02	310.24	66.07	7.62	1.62	120.88	25.74	417.63
	XI	N.D.	0.00	8.86	4.07	112.86	51.81	N.D.	0.00	96.13	44.13	183.43
	XII	0.02	0.08	2.18	6.86	23.82	74.83	0.88	2.76	4.93	15.47	40.00
Range		N.D.–7.29	0.00–1.19	0.83–49.78	0.53–9.57	14.22–402.28	14.70–74.83	N.D	0.00–11.59	4.93–378.38	15.47–83.00	38.04–865.00
Average		2.85	0.62	15.39	4.21	168.06	44.85	22.12	5.61	153.50	44.71	350.06
SD		2.73	0.42	15.28	2.57	143.33	18.59	27.53	4.25	120.31	20.12	268.63

Note: ND, not detected(below the detection limit)

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3.1. *Total metal concentrations*

Cadmium inputs to the marine environment are derived from both natural (volcanoes, dusts and run-off) and anthropogenic sources [18]. In the present study, Cd ranged between 0.07 and 2.75 $\mu g \cdot g^{-1}$. Except for station I, the concentrations of Cd are greater than the recommended value for unpolluted marine sediments (0.11 $\mu g \cdot g^{-1}$ dry weight) [19], and indicate that there is a source of Cd contamination. The levels of Cd in the present study are relatively higher than those reported for Wadi EL-Gemal area (0.02–0.16 $\mu g \cdot g^{-1}$) [20] and lower than those observed for Hurghada region (1–5.25 $\mu g \cdot g^{-1}$) [12]. Both are located on the Egyptian Red Sea.

The concentration of Cu in the studied sediments was in the range 0.20–5.75 $\mu g \cdot g^{-1}$. These levels are below the contamination levels stated by the Swedish Environmental Protection Agency (EPA) (80 $mg \cdot kg^{-1}$) [21]. The Swedish EPA is responsible for a wide range of issues including pollution control, nature conservation and the establishment of national parks, and hunting regulation. The concentrations of Cu in the present study are considerably lower than those previously reported for Red Sea sediments (5.2–453.6 $\mu g \cdot g^{-1}$ and 2.5–95.3 $\mu g \cdot g^{-1}$) [12,20]. Zn fluctuated within a wide range (10.65–515.23 $\mu g \cdot g^{-1}$). Except for stations I and IV, the concentrations of Zn found in the present study are quite low and below the contamination limit. Thus according to the Swedish EPA, the level of Zn contamination is 360 $mg \cdot kg^{-1}$ [21]. Comparison of our results with former data on the Egyptian Red Sea sediments shows that our results are higher than those mentioned for Hurghada and Wadi EL-Gemal (8.8–245 $\mu g \cdot g^{-1}$ and 18.2–283.03 $\mu g \cdot g^{-1}$, respectively) [12,20].

Lead inputs into the marine environment are derived from anthropogenic sources, including mining and the combustion of coal, wood and other organic matter. It has been estimated that as much as 90% of the atmospheric input into the sea may be of anthropogenic origin [18]. There is evidence from analyses of inshore sediments that lead inputs have increased in recent years. Indeed, the greatest metal concentration in the studied sediment was for Pb (38.04–865.00 $\mu g \cdot g^{-1}$). These levels exceeded the recommended value for unpolluted marine sediments (19 $\mu g \cdot g^{-1}$) [19]. The concentrations of Pb in the present study are considerably higher than those reported in previous studies for Egyptian Red Sea sediments (9.9–114.4 $\mu g \cdot g^{-1}$ and 12.8–96.3 $\mu g \cdot g^{-1}$) [12,20]. It seems that the use of leaded petrol in engines associated with tourism equipment, including submarines, is one of the factors affecting the concentration of Pb in the studied sediments and this effect may increase over time.

Pearson's correlations between the four studied metals and the depth were investigated (Table 8). Apparently, Cu, Zn and Pb were significantly correlated. The correlation coefficients between Cu and Zn, Cu and Pb, Zn and Pb were 0.902 ($p = 0.00$), 0.709 ($p = 0.010$) and 0.641 ($p < 0.05$), respectively. Moreover, negative correlations exist between the depth and the concentrations of Cu ($r = -0.663$, $p < 0.05$), Zn ($r = -0.850$, $p = 0.00$) and Pb ($r = -0.586$, $p < 0.05$),

Table 8. Correlation matrices for the studied metals and depth.

	Depth	*Cd*	*Cu*	*Zn*
Cd	0.519			
	0.084			
Cu	**−0.663**	−0.163		
	0.019	0.612		
Zn	**−0.850**	−0.452	**0.902**	
	0.000	0.140	**0.000**	
Pb	**−0.586**	−0.107	**0.709**	**0.641**
	0.045	0.740	**0.010**	**0.025**

Note: The bold data represent significant correlations.

respectively. This means that these metals probably originate from a common source which is mostly derived from a terrestrial source close to the sea. Indeed, Madkour *et al.* [22] asserted that the Red Sea lagoons receive sediments from two different sources; the terrigenous inputs from the Hinterland Mountains and skeletal carbonates from the sea. However, no significant relationship between the concentrations of the metals (Cu, Zn and Pb) and Cd was observed, suggesting that Cd is not associated with these metals. Furthermore, Cd might have different anthropogenic and/or natural sources. In general, the present study shows that the total metal concentrations in the sediments tended to vary among stations, at the same time some stations (especially station IV) displayed particularly high levels. This variation may be due to the differences in the sources of metal and physical–chemical conditions favoring sediment contamination.

3.2. *Fractionation of the studied metals*

3.2.1. *Exchangeable fraction*

It was found that the concentrations of the studied metals in the exchangeable fraction are generally low. The levels of Cd and Cu are nil for almost stations and the maximum concentrations does not exceed 0.03 and 0.13 $\mu g \cdot g^{-1}$ for Cd and Cu, respectively. These values are accounted for < 3 and 8% of the total Cd and Cu contents, respectively. The concentration of Zn ranged between 0.01 and 1.02 $\mu g \cdot g^{-1}$. Among the studied metals, the obtained Pb values for this fraction are the highest especially at stations V and VII (7.10 and 7.29 $\mu g \cdot g^{-1}$, respectively). The exchangeable fraction accounted for almost $< 1\%$ of the total Zn and Pb contents. Marin *et al.* [23] stated that the exchangeable fraction includes weakly adsorbed metals retained on the solid surface by relatively weak electrostatic interaction, metals that can be released by ion-exchange processes. Changes in the ionic composition, influencing adsorption–desorption reactions or lowering of pH could cause remobilisation of metals from this fraction. Exchangeable metal ions are a measure of those trace metals which are released most readily into the environment [24].

3.2.2. *Carbonate fraction*

Carbonate can be an important adsorbent for many metals when organic matter and Fe–Mn oxides are less abundant in the aquatic system [24]. The carbonate form is a loosely bound phase and liable to change with environmental conditions [25]. The concentrations of studied metals in the carbonate fraction varied between 0.02 and 1.45 $\mu g \cdot g^{-1}$, 0.01 and 0.64 $\mu g \cdot g^{-1}$, not detected (ND) and 2.67 $\mu g \cdot g^{-1}$, and 0.83 and 49.78 $\mu g \cdot g^{-1}$ for Cd, Cu, Zn and Pb, respectively. The results showed that there are high percentages of Cd bound to carbonate fraction (32.72–51.16%) in comparison with Cu (4.26–18.56%), Zn (0.00–1.41%) and Pb (0.53–9.57%). This is because Cd has a special affinity with carbonate and may co-precipitate with carbonate minerals at high pH [26]. The preferential association between Cd and carbonate was also mentioned in previous studies [8,9,27].

3.2.3. *Reducible fraction*

Hydrous oxides of manganese and iron are extracted together in this fraction, the well-known 'sinks' in the surface environment for heavy metals [28]. Scavenging by these secondary oxides, present as coatings on mineral surfaces or as fine discrete particles, can occur by any or a combination of the following mechanisms: co-precipitation, adsorption, surface complex formation, ion exchange and penetration of the lattice [29]. They are thermodynamically unstable under the anoxic circumstances and are attacked by benthic organisms [30]. These oxides are present in large

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proportions in soil and sediments [31]. Indeed, in the present study, the concentration ranges of Cd, Cu, Zn and Pb associated with the reducible fraction are appreciable (0.02–0.50, 0.04–1.90, 0.48–83.26 and 14.22-402.28 $\mu g \cdot g^{-1}$, respectively). These levels accounted for 14.00 ± 7.64, 26.73 ± 12.98, 16.43 ± 9.09 and 44.85 ± 18.59 average percentages of the total Cd, Cu, Zn and Pb content, respectively. The results showed that the levels and percentages of Pb adsorbed to Fe–Mn oxides are the highest. Similarly, Jones and Turki [32] found that most of lead was present in the Fe–Mn oxide fraction in the sediments of the Tees estuary (north-east England). This is may be because Pb can form stable complexes with Fe and Mn oxides [33]. Moreover, Perin *et al.* [34] stated that not only do manganese and iron act as adsorbants during oxide/hydroxide co-precipitation, but lead reacts with Fe or with itself to form a stable and solid compound. This may account for the high concentration of Pb in this fraction. It was observed that appreciable concentrations of Zn are bound with the reducible fraction. Davis and Leckie [35] reported that amorphous sesquioxides have a greater ability to retain the heavy metal relative to their specific surface area. Zn is absorbed by oxides as well as being occluded in the structure. The similarity between the atomic radius of Zn and Fe makes their exchange possible. The significant association of Zn with this fraction has been extensively observed in previous studies [6, 36]. The sequential extraction results of the current study suggest that Fe–Mn oxides may be the main carriers for Pb and to a lesser degree for Zn in sediments.

3.2.4. *Oxidisable fraction (organic matter/sulfide-bound fraction)*

Heavy metals have great affinity with organic ligands [37]. The metals may be associated through complexation or bioaccumulation process with various forms of organic material such as living organisms, detritus or coatings on mineral particles [30]. In the present study, Tables 2–5 show that, in general, the levels of Cd, Cu, Zn and Pb associated with the organic fraction are appreciable (ND–0.48, 0.02–1.06, 0.52–168.08 and ND–76.10 $\mu g \cdot g^{-1}$, respectively). Based on average values, the order of binding strength for metal ion percentages onto organic matter is Cd > Cu > Zn > Pb. Bruland [38] showed that the biogeochemistry of Cd is strongly dominated by the organic matter cycle. In the marine environment, Cd is fixed by phytoplankton in the surface water and is transported towards the floor with the remains of these organisms, when organic detritus is decomposed Cd is liberated with other mineralisation products. Organic matter plays an important role in the immobilisation of Cu. This is probably due to the well-known tendency of copper to form organic complexes, e.g. with humic acids and the various metabolites deriving from algal biomass decomposition and other biochemical reactions [39]. Copper can easily complex with organic matter because of the high formation constants of organic–Cu compounds [40]. The high percentage of Zn in the organic fraction may be related to the tendency of the metal to be readily adsorbed by organic molecules [41]. Degradation of organic matter under oxidising conditions can lead to a release of soluble trace metals bound to this component [42]. However, the organic fraction released in the oxidisable step is not considered very mobile or available since it is thought to be associated with stable high molecular mass humic substances that release small amounts of metals in a slow manner [43].

3.2.5. *Residual fraction*

This fraction mainly contains crystalline-bound trace metals [27]. Tables 2–5 show that the residual fraction was within the ranges 0.03–0.58, 0.08–1.85, 7.30–257.98 and 4.93–378.38 $\mu g \cdot g^{-1}$ for Cd, Cu, Zn and Pb respectively. Based on average values, this fraction is the most important phase for binding Zn ($72.11 \pm 14.56\%$) and to a lesser degree for Cu and Pb (45.36 ± 13.81 and $44.71 \pm 20.12\%$, respectively). The higher percentages of Zn in the residual fraction indicating that this

metal is derived from natural geological sources [6] and has less potential for mobilisation from the studied sediment. Indeed, metals found in the residual fraction are expected to be chemically stable and biologically inactive. This means that the greater the percentage of heavy metal present in this fraction, the lower the degree of pollution [27]. The high percentage of Zn in the residual fraction found in this study agrees with the results of Singh *et al.* [27]. By contrast, the lower percentages of Cd in this fraction (24.25 ± 5.97) indicate that either the anthropogenic inputs to surface sediments from the recent industrial development and/or urbanisation in the surrounding areas.

3.3. *Principal component analysis*

Chemical fractionation studies are usually carried out using univariate procedures (element to element or sample to sample), but multivariate methods such as principal component analysis (PCA) can provide further interpretation of results [44]. PCA is a data reduction procedure the main goal of which is to provide an easy visualisation of the relationships existing amongt the variables determined in large or complex datasets, including those obtained in fractionation studies [45]. In the present study, the dataset used was the percentages of metals in the different fractions as objects (lines), with the metals measured as variables (colums). Two significant factors explain 88.3% of the total variance. PC1 accounts for 63.2% of the total variance and PC2 for 25.1% (Table 9). The results show that PC1 is negatively related to the concentrations of Cu, Zn and Pb (-0.606, -0.570 and -0.555, respectively), indicating that there exists an association between these metals. Indeed, these metals are mostly associated with appreciable percentages in the residual fraction of sediments. The behaviour of Cd is completely different and is strongly associated with PC2 (positive loading; 0.996). This may be due to the lower percentage of Cd in the residual fraction. In order to test whether the distribution of metallic fractions follows a similar trend, a new PCA was applied. In this case, the normalised matrix was composed of lines (metals) and columns (% of fractions). Table 9 shows that two principal components were extracted, together explaining 69.6% (PC1: 41.2%; PC2: 28.4%) of the information contained in the initial variables. It was observed that the residual fraction was the only one related positively to both factors (PC1: 0.539; PC2: 0.512). So, the results of the PCA confirmed the previous observations and comments.

3.4. *Risk Assessment Code*

The percentages of studied metals associated in the carbonate and exchangeable fractions for the studied sampling sites were calculated, and their average percentages in different sections (a, b, c and d) are presented in Figure 3. For Cd, the average percentages in the samples analysed were 45.41 ± 9.21, 42.26 ± 9.30, 43.54 ± 6.00 and 47.76 ± 4.61 for sections a, b, c and d, respectively. Cadmium values are high, however, no spatial pattern was observed. These results suggest that Cd poses a high risk to the environment. The association of Cu in carbonate and exchangeable fractions in different sections was in the order: section a $<$ section b $<$ section c $=$ section d.

Table 9. Principal component analysis (PCA) results.

Variable	PC1	PC2	Variable %	PC1	PC2
Cd	−0.020	0.996	Exchangeable	−0.144	−0.226
Cu	−0.606	0.024	Carbonate	−0.620	−0.026
Zn	−0.570	0.021	Reducible	0.214	−0.766
Pb	−0.555	−0.085	Oxidizable	−0.509	0.316
—	—	—	Residual	0.539	0.512
Total variance %	63.2	25.1	Total variance %	41.2	28.4
Cumulative variance %	63.2	88.3	Cumulative variance %	41.2	69.6

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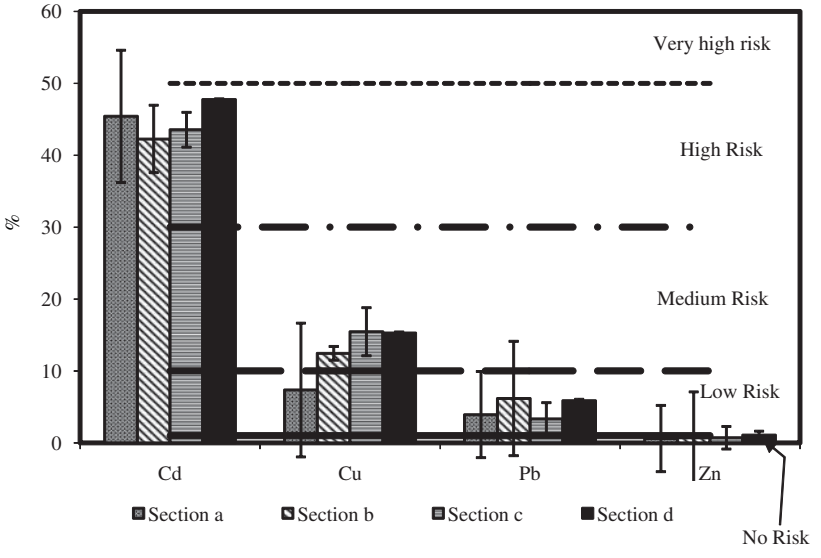

Figure 3. Percentages of studied metals in carbonate and exchangable fractions at different sections.

Their values reveal that Cu is medium risk (sections b, c and d) and in some cases it poses low risk (section a). Similarly, Pb poses a low risk where their percentages were 3.93 ± 2.42, 6.18 ± 3.35, 3.33 ± 2.26 and 5.85 ± 1.56 for sections a, b, c and d, respectively. For all studied sections, Zn shows low affinity towards binding with the carbonate and exchangeable fractions where its maximum affinity does not exceed 1.08 ± 0.56 (section d). This is because Zn is present as a major portion in the residual fraction. In general, for almost all samples, the data show that Zn has no risk ($< 1\%$). Overall, the data suggest that the rates of mobilisation and availability of metals were significantly higher for Cd and to some extent for Cu. However, this availability depends greatly on the properties of particle's surface, on the kind of strength of the bond, and on external conditions such as pH, Eh, salinity, and concentration of organic and inorganic complexation agents [46].

4. Conclusions

The results of this study supply valuable information about fractionation analysis and the potential mobility of cadmium, copper, lead and zinc in sediments from 12 sample sites in the north-western part of the Red Sea, where improper recreational facilities have resulted in diverse impacts on the coastal environments fronting some of the recreation projects. The results showed that, among the studied sediment fractions, the exchangeable fraction percentages were lowest for all the metals. For Cd, the carbonate fraction was predominant, followed by the residual fraction. Cd was retained almost equally by organic and reducible phases fractions. Cu and Zn were concentrated in the residual fraction. Proportions of these Cu and Zn were second in the reducible phase fraction followed by the organic matter and carbonate fractions. For Pb, the fractions bounded to the residual fractions and the reducible phases are equal and exhibited the highest percentages. However, the carbonate and organic fractions associated with Pb were small in terms of percentage and almost the same. Based on the RAC, we suggest that the rates of mobilisation and availability of metals were significantly higher for Cd and to some extent for Cu. Finally, this study was not detailed enough to estimate a number of pollutants. Hence, more comprehensive studies, covering this region and other resources in the Egyptian coast of the Red Sea, are needed.

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