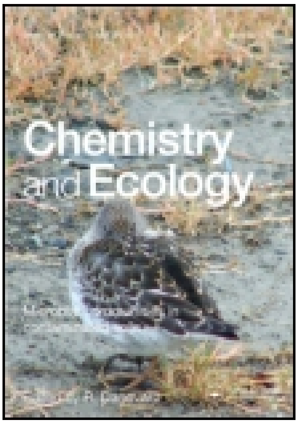

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Fractionation of trace metals (Mn, Zn, Cu, Pb) in Red Sea sediments, Gulf of Aden, Yemen

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A sequential extraction technique was applied to estimate the chemical association of Mn, Zn, Cu and Pb in five chemical phases (exchangeable, carbonate, Fe–Mn oxides, organic matter and residual) in sediments of the Gulf of Aden, Yemen. The results indicated that a higher level of Mn was associated with the residual fraction (natural sources) than the non-residual fraction (anthropogenic sources). Zn fractionations revealed that it was associated more with Fe–Mn oxides and organic fractions than exchangeable and carbonate fractions. Most of the Cu was present in the residual form (60–72%) except for in the main port area (zone III), where it was associated with the organic phase (77% of the total Cu content, the organic matter content was 5%). Similarly, most Pb was bound in the residual fraction (56–71%) except the main port area where $\sim$ 62% of the total Pb was bound in non-residual fractions. It was also found that the Pb concentration in the exchangeable fraction was very high compared with other metals. The risk assessment code for the metals showed a low risk for Zn and Cu, but low to medium risk for Mn. Fractionation of Pb showed medium risk at most of the regions except at the eastern area, which revealed a high risk for the aquatic environment.

Keywords: sequential extraction; heavy metals; risk assessment; Gulf of Aden

1. Introduction

The Gulf of Aden consists of the inner harbour, the oil harbour serving the Aden refinery, and the anchorage and approach channels of the outer harbour. The Gulf of Aden is an essential waterway for the transportation of oil from the Persian Gulf, making it very important for the world economy. It has a rich marine life in terms of both quantity and variety. Different habitats such as mangroves, sea grasses and coral-reef territories are fairly widespread within the Red Sea/Gulf of Aden region. Problems of physical alteration and the destruction of habitats are a result of dredging and filling operations associated with urban expansion, tourism and industrial development. In general, the main sources of marine pollution are from land-based activities, including urbanisation and coastal development, industries including power and desalination plants, refineries, recreation and tourism, wastewater treatment facilities, coastal mining and quarrying activities, and oil bunkering. Marine sediments can be sensitive indicators for monitoring contaminants in aquatic environments [1].

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Sequential extraction of elements from sediment is a common analytical tool and is a widely applied technique in geochemical exploration and environmental geochemistry [2]. A large number of sequential extraction methods have been reported, many of which are variants on Tessier's procedure [3] in which the different fractions are extracted with different reagents [4]. Although the reagents used in sequential extraction procedures may be insufficiently specific to exclusively dissolve the 'target' phases, and the results obtained can vary widely when different extraction schemes and experimental conditions are used, useful information has been gained from such studies [5–7]. For years, sequential extraction procedures have been developed and applied to extract elements from sediment under different conditions [8]. To assess the environmental impact of sediment pollution, chemical partitioning of trace metals among the various geochemical phases is more useful than measurement of the total metal content. Metal speciation gives more information about the potential release of contaminants, migration and toxicity of the metals, as well as a risk assessment of these metals [9]. Most studies have focused on trace metal bioaccumulation in mussels and molluscs, as well as oil pollution. A number of studies have been carried out to determine the levels of heavy metals in the Red Sea sediments of Yemen [10–12]. This tudy is the first in the region to be focused on the assessment and chemical fractionation of trace metals in sediments of the Gulf of Aden, Yemen.

2. Material and methods

2.1. *Study area*

The Gulf of Aden (Figure 1) is a deepwater basin forming a natural link between the Red and Arabian Seas. This region is characterised by an arid climate, with low rainfall in the form of showers of short duration, with thunderstorms and occasionally with dust storms. Geographically, Aden is situated at latitude 12° 47′ N and longitude 44° 57′ E. It is located at the south west tip of Yemen and the Arab peninsula. It is one of the largest natural harbours in the world with an

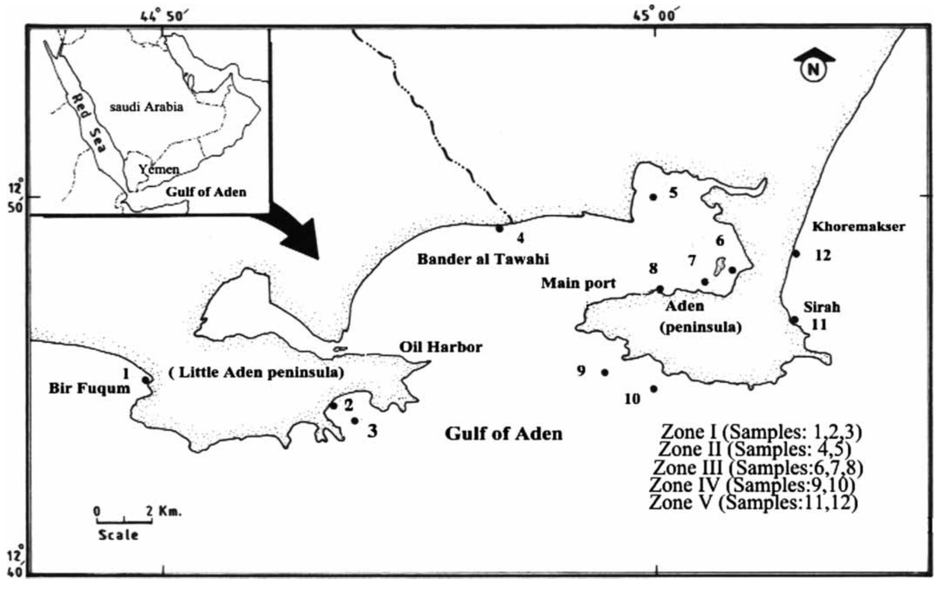

Figure 1. Sampling sites, Aden port.

area of ~ 70 km^2 of sheltered water, surrounded by Jebel Shamsan, Khoremakser and the shore which extends to the hills of Little Aden.

2.2. *Sample collection and analysis*

Duplicate sediment samples were collected during 2004 from 12 sites across the Gulf of Aden region (Figure 1). Sampling sites were chosen to assess spatial differences in trace metal concentrations of the Gulf sediments. The area was divided into five zones for a proper evaluation of the area. Zone I is located on the western part of the port of Aden (samples 1–3), zone II (samples 4 and 5) is located north of the port (polluted by industrial waste), zone III is a highly polluted area due to more human activity, represents the main port, and consists of three samples (6–8), and zone IV (samples 9 and 10) and zone V are located in the eastern area of the port (samples 11 and 12). Sediments were collected using a van Veen grab sampler and were placed into sealed polyethylene bags, carried to the laboratory in an ice box and stored at 4 °C in the dark.

For total heavy metals analysis, powdered samples (0.3 g) were digested with HNO_3, HF, aqua regia (HNO_3:HCl) and $HClO_4$ [13]. The samples were analysed using a Perkin–Elmer atomic absorption spectrophotometer (model 2830). The concentrations of the trace metals were determined in $\mu g \cdot g^{-1}$. Total carbonate content was determined using the method described by Dean [14]. Organic matter in the sediments was determined using the wet oxidation method as described by El-Wakeel and Riely [15].

2.3. *Sequential extraction procedure*

Sediments were sequentially extracted (Table 1) according to Tessier's procedure [3]. The residual fraction was determined after digestion with an acid mixture ($HNO_3/HClO_4$/HF, 3:2:1) [16].

2.4. *Quality control studies*

Quality control studies for the total concentrations of metals were carried out using a reference material as shown in Table 2 (HISS-1, National Research of Council of Canada). The reference material was analysed in duplicate in six batches, and the accuracy of the results ranged between 90 and 110%, whereas precision was agreed to be within 10%. Table 2 illustrates the concentrations of different metals in the reference materials. The variation coefficients were 8.5 for Mn, 7.4 for Zn, 4.2 for Cu and 6.5 for Pb. Comparison of the sum of the fractions with the results from the total concentrations (a separate strong acid digestion) was used to assess quality control for the sequential extractions procedure; the percentage recovery of the metals was found to be within ±20%.

Table 1. Extraction procedures for different heavy metal fractions.

Fraction	Extraction reagent	Extraction conditions
Exchangeable	1 M $MgCl_2$, pH 7.0	Shaken at room temperature for 1 h with continuous agitation
Carbonate	1 M NaOAC adjusted to pH 5 with HOAC	Shaken at room temperature for 5 h with continuous agitation
Fe-Mn oxides	0.04 M $NH_2OH.HCl$ in 25% (v/v) HOAC	Heat in water bath at 96 ± 3 °C for 6 h
Organic matter	0.02 M HNO_3 + 30% H_2O_2 (adjusted to pH 2 with HNO_3). On cooling add 3.2 M NH_4OAC in 20% (v/v) HNO_3	Shaken occasionally at 85 °C for 5 h then shaken on the addition of NH_4OAC for a further 0.5 h
Residual	Digested with acid mixture ($HNO_3/HClO_4$/HF; 3:2:1)	Evaporated to near dryness at 80 °C, complete with 0.1 M HCl to 25 mL volumetric flask

Table 2. The concentrations of different metals (mg·kg^{-1}) in the reference materials (HISS-1, National Research of Council of Canada).

Metal	Found	Certified
Mn	60.85 ± 4.2	61.24 ± 2.30
Zn	4.74 ± 0.79	4.60 ± 1.21
Cu	2.19 ± 0.37	2.08 ± 0.08
Pb	3.03 ± 0.40	2.83 ± 0.74

3. Results and discussion

3.1. *Grain size, carbonate and organic matter studies*

Heavy metal distributions in marine deposits are influenced by sediment texture, organic carbon and carbonates [17]. The results of grain size analysis for the studied sediments, carbonates and organic matter are listed in Table 3. Sediments were composed mainly of sand and silt, except for zone IV which is characterised by a relatively high clay content (24.0%). The organic matter varied from 0.69% at zone IV to 2.98% at zone III. The carbonate content was highest (64.50%) at zone IV and lowest at zone V (9.34%). The variation in the carbonate content was due to variability in the mineralogical components.

3.2. *Fractionation of heavy metals*

Manganese is mostly concentrated in the residual fraction, it represented >64% of the total concentration in zones I–IV, whereas it was <20% in zone V. The other important Mn phase is the non-residual form. Associations of Mn with different fractions in five zones are given in Table 4 and Figure 2. Mn content in the five fractions of the five zones (Table 4) can be arranged in the following order: residual (243.83 µg·g^{-1}) > Fe–Mn oxides (44.80 µg·g^{-1}) > organic form (25.00 µg·g^{-1}) > carbonate (23.90 µg·g^{-1}) > exchangeable (1.44 µg·g^{-1}).

Zinc fractionation revealed that a major part is found to be associated with the Fe–Mn oxides and organic phases compared with the exchangeable and carbonate phases. Zn in oxides and

Table 3. Physical and chemical characteristics of sediments from the Gulf of Aden, Yemen (2004).

	Grain size analysis (%)					
Zones	Sand	Silt	Clay	Sediment type	$CaCO_3$ (%)	Organic matter (%)
I	80.4	12.3	7.3	Loamy sand	36 (29.67–58.0)	1.24 (1.18–2.05)
II	75.0	10.5	14.5	Sandy loam	34 (18.33–49.67)	1.72 (1.06–2.09)
III	43.0	38.7	18.3	Sandy loam	38.28 (28.4–50.0)	2.98 (1.47–5.04)
IV	72.50	3.50	24.0	Sandy clay loam	64.5 (51.33–78.67)	0.69 (0.66–0.72)
V	80.5	2.00	17.5	Sandy loam	9.34 (5.67–13.00)	0.87 (0.80–0.93)

Table 4. Average (range) concentrations of Mn (µg·g^{-1}) in five fractions of Gulf of Aden sediments.

Zone	Exchangeable form	Carbonate form	Oxides form	Organic form	Residual form
I	1.3 (0.70–1.69)	14.0 (7.16–25.76)	30.7 (21.35–42.16)	15.5 (9.80–19.22)	270 (155–320)
II	1.9 (1.65–2.07)	41.0 (32.71–50.23)	52.7 (45.77–54.60)	21.1 (16.9–25.4)	346 (153–504)
III	2.0 (1.93–2.21)	26.1 (16.69–37.38)	63.2 (52.41–73.78)	41.7 (19.3–79.3)	237 (156–301)
IV	0.8 (0.78–0.84)	8.30 (8.00–8.60)	29.7 (29.0–30.40)	11.0 (9.61–12.4)	339 (156–481)
V	1.1 (0.84–1.26)	29.80 (29.0–31.60)	47.6 (39.85–55.4)	35.9 (24.4–47.35)	26.0 (29.4–33.7)

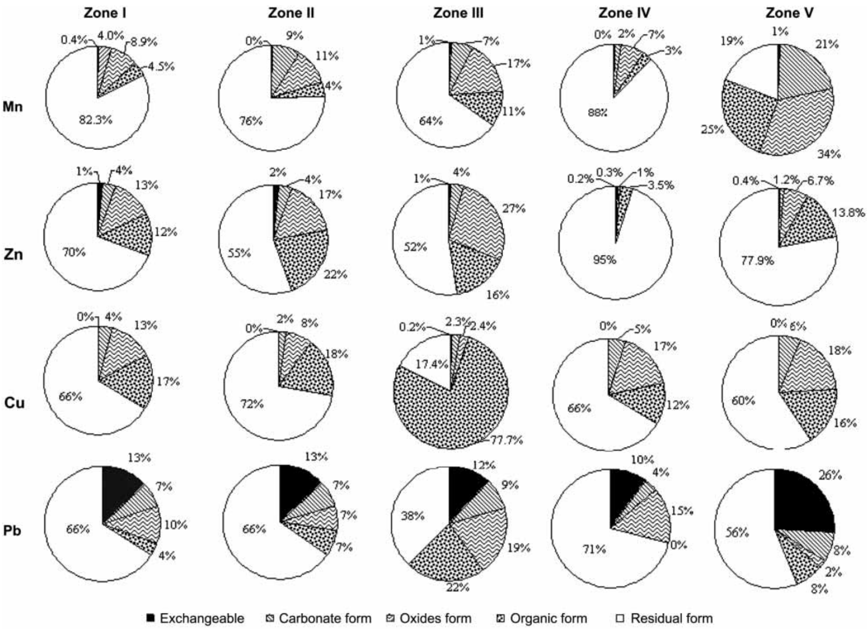

Figure 2. Percentage Mn, Zn, Cu and Pb fractionation from total content in Gulf of Aden sediments.

Table 5. Average (range) concentrations of Zn ($\mu g \cdot g^{-1}$) in five fractions of Gulf of Aden sediments.

Zone	Exchangeable form	Carbonate form	Oxides form	Organic form	Residual form
I	0.63 (0.48–0.86)	1.60 (0.96–2.79)	5.58 (1.99–10.26)	5.27 (3.79–6.98)	27.8 (11.88–40.1)
II	0.65 (0.60–0.70)	1.64 (1.14–2.13)	6.92 (2.2–11.64)	9.15 (7.49–10.81)	21.3 (16.24–29.7)
III	1.13 (0.42–1.80)	7.14 (2.87–13.12)	50.5 (15.64–106.1)	30.5 (12.84–63.45)	93.5 (59.9–113.1)
IV	0.36 (0.35–0.360	0.47 (0.34–0.59)	1.64 (1.59–1.69)	5.69 (5.24–6.13)	137.9 (73–203)
V	0.29 (0.26–0.36)	0.93 (0.38–1.48)	5.39 (2.40–8.37)	11.1 (8.22–13.90)	55.9 (61.0–49.9)

organic fractions constitutes ~ 4.5% of the total Zn in zone IV, reaching 43% in zone III. Zn bound to the exchangeable fraction is very low. Associations of Zn with the different fractions are given in Table 5 and Figure 2. The average values of Zn in the five fractions of the five zones are shown in Table 2. They are arranged as follows: residual ($71.21\,\mu g \cdot g^{-1}$) > Fe–Mn oxides ($14.0\,\mu g \cdot g^{-1}$) > organic form ($12.3\,\mu g \cdot g^{-1}$) > carbonate ($2.69\,\mu g \cdot g^{-1}$) > exchangeable ($0.60\,\mu g \cdot g^{-1}$).

Copper (Figure 2 and Table 6) is concentrated in the organic fraction rather than in other forms, indicating its association with the organic phase. The exchangeable fraction was not detected in the study area, except in zone III ($0.1\,\mu g \cdot g^{-1}$). Average values of Cu in the five fractions of the five zones are shown in Table 6. They are arranged as follows: organic form ($9.6\,\mu g \cdot g^{-1}$) > residual ($9.1\,\mu g \cdot g^{-1}$) > Fe–Mn oxides ($1.8\,\mu g \cdot g^{-1}$) > carbonate ($0.7\,\mu g \cdot g^{-1}$) > exchangeable (not detected).

Lead in the environment may be derived from either natural or anthropogenic sources. Natural sources include geological weathering and volcanic emissions. Pb and its compounds may enter the environment at any point from industrial effluent, sewage sludge, domestic waste, pigments, petrol (gasoline) additives, steel products and the combustion of fossil fuels. In our study area, a major part of Pb is concentrated in the residual fraction. The concentration of Pb bound in residual fraction varies from 38% in zone III to 56% in zone V and 71% in zone IV. The next important

Table 6. Average (range) concentrations of Cu ($\mu g \cdot g^{-1}$) in five fractions of Gulf of Aden sediments.

Zone	Exchangeable form	Carbonate form	Oxides form	Organic form	Residual form
I	ND	0.72 (0.54–1.04)	2.23 (1.69–3.24)	2.84 (1.8–3.23)	11.22 (8.21–13.68)
II	0.12 (ND to 0.16)	0.41 (0.39–0.42)	1.46 (0.98–1.94)	3.25 (2.03–4.46)	12.14 (9.26–14.3)
III	ND	1.12 (0.44–2.23)	1.21 (0.79–1.50)	38.6 (7.90–98.70)	10.7 (9.03–14.8)
IV	ND	0.61 (0.53–0.69)	2.31 (1.70–2.91)	1.56 (1.48–1.63)	9.19 (8.89–9.48)
V	ND	0.62 (0.67–1.04)	1.81 (1.65–3.24)	1.62 (1.64–3.23)	5.7 (4.56–13.68)

Note: ND, not detected.

Table 7. Average (range) concentrations of Pb ($\mu g \cdot g^{-1}$) in five fractions of Gulf of Aden sediments.

Zones	Exchangeable form	Carbonate form	Oxides form	Organic form	Residual form
I	11.3 (0.59–12.15)	6.1 (5.52–6.81)	6.03 (ND to 14.37)	3.08 (2.63–3.64)	50.47 (37.6–60.3)
II	10.1 (10.1–10.16)	5.76 (5.65–5.86)	5.48 (12.86–8.1)	5.7 (2.29–9.10)	46.38 (36.3–51.5)
III	11.4 (10.58–12.4)	8.0 (6.43–9.55)	18.22 (12.64–29.3)	20.99 (10.11–40.9)	34.36 (22.9–42.1)
IV	11.7 (11.2–12.24)	4.31 (4.1–4.57)	17.9 (15.73–20.1)	ND	77.9 (58.0–92.0)
V	8.28 (6.2–10.35)	1.51 (0.92–2.1)	0.42 (0.04–0.8)	1.66 (0.61–2.70)	10.64 (4.41–16.9)

Note: ND, not detected.

phase of Pb concentration is in the non-residual fraction (labile form). The association of Pb with different fractions is shown in Figure 2 and Table 7. As shown in Table 4, the average values for the five fractions from the study area are arranged as follows: residual ($45.18\,\mu g \cdot g^{-1}$) > Fe–Mn oxides ($10.3\,\mu g \cdot g^{-1}$) > exchangeable ($10.1\,\mu g \cdot g^{-1}$) > organic form ($8.0\,\mu g \cdot g^{-1}$) > carbonate ($5.3\,\mu g \cdot g^{-1}$).

The relative percentage of Mn about the fractionation revealed a similarity in the exchangeable fraction for the five zones; very small amounts of Mn ($<1\%$) were found in the exchangeable fraction for all samples. This indicates the low contribution of Mn from anthropogenic activities. The concentrations of Mn associated with carbonate were high in zone V, representing 21% of the total Mn (Figure 2). Mn in the exchangeable and carbonate fractions is considered to be weakly bound and may equilibrate with the aqueous phase, thus becoming more bioavailable [18]. Caplat et al. [19] found that Mn is mainly present in the acid-soluble fraction (carbonate form) and showed significant affinity for the residual fraction (up to 50%). Manganese bound with both Fe–Mn oxides and organic fractions was high in zone V, representing 59% of the total Mn. We found $\sim 28\%$ of Mn in zone III, which decreased to 13 and 15% in zones I and II, respectively. In general, Mn may be present as oxides, hydroxides or in association with iron oxides/hydroxides. Mn ions can be adsorbed and/or partially ion-exchanged on the surface of MnO_2 and they can be environmentally mobile under certain conditions [20]. Mn also bound to carbonates or was specifically adsorbed and bound to organic matter and sulfides [21]. The relative percentage of Mn associated with residual fraction is high, $> 64\%$ in zones I, II, III and IV. The high concentration of Mn in the residual fraction may be due to variation in the mineralogical composition of sediments in the study area. As shown in Table 3, the binding behaviour of Mn bound to the sediment fractions revealed high positive correlations between the Mn concentration in the organic phase and Zn, Cu and Pb in the same fraction ($r = 0.92$, 0.86 and 0.85, respectively). The relationships between Mn in the fractions with the other metals are: Mn-Oxide $= 38.793 + 0.390$ Zn-Oxide ($r = 0.71$, $p < 0.01$); Mn-OM $= 10.350 + 1.152$ Zn-OM ($r = 0.92$, $p < 0.01$); Mn-$OM = 18.612 + 0.614$ Cu-OM ($r = 0.86$, $p < 0.01$); Mn-OM $= 15.034 + 1.443$ Pb-OM ($r = 0.85$, $p < 0.01$).

Zinc is the most labile metal, recovered in the first extraction stages, and is associated with the non-residual fraction of the sediment. Zn is mainly bound to non-residual fractions [19]. Low levels of Zn are obtained in the non-residual fractions (labile form), and range from 5% in zone IV to 48% in zone III. The results shown in Figure 2 indicate that Zn is not reflecting any anthropogenic impact on the sediments in zone IV, but the relatively high concentration found in the other zones may be an indicator that these zones are releasing relatively large amounts of Zn into the aquatic environment. Fe–Mn oxides and organic fractions were reported to be the main carriers of Zn for the aquatic environment in Gulf of Aden sediments, in agreement with Fernandes [22]. Zn-bound to the oxide form ranged from 3.5% of total Zn in zone IV to 27% in zone III. Zn adsorption in the oxide fraction has a higher stability constant than in the carbonate fraction [22,23]. The percentage of Zn associated with residual fractions was in the order: zone IV (95%) $>$ zone V (77.9%) $>$ zone I (70%) $>$ zone II (55%) $>$ zone III (52%). In generally, the results indicate that $>$ 50% of the total Zn was recorded in the non-residual fraction for zones II and III, this may be due to the disposal of untreated sewage from domestic drainage and human activities in the area.

Copper bound to the different fractions of the study area as follows: organic form (11.44 $\mu g \cdot g^{-1}$) $>$ residual (9.10 $\mu g \cdot g^{-1}$) $>$ Fe–Mn oxides (1.79 $\mu g \cdot g^{-1}$) $>$ carbonate (0.73 $\mu g \cdot g^{-1}$) $>$ exchangeable (0.03 $\mu g \cdot g^{-1}$). A high concentration of Cu associated with the organic fraction was recorded in zone III (98.66 $\mu g \cdot g^{-1}$; 89% of total Cu). Zone III is characterised by a relatively high percentage (5%) of organic matter. This indicates that Cu occurs in the form of organic complexes. Cu is preferentially retained in organic matter by complexation rather than by ion exchange [24,25]. As expected from previous studies on polluted sediments [23,24], extractable Cu is mainly associated with the oxidisable phase, where it is likely to occur as organically complex metal species. This can be explained by the well-known high affinity of Cu for humic substances, which are chemically very active in Cu complexion [26,27]. Although substantial percentages of Cu are extracted in the four equivalent fractions, the most abundant is the oxidisable fraction (coinciding with organic and sulfur compounds). This agrees with the results of many studies [28–30], which state that a high proportion of Cu in the sediments may form part of the organic matter. Rapin et al. [31] reported that Cu WAS mostly bound to the organic matter/sulfide fraction (70–80%) of the marine sediment in a highly polluted area of Villefranche Bay (NW Mediterranean Sea). Cu can easily form a complex with organic material because of the high formation constants of organic-Cu compounds [32]. In aquatic systems, the distribution of Cu is mainly affected by natural organic matter, such as humic material and amino acids. However, most of the Cu is present in the residual fraction (60–72%) in the all zones except zone III (17%). The higher association with the residual fraction indicates the low bioavailability of Cu [33]. The percentage of metal in the residual fraction cannot be easily released into the environment because the metal forms a crystal lattice. The association of Cu with Fe–Mn oxides ranges between 1.21 $\mu g \cdot g^{-1}$ (2.43% of the total) in zone III and 2.31 $\mu g \cdot g^{-1}$ (17%) in zone IV. Several investigators have demonstrated that the sorption of Cu onto hydrous Fe–Mn oxides is due to co-precipitation of Cu in the Fe–Mn oxide lattice [34]. The low Cu content in the exchangeable (not detected to 0.24%) and carbonate (2.25–6.2%) fractions in our study indicates that the bioavailability of Cu to the sediments may be lower.

The residual and labile concentration of Pb in this study is similar to that recorded by El-Sikaily et al. [34] for the sediments of the Gulf of Suez (71.5–100 $\mu g \cdot g^{-1}$ dry weight) which shows that $\sim$ 50 $\mu g \cdot g^{-1}$ of the total Pb content is bound to the labile form (non-residual fraction). The residual form of Pb in the sediments of the Athens Sea is 31.2% of the total Pb [29]. High positive correlations are recorded between the concentrations of Pb and the other metals (Mn, Zn, Cu) in the organic form (Table 3). This correlation indicates that Pb and Cu are mainly discharged from urban wastes. Metals which are associated in the residual fraction are at low risk of mobility [35]. The data obtained in the exchangeable Pb fraction are similar in all zones (10.28 $\pm$ 2.92 $\mu g \cdot g^{-1}$). This indicates that Pb is highly distributed in the study area. The large amounts of Pb in the exchangeable fraction (Figure 2) indicate that Pb is from an anthropogenic source. The average concentration of Pb associated with carbonate is 5.59 $\pm$ 2.44 $\mu g \cdot g^{-1}$, the high concentration is recorded in zone III (8.33 $\mu g \cdot g^{-1}$). Pb associated with the exchangeable and carbonate fractions is considered to be weakly bound and may equilibrate with the aqueous phase, becoming more bioavailable [21]. These data might reflect the dangers of Pb in the study area. Also, Pb bound to the organic fraction and the Fe–Mn oxides fraction which is high in polluted zone III ($\sim$ 80% of the total Pb). Organic matter and Fe–Mn oxide have a high scavenging effect and may provide a sink for Pb [21,36]. In general, in the highly polluted zone III, Pb is concentrated in the non-residual fraction (anthropogenic sources). The association of Pb with the residual fraction was high in zones I, II, IV and V, representing >56% of the total Pb, and the residual solid should contain primary and secondary minerals which may hold heavy metals within their crystal structures [21,37]. This indicates a large amount of Pb discharging into the water of the study area. The behaviour of Pb bound to the sediment fractions, as shown in Table 3, revealed a high positive correlation between Pb and the carbonate phase with Zn and Cu, and significant relationships between Pb bound to oxide and Zn-oxide, and Pb bound to the organic form and Mn, Zn and Cu. The relationships with Pb in fractions with the other metals are as follows: Pb-Carb. $= 4.11 + 0.550$ Zn-Carb ($r = 0.64$, $p < 0.01$); Pb-Carb. $= 4.11 + 0.550$ Zn-Carb ($r = 0.64$, $p < 0.01$); Pb-Oxide $= 6.710 + 0.209$ Zn-Oxide ($r = 0.66$, $p < 0.025$); Pb-OM $= -5.53 + 0.502$ Mn-OM ($r = 0.85$, $p < 0.01$); Pb-OM $= -2.202 + 0.720$ Zn-OM ($r = 0.97$, $p < 0.01$); Pb-OM $= 2.704 + 0.406$ Cu-OM ($r = 0.96$, $p < 0.01$).

3.3. *Risk Assessment Code*

According to the Risk Assessment Code (RAC) [38,39], the metals in the sediments are bound to the fractions with different strengths. Because there are differences in the toxic effects of the metals, as well as differences in their concentrations and the length of exposure [40], the RAC assesses the availability of metals in sediments by applying a scale to the percentage of exchangeable and carbonate fractions. This is important because fractions introduced by anthropogenic activities were typified by being adsorptive, exchangeable and bound to carbonate fractions, i.e. weakly bonded metals that might equilibrate with the aqueous phase and thus become more rapidly bioavailable [39]. This classification is given in Table 8. It is evident from the results of the fractionation studies that metals in the sediments are bound to different fractions with different strengths. These strengths can, therefore, give a clear indication of sediment reactivity, which in turn assesses the risk connected with the presence of metals in an aquatic environment. This criterion of RAC indicates that sediment which can release <1% of the total metal in exchangeable and carbonate fractions is considered safe to the environment. By contrast, sediment releasing >50% of the total metal in the same sediment is considered highly dangerous and can easily enter the food chain [41]. The RAC for Pb showed medium risk for most of the stations except zone IV, which revealed a high risk for the aquatic environment. The fractionation pattern of Zn and Cu shows low risk, whereas Mn shows low to medium risk to aquatic environment.

Table 8. Risk Assessment Code (RAC).

		This study % of Exch. + Carb.			
Risk	Criteria (%) [38,39]	Mn	Zn	Cu	Pb
No risk	<1	2.23–21.75	0.51–5.5	2.25–6.20	13.59–34.06
Low risk	1–10				
Medium risk	11–30				
High risk	31–50				
Very high risk	>50				

4. Conclusion

Sequential extraction of Mn, Zn, Cu and Pb in sediments of the Gulf of Aden did not detect an exchangeable Cu fraction in the study area and only small amounts of Mn and Zn were found in this fraction for all samples ($<2\%$ of the total). This indicates a lower effect of anthropogenic material on the distribution of Mn, Zn and Cu. The low content of these metals in the exchangeable fraction indicated low bioavailability.

The large amounts of Pb extracted from the exchangeable and carbonate fractions indicated an anthropogenic source which spread to $>40\%$ of zone V. Also, Pb bound to the organic and Fe–Mn oxides fractions were found from the highly polluted zone III ($\sim$ 80% of the total Pb).

It is clear from the results that the residual fraction is the most important. Among non-residual fractions, Mn and Zn were mostly associated with the Fe–Mn oxides fraction.

The association of the metals with organic fraction was observed in the following order namely Cu $>$ Zn $>$ Mn $>$ Pb.

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