Chemical fractionation of Mn, Zn, Cu and Pb in the Sediments of Gulf of Aden, Yemen

Samir M. Nasr[1], Mohamed A. Okbah*[2], Shaif M. Kasem[3]

[1]*Department of Environmental Studies, Institute of Graduate Studies and Research, University of Alexandria, Alexandria, Egypt*

[2] Corresponding author: National Institute of Oceanography and Fisheries, Kayet Bay, Alexandria, Egypt

[3]*University of Aden, Faculty of Education, Chemistry Department, PO Box 6014, Khormaksar, Aden, Yemen*

Abstract

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 the sediments of Gulf of Aden, Yemen. The results indicated that high level of Mn was associated with the residual fraction (natural sources) than in the non-residual fraction (anthropogenic sources). Zn fractionations revealed that it was associated 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 the main port area (zone III) where it was associated with organic phase (77% of the total Cu content). Similarly most of Pb was bound in the residual fraction (56-71%) except the main port area where about 62% of the total Pb was bound in non-residual fractions. It was also found that Pb concentration in the exchangeable fraction was very high comparing with other metals.

The risk assessment code of the metals showed low risk for Zn and Cu, while it was low to medium risk for Mn. The fractionation of Pb showed medium risk at most of the regions except at the eastern area which revealed high risk for aquatic environment.

Keywords: Sequential extraction; Heavy metals, Risk assessment, Gulf of Aden.

INTRODUCTION

The Gulf of Aden consists of the inner harbor, the oil harbor serving for Aden refinery and the anchorage and approach channels of the outer harbor. The Gulf of Aden is an essential waterway for transportation oil from the Persian Gulf, making it very important for the world economy. It has rich marine life 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. The problems of physical alteration and 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 comes from land-based activities, including urbanization 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].

Sequential extraction of elements from sediment is a common analytical tool and 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 the Tessier procedure [3] in which the different fractions were extracted with different reagents [4]. Although the reagents used in sequential extraction procedures may be insufficiently specific to dissolve exclusively the ''target'' phases, and results obtained can vary widely when different extraction schemes and experimental conditions are used, useful information has been gained from such studies [5,6,7]. 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 sediments pollution, chemical partitioning of trace metals among the various geochemical phases is more useful than measurement of the total content. The metal speciation will give more information about the potential release of contaminants, migration and toxicity of the metals as well as the risk assessment of these metals [9]. Most of the studies focused on the studying of trace metals bioaccumulation in the mussels and mollusks 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 [10,11,12] .The present work is the first study in the region which is focused on the assessment and chemical fractionation of trace metals in the sediments of Gulf of Aden, Yemen.

STUDY AREA

The Gulf of Aden (Fig. 1) is a deepwater basin forming a natural link between the Red and Arabian Sea. This region is characterized by 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 at 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 harbors in the world with an area of about 70 km^2 of sheltered water surrounded by Jebel Shamsan, Khoremakser and the shore which extends to the
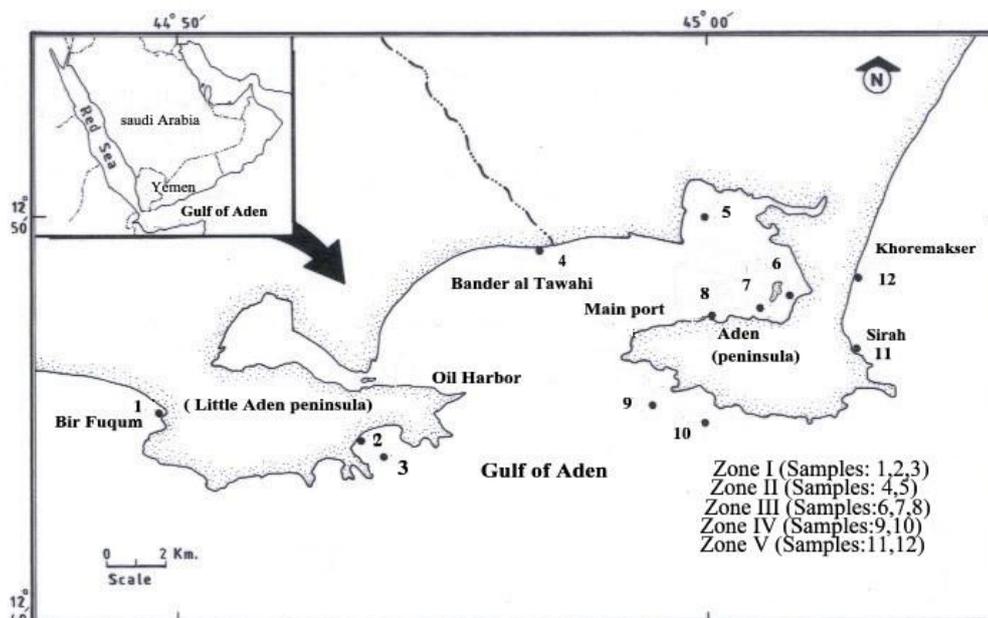
hills of Little Aden.

Fig.1: Sampling Sites of Aden Port

MATERIAL AND METHODS

Sample Collection and analysis

Twelve sediment samples were collected during 2004 from the Gulf of Aden (Fig. 1). This was divided into five zones for a proper evaluation of the area. Zone 1 is located on the western part of the Aden port, (samples1- 3); zone II (samples 4 & 5) located north of the port (polluted with industrial waste); zone III is a highly polluted area due to more human activity, represents the main port, consists of three samples (6, 7 and 8); zone IV (samples 9 and 10) in additions zone V located in the eastern area of the port (samples 11 and 12). The sediments were collected using 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 dark room.

For heavy metals analysis, the powdered samples (0.3g) were digested with HNO_3, HF, Aqua regia (HNO_3: HCl) and $HClO_4$ [13]. The samples were analyzed using Parkin Elmer Atomic Absorption Spectrophotometer (Model 2830). The concentrations of the trace metals were determined in $\mu g\ g^{-1}$. Total carbonate content was determined using the method described by Dean [14]. Organic matter of the sediments was determined by wet oxidation method as described by El-Wakeel and Riely [15].

Sequential Extraction Procedure

The sediments were sequentially extracted according to the Tessier method [3]. The residual fraction was determined after digested with acid mixture (HNO_3, $HClO_4$, HF ratio 3:2:1) [16]. Quality control for the total concentrations of metals was done using a reference material (HISS-1, National Research of Council of Canada). It was analyzed in duplicate in six batches, the accuracy of the results ranged between 90-110%, while precision was agreed to be within 10%. The variation coefficients were 8.5% for Mn; 7.4% for Zn; 4.2% for Cu and 6.5% for Pb. The comparison of the sum of the fractions with the results from the total concentration (a separate strong acid digestion) was performed to study the quality control for sequential extractions procedure; the percentage recovery of the metals was within ±20 %.

RESULTS

The study highlighted at the content of Mn, Zn, Cu and Pb in the sediments from Gulf of Aden. Heavy metal distributions in marine deposits are influenced by sediment texture, organic carbon, and carbonates [17]. Particle size distribution, calcium carbonate, and organic matter contents in the sediments of the study area are given in Table 1. Calcium carbonate in the sediment samples ranges from 9.34 to 64.5 %.

Table 1: Physical and chemical characteristics of sediments, Gulf of Aden, Yemen (2004)

Zones	Grain size analysis			Sediment Type	CaCO$_3$ %	OM%
	Sand	Silt	Clay			
	-	%	-			
I	80.4	12.3	7.3	Loamy sand	36.00	1.24
II	75.0	10.5	14.5	Sandy loam	34.00	1.72
III	43.0	38.7	18.3	Sandy loam	38.28	2.98
IV	72.50	3.50	24.0	Sandy clay loam	64.50	0.69
V	80.5	2.00	17.5	Sandy loam	9.34	0.87

Fractionation of heavy metals

Mn is mostly concentrated in the residual fraction, it represent more than 64% of the total concentration from zones I - IV, while in zone V it is < 20%. The other important phase of Mn is non-residual form. Mn associations with different fractions in five zones are given in Table 2 and Fig. 2. Mn content in the five fractions of the five zones (Table 2) can be arranged in the following order: Residual (243.83μg/g;73.02 %) > Fe-Mn oxides (44.80μg/g, 12.75 %) > Organic form (25.00μg/g, 7.24 %) > Carbonate (23.90μg/g, 6.58 %) > Exchangeable (1.44μg/g, 0.41 %).)
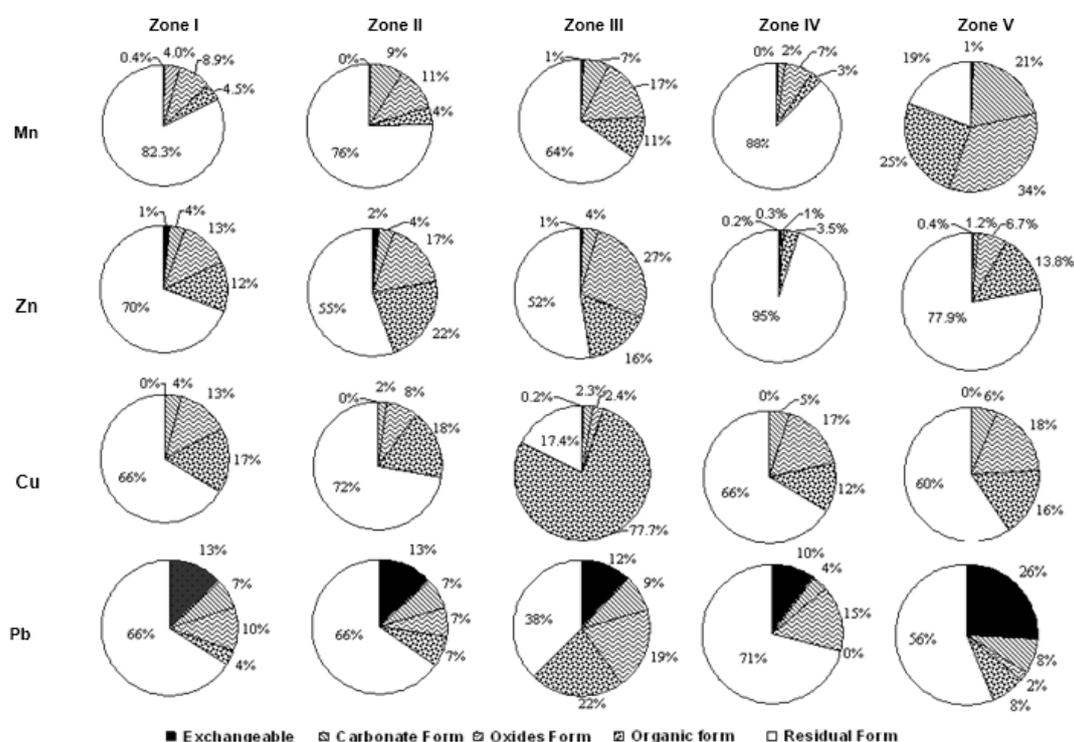
Figures (2). Percentage of Mn, Zn, Cu and Pb fractionation from the total content in the Gulf of Aden sediments

Zn fractionation reveals that a major part is found to be associated with Fe-Mn oxides and organic phases compared to exchangeable and carbonate phases. Zn in oxides and organic fractions constitute about 4.5% of the total Zn in Zone IV and reaching to 43% in zone III. Zn bound to exchangeable fraction is very low. The associations of Zn with the different fractions are given in Table 2& Fig.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 µg/g, 68.69%) > Fe-Mn oxides (14.0 µg/g, 15.53%) > organic form (12.3 µg/g, 12.60%) > carbonate (2.69 µg/g, 2.4%) > exchangeable (0.60µg/g, 0.62%).

Table 2: The average values of heavy metals (µg/g) in the five fractions of Gulf of Aden sediments

Zones	Mn					Zn					Cu					Pb				
	Chemical fractions					**Chemical fractions**					**Chemical fractions**					**Chemical fractions**				
	F1	F2	F3	F4	F5	F1	F2	F3	F4	F5	F1	F2	F3	F4	F5	F1	F2	F3	F4	F5
I	1.3	14.0	30.7	15.5	270.4	0.6	1.6	5.6	5.3	27.8	ND	0.7	2.2	2.8	10.8	11.3	6.1	9.1	3.1	52.5
II	1.9	41.5	52.7	21.1	346.5	0.7	1.6	6.9	9.2	21.7	ND	0.4	1.5	3.3	12.4	10.1	5.8	5.5	5.7	48.6
III	2.0	26.1	63.2	41.7	237.1	1.1	7.1	50.5	30.5	96.2	0.1	1.1	1.2	38.6	8.0	11.4	8.3	18.6	21.3	33.4
IV	0.8	8.3	29.7	11.0	339.1	0.4	0.5	1.6	5.7	150.5	ND	0.6	2.3	1.6	8.7	11.7	4.3	17.9	ND	79.2
V	1.1	29.8	47.6	35.9	26.0	0.3	0.9	5.4	11.1	59.8	ND	0.6	1.8	1.6	5.6	5.9	1.9	0.5	1.8	12.3
Average	1.4	23.9	44.8	25.0	243.8	0.6	2.4	14.0	12.3	71.2	0.0	0.7	1.8	9.6	9.1	10.1	5.3	10.3	8.0	45.2
± SD	0.5	13.1	14.4	13.2	130.2	0.3	2.7	20.5	10.5	53.3	0.0	0.7	1.7	10.9	8.8	2.4	2.4	7.9	9.1	24.7

Cu (Fig. 2 & Table 2) is concentrated in the organic fraction than in other forms indicating its association with organic phase. The exchangeable fraction is not detected in the study area except in zone III (12 µg/g -0.2% of the total Cu). The average values of Cu in the five fractions of the five zones are shown in Table 2. They are arranged as follows: organic form (9.6µg/g, 45.3%) > residual (9.1 µg/g, 42.9%) > Fe-Mn oxides (1.8 µg/g, 8.5%) > carbonate (0.7µg/g, 3.3%) > exchangeable (ND).

Pb 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 the inputs of industrial effluents, sewage sludge, domestic wastes, pigments, petrol (gasoline) additives, steel products and the combustion of fossil fuels. In the present study area a major part of Pb is concentrated in the residual fraction. The concentration of Pb bound in residual fraction vary from 38% in zone III, 56% in zone V and 71% in zone IV, The next important phase of Pb concentration is in the non-residual fraction (labile form). The associations of lead with different fractions are shown in Fig.2 & Table 2. As shown in Table 2 the average values of the five fractions of the study area arranged in the following order: Residual (45.18 µg/g; 58.94 %) > Fe-Mn oxides (10.3 µg/g, 13.60 %) > Exchangeable (10.1 µg/g, 12.66 %) > Organic form (8.0 µg/g, 10.85 %) > Carbonate (5.3 µg/g, 6.88%).

DISCUSSION

The relative percentage of Mn about the fractionation revealed similarity in 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 by anthropogenic activities. The concentrations of Mn associated with carbonate were high in zone (V) representing 21% of the total Mn (Fig. 2). The metal in the exchangeable and carbonate fractions are considered to be weekly bound and may equilibrate with the aqueous phase, thus becoming more bioavailability [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%). Mn bound with both Fe-Mn oxides and organic fractions was high in zone V; representing 59% of the total Mn. It was found that about 28% in zone III and get decreased to13% and 15% in zones I and II, respectively. In general, Mn can be presented as oxides, hydroxides or in association with iron oxides / hydroxides, Mn ions can be adsorbed and / or partially ion-exchanged on the surface of MnO_2 and they can be environmentally mobile in certain conditions [20]. Mn, also, bound to carbonates or specifically adsorbed and bound to organic matter and sulfides [21]. The relative percentage of Mn associated with residual fraction is high, more than 64% in zones I, II, III and IV. The high concentration of Mn in the residual fraction may be due to the variation in mineralogical composition of sediments of the study area. As shown in Table (3), the binding behavior of Mn bound to the sediment fractions revealed high positive correlation of Mn concentration in the organic phase with 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 given below

Mn-Oxide = 38.793 + 0.390 Zn-Oxide	r = 0.71	P-value < 0.01
Mn-OM = 10.350 + 1.152 Zn-OM	r = 0.92	P-value < 0.01
Mn-OM = 18.612 + 0.614 Cu-OM	r = 0.86	P-value < 0.01
Mn-OM = 15.034 + 1.443 Pb-OM	r = 0.85	P-value < 0.01

Table 3: Correlation Matrix of heavy metal binding fractions   bound to a) Exchangeable b) Carbonate c) Oxides d) Organic matter e) Residual in the Gulf of Aden sediments (No.=12,significance at <0.025 & 0.01).

a)

	Mn-Exch	Zn-Exch	Cu-Exch	Pb-Exch
Mn-Exch	1.00			
Zn-Exch	0.55	1.00		
Cu-Exch	0.51	0.91	1.00	
Pb-Exch	-0.05	0.52	0.47	1.00

b)

	Mn-Carb)	Zn-Carb.	Cu-Carb.	Pb-Carb.
Mn-Carb.	1.00			
Zn- Carb.	0.34	1.00		
Cu- Carb.	0.15	0.89	1.00	
Pb- Carb.	0.12	0.81	0.64	1.00

c)

	Mn-Oxide	Zn-Oxide	Cu-Oxide	Pb-Oxide
Mn-Oxide	1.00			
Zn-Oxide	0.71	1.00		
Cu-Oxide	-0.54	0.50	1.00	
Pb-Oxide	0.27	0.65	-0.21	1.00

d)

	Mn-OM	Zn-OM	Cu-OM	Pb-OM
Mn-OM	1.00			
Zn-OM	0.92	1.00		
Cu-OM	0.86	0.98	1.00	
Pb-OM	0.85	0.97	0.96	1.00

e)

	Mn-Resid.	Zn-Resid	Cu-Resid	Pb-Resid
Mn-Resid	1.00			
Zn-Resid	-0.14	1.00		
Cu-Resid	0.16	-0.23	1.00	
Pb-Resid	0.30	0.42	0.47	1.00

Zn is the most labile metal, recovered in the first extraction stages, and is associated with the non-residual fraction of sediment. Zinc is mainly bound to non-residual fractions [19]. Low level of Zn concentration is obtained in the non-residual fractions

(labile form), it ranges from 5% in zone IV to 48% in zone III. The results as shown in Fig. 2, indicates that Zn is not reflecting any anthropogenic impact into sediments at zone IV but the relatively high concentration which found in the other zones can be an indicator for that, these zones are releasing relatively large amounts of zinc in 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, this in agreement with that reported by Fernandes [22]. Zn-bounded to the oxide form ranged from 3.5% of the total Zn at zone IV to 27% at zone III. Zn adsorption in the oxides fraction has higher stability constant than 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 %). Generally, the results indicate that more than 50 % of the total Zn was recorded in the non-residual fraction for zones II and III, this may be possible by disposal of untreated sewage wastes from domestic drainage and human activities in the area.

Cu bound to different fractions in the study area were recorded as the following: organic form (11.44 µg/g, 48.29%) > residual (9.10 µg/g, 40.95%) > Fe-Mn oxides (1.79µg/g, 7.56%) > carbonate (0.73µg/g, 3.08%) > exchangeable (0.03µg/g, 0.13%). The high concentration of Cu associated with organic fraction was recorded in zone III (98.66 µg/g; 89 % of the total Cu). Zone III is characterized by relatively high organic matter percentage (5%). This indicates that Cu occurs in the forms of organic complexes. Cu is preferentially retained in organic matter by complexation rather than by ion exchange [24, 25]. As expected from a number of previous studies on polluted sediments [23, 24] extractable Cu is mainly associated with the oxidizable phase, where it is likely to occur as organically complex metal species. This behavior can be explained by the well-known high affinity of Cu to humic substances, which are chemically very active in Cu complexion [26, 27]. Although substantial percentages of Cu are extracted in the four equivalent fractions, the most abundant is the oxidizable fraction (coinciding with organic and sulfur compounds). This agrees with the results of many studies [28, 29, 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 is mostly bound to the organic matter/sulfide fraction (70–80%) in marine sediment in highly polluted area of Villefranche Bay. Cu can easily complex with organic matters 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 materials and amino acids. On the other hand, most of the Cu is presented in the residual fraction (60–72%) in the all zones except zone III (17%). The higher association with the residual fraction indicates its low bioavailability [33]. The percentage of metal in the residual fraction can not be easily released to the environment since the metal is about to crystal lattice. The association of Cu with Fe-Mn oxides ranges between 1.21µg/g (2.43% of the total) in zone III to 2.31 µg/g (17%) in zone IV. Several investigators have demonstrated that the sorption of Cu on to hydrous Fe–Mn oxides is due to co-precipitation of Cu in the Fe–Mn oxide lattice [34]. The low Cu content in the exchangeable (ND-0.24%) and carbonate fraction (2.25-6.2 %) in the present study indicates that the bioavailability of Cu to the sediments may be less.

The residual and labile concentration of Pb of the present study is similar to that recorded by El-Sikaily et al., [34] for the sediments of Suez Gulf, (71.5-100 μg/g dry wt) which shows that about 50μg/g of the total content of Pb is bounded to the labile form (non-residual fraction).The residual form of Pb in the sediments of Athens sea is 31.2% of the total Pb [29]. High positive correlations are recorded between Pb concentration 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 residual fraction are of low risk of mobility [35]. The data obtained in the exchangeable fraction of Pb are similar in the all zones (10.28 ± 2.92 μg/g). This indicates that Pb is highly distributed in the study area. The large amounts of Pb in the exchangeable fraction (Fig. 2) indicate that Pb is from anthropogenic source. The average concentration of Pb associated with carbonate is 5.59 ± 2.44 μg/g, the high concentration is recorded in zone III (8.33 μg/g). Pb associated with exchangeable and carbonate fractions are considered to be weekly bound and may equilibrate with the aqueous phase, and so becoming more bioavailability [21]. These data could reflect the dangerous of Pb in the study area. Also, Pb bound to organic fraction and Fe-Mn oxides fraction which is high polluted zone III (about 80% of the total Pb). Organic matter and Fe-Mn oxide have high scavenging affect on Pb 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 associated of Pb with residual fraction were high in zones I, II, IV and V, represent more than 56% in the total Pb, the residual solid should contain primary and secondary minerals which may hold heavy metals within their crystal structure [21, 37]. This result indicates that an abundant amount of Pb discharging into the water of the study area. The binding behavior of Pb bound to the sediment fractions as shown in Table (3) revealed high positive correlation of Pb with carbonate phase with Zn and Cu, and significant relationships between Pb bound to oxide with Zn-oxide, Pb bound to organic form with Mn, Zn and Cu. The relationships between Pb in the fractions with the other metals are as follows

$$Pb\text{-}Carb. = 4.11 + 0.550\ Zn\text{-}Carb \qquad r = 0.81 \qquad P\text{-value} < 0.01$$

$$Pb\text{-}Carb. = 4.11 + 0.550\ Zn\text{-}Carb \qquad r = 0.64 \qquad P\text{-value} < 0.01$$

$$Pb\text{-}Oxide = 6.710 + 0.209\ Zn\text{-}Oxide \qquad r = 0.66 \qquad P\text{-value} < 0.025$$

$$Pb\text{-}OM = -5.53 + 0.502\ Mn\text{-}OM \qquad r = 0.85 \qquad P\text{-value} < 0.01$$

$$Pb\text{-}OM = -2.202 + 0.720\ Zn\text{-}OM \qquad r = 0.97 \qquad P\text{-value} < 0.01$$

$$Pb\text{-}OM = 2.704 + 0.406\ Cu\text{-}OM \qquad r = 0.96 \qquad P\text{-value} < 0.01$$

RISK ASSESSMENT CODE (RAC):

According to the RAC [38, 39], the metals in the sediments are bound with different strengths to the fractions. The RAC assesses the availability of metals in solution by applying a scale of the relative percentage in the exchangeable and carbonate fractions. This classification is tabulated in Table (4). It is evident from the results of

the fractionation studies that the metals in the sediments are bound to different fractions with different strengths. The strength values can, therefore, give a clear indication of sediment reactivity, which in turn assess the risk connected with the presence of metals in an aquatic environment. This criterion of RAC as given below indicates that sediment which can release in exchangeable and carbonate fractions, less than 1% of the total metal will be considered safe for the environment. On the contrary, sediment releasing in the same fraction more than 50% of the total metal has to be considered highly dangerous and can easily enter the food chain [40]. The risk assessment code of Pb showed medium risk at most of the stations except at zone IV which revealed high risk for aquatic environment. Fractionation pattern of Zn and Cu shows low risk, while Mn shows low to medium risk to aquatic environment.

Table 4: Risk assessment code (RAC)

Risk	Criteria (%),(Perin *et al.,* 1985 ; Singh *et al.,* 2005)	Present study % of Exch. + Carb.			
		Mn	Zn	Cu	Pb
No risk	< 1				
Low risk	1 -10				
Medium risk	11 - 30	2.23-21.75	0.51-5.5	2.25-6.20	13.59-34.06
High risk	31 - 50				
Very high risk	>50				

CONCLUSION

1) Sequential extraction of Mn, Zn, Cu and Pb in sediments of Gulf of Aden indicated that the exchangeable Cu fraction was not detected from the study area and small amounts of Mn and Zn were found in this fraction for all samples (< 2 % of the total). This indicates the lower effect of the anthropogenic material on the distribution of Mn, Zn and Cu content. The low content of these metals in the exchangeable fraction showed low bioavailability.

 2) Large amounts of Pb extracted from the exchangeable and carbonate fractions indicated its anthropogenic source which spreaded to more than 40 % of zone V. Also, Pb bound to organic fraction and Fe-Mn oxides fractions were found from the highly polluted zone III (about 80% of the total Pb).

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

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

References

[1]   Balls, P.W., Hull, S., Miller, B.S., Pirie, J.M., and Proctor, W., 1997, "Trace metal in Scottish Estuarine and coastal sediments," *Marine Pollution Bulletin*, **34**, pp. 42–50.

[2]   Sutherland, A. R., and Tack, F. M.G., 2002,"Determination of Al, Cu, Fe, Mn, Pb and Zn in certified reference materials using the optimized BCR sequential extraction procedure" *Analytica Chimica Acta*, **454**, pp. 249–257.

[3]   Tessier, A., Campbell, P. G. C., and Bisson, M., 1979,"Sequential extraction procedure for the speciation of particulate trace metals" *Analytical Chemistry*, **51** (7), pp.844-851.

[4]   Sobczynski, T., and Siepak, J., 2001,"Speciation of heavy metals in bottom sediments of lakes in the area of Wielkopolski National Park. Polish" *Journal of Environmental Studies*, **10**, pp. 463 –74.

[5]   Dollar, N. L., Souch C. J, Filippelli G.M., and Mastalerz, M., 2001,"Chemical fractionation of metals in wetland sediments: Indiana Dunes National Lakeshore" *Environmental Science and Technology*, **35**, pp.3608–15.

[6]   Dold B., 2003," Speciation of the most soluble phases in a sequential extraction procedure adapted for geochemical studies of copper sulfide mine waste" *Journal of Geochemical Exploration*, **80**, pp.55–68.

[7]   Fytianos, K., and Lourantou, A., 2004," Speciation of elements in sediment samples collected at lakes Volvi and Koronia, N. Greece" *Environment International*, **30**, pp.11 – 17.

[8]   Bruder-Hubscher, V., Lagarde, F., Leroy, M. J. F., Coughanowr, C., and Enguehard, F., 2002, "Application of a sequential extraction procedure to study the release of elements from municipal solid waste incineration bottom ash" *Analytica Chimica Acta*, **451**, pp. 285-295.

[9]   Usero, J., Gamero, M., Morillo, J., and Gracia, I., 1998,"Comparative study of three sequential extraction procedures for metals in marine sediments" *Environment International*, **24**, (4), pp. 487-496.

[10] Hassan, M. A. H. and Nadia, A. A., 2000, "Trace metals in fish, mussles, shrimpand sediment from Red sea coast of Yemen" *Bull. Nat. Inst. of Oceanagr. & Fish., A. R. E.,* **26**, pp.339-353.

[11] Al-Edressi, M. A. M. Abdelmuneim, M. A. Al-Saad, H. T. and Heba, H. M. A., 2002, "Heavy metal contents of some mollusks and crustaceans along Al-Hodeidah Red Sea coast of Yemen" *Bull. Nat. Inst. of Oceanagr. & Fish., A. R. E.,* **28** 319-331.

12]   Samir, M. N., Okbah,M.A. Kasem,Sh,M., 2006, " Environmental Assessment of Heavy Metal Pollution in Bottom Sediments of Aden Port, Yemen" *International Journal of Oceans and Oceanography*,**1**, pp. 99-109

[13] Loring, D. H., and Rantala, R. T. T., 1992," Manual for geochemical analysis of marine sediments and suspended particulate matter" *Earth Science Reviews*, **32**, pp.235-283.

[14] Dean, W.E., 1974, "Determination of carbonate and organic matter in calcareous sediments and sedimentary rocks by loss on ignition. Comparison with other methods" *Journal of sedimentary petrology*, **44**, pp.242-248.

[15] El-Wakeel, S.K., and Riley, J. P., 1957, **"**Determination of organic carbon in marine mud" *Journal du Conseil international pour l'Exploration de la Mer*, **22**, pp.180-183.

[16] Oregioni, B., and Aston, S. R., 1984,"The determination of selected trace metals in marine sediments by flume atomic absorption spectrophotometery" *IAEA Monaco Laboratory International Report. UNEP, reference methods for marine pollution studies No* **38**.

[17] Salomons, W., and Forstner, U., 1984," Metals in the hydrocycle" *Springer-Verlag, Berlin, Heidelberg, New York, Tokyo,* ISBN 3540127550.

[18] Fytianos, K., Bovolenta, S., and Muntau, H., 1995," Assessment of metal mobility from sediment of Lake Vogoritis" *Journal Environmental Science and Health,* **A30** (6), pp.1169-1190.

[19] Caplat C., Texier H., Barillier D., and Lelievre C., 2005, "Heavy metals mobility in harbour contaminated sediments" *Marine Pollution Bulletin*, **50**,pp 504 -11.

[20] Weisz, M., Polyák, K., and Hlavay, J., 2000,"Fractionation of elements in sediment samples collected in rivers and harbors at Lake Balaton and its catchment area" *Microchemical Journal*, **67**, pp. 207-217.

[21] Dong, D., Zhu, X., Yang, B., and Liu M., 1998, "Evaluation of sampling and analytical errors in the determination of manganese in soils" *Microchemical Journal*, **59**, pp.356–363.

[22] Fernandes, H. M., 1997, "Heavy metal distribution in sediments and ecological risk assessments: the role the digenetic processes in reducing metal toxicity in bottom sediments" *Environmental Pollution*, **97**, pp.317-325.

[23] Li, X; Shen, Z., Wai, O. W. H., and Li, Y. S., 2001," Chemical forms of Pb, Zn and Cu in the sediment Profiles of the Preal River estuary" *Marine Pollution Bulletin*, **42**, (3),pp. 215-223.

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

[25] Wu, J., Laird, D.A. and Thompson, M.L., 1999," Sorption and desorption of copper on soil clay components, *J. Envir. Qua*l., **28**, pp. 334–338.

[26] Pardo, R., Barrado, E., Castrillejo, Y., Velasco, M. A., and Vega, M.,

1993,"Study of the contents and speciation of heavy metals in River sediments by factor analysis" *Analytical Letters,* **26**, pp.1719–39.

[27] Marin, B., Valladon, M., Polve, M., and Monaco, A., 1997,"Reproducibility testing of a sequential extraction scheme for the determination of trace metal speciation in a marine reference sediment by inductively coupled plasma-mass spectrometry" *Analytica Chimica Acta,* **342**, pp.91 – 112.

[28] Pempkowiak, J., Sikora, A., and Biernacka, E., 1999,"Speciation of heavy metals in marine sediments vs their bioaccumulation by mussels"*Chemosphere*, **39**, (2),pp. 313-321.

[29] Savvides C., Papadopoulos, A., Haralambous K. J., and Loizidou M., 1995,"Sea sediment contaminated with heavy metals: metal speciation and removal" *Water Science and Technology*, **32**, (9) pp.65-73.

[30] Parkman, R. H., Curtis, C. D., and Vaughan, D. J., 1996,"Metal fixation and mobilisation in the sediments of the Afon Goch Estuary – Dulas Bay, Anglesey" *Applied Geochemistry*. **11**, pp.203-210.

[31] Rapin, F., Membrine, G. P., Förstner, U., and Gracia, J. L., 1983,"Heavy metals in marine sediment phases deter-mined by sequential chemical extraction and their inter-action with interstitial water" *Environmental Technology Letters*, **4**, pp.387–396.

[32] Stumm, W., and Morgan, J. J., 1981,"Aquatic chemistry: An introduction emphasizing chemical equilibria in natural water". 2nd ed. John Wiley & Sons, New York.

[33] Kotoky, P., Bora, B. J., Baruah, N. K., Baruah, J., Baruah P., and Borah, G. C., 2003, "Chemical fractionation of heavy metals in soils around oil installations, Assam" *Chemical Speciation and Bioavailability*, **15**(4),pp. 115-126.

[34] El-Sikaily, A., Khaled, A., and El-Nemr, A., 2005, "Leachable and total nine heavy metals in muddy and study sediment collected from Suez Gulf" *Egyptian Journal of Aquatic Research*, **31**, pp.99-119.

[35] Filgueiras, A.V., Lavilla, I., and Bendicho, C., 2004, "Evaluation of distribution, mobility and binding behaviour of heavy metals in surficial sediments of Louro River (Galicia, Spain) using chemometric analysis: a case study" *Science of the Total Environment*, **330**, pp.115 –129.

[36] Yu, K.C., Tsai, L. G., Chen, S. H., and Ho, S. T., 2001,"Correlation analyses on binding behavior of heavy metals with sediment matrices" *Water Research*, , **35**, (10), pp. 2417 -2428.

[37] Nasr, S. M., Elsokkary, I. H., Fakhry, A. A., and El-Shibiny, I. H., 1990," Fractionation of some heavy metals in the costal belt sediments off Alexandria" *Regional Symposium Environmental Studies (UNARC), Alexandria*, pp.415-436.

[38] Perin, G., Craboledda, L., Lucchese, M., Cirillo, R., Dotta, L., Zanetta, M. L.,

and Oro, A. A., 1985,"Heavy metal speciation in the sediments of northern Adriatic sea. A new approach for environmental toxicity determination. In: Lakkas, T.D. (Ed.), Heavy Metals in the Environment, vol. 2. CEP Consultants, Edinburgh.

[39] Singh, K. P., Mohan, D., Singh, V. K., and Malik A., 2005," Studies on distribution and fractionation of heavy metals in Gomti river sediments—a tributary of the Ganges, India" *Journal of Hydrology* , **312**, pp. 14-27.

[40] Jain, C.K., 2004,"Metal fractionation study on bed sediments of River Yamuna, India" *Water Research*, **38**,pp. 569-578.