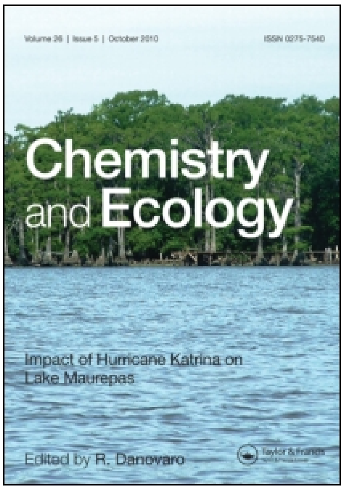

Chemistry and Ecology
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713455114

Heavy metals availability (Fe, Mn, Zn, Cu and Cr) in Aden Gulf sediments under aerobic and anaerobic conditions

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To cite this Article Okbah, Mohamed A. , Nasr, Samir M. and Kasem, Shaif M.(2008) 'Heavy metals availability (Fe, Mn, Zn, Cu and Cr) in Aden Gulf sediments under aerobic and anaerobic conditions', Chemistry and Ecology, 24: 2, 109 — 117

To link to this Article: DOI: 10.1080/02757540801919305

URL: http://dx.doi.org/10.1080/02757540801919305

Chemistry and Ecology
Vol. 24, No. 2, April 2008, 109–117

Heavy metals availability (Fe, Mn, Zn, Cu and Cr) in Aden Gulf sediments under aerobic and anaerobic conditions

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(*Received 02 November 2007; final version received 10 January 2008*)

The present study aims to analyse the chemical speciation of heavy metals in relation to aerobic and anaerobic conditions. Two sediment samples (from the Gulf of Aden, Yemen) were incubated under flooded conditions. In particular, the chemical forms of Fe, Mn, Zn, Cu and Cr under the experimental conditions were studied using a sequential chemical extraction method. The pH and Eh of the suspension were measured as critical parameters controlling the fate of the metals in the environment. The results showed that the metals concentration in the different forms varied with time incubation and affected by the variation of redox potential and pH value. Also, the changes in both redox potential (Eh) and pH values had evident effects on heavy metals transformation. It is obvious that the highest redox potential affected the amount of iron and manganese in the oxides form. When the redox potential decreased to −133 and −170 mV, it caused a significant transformation of the Fe-Mn oxide form to the water-soluble and exchangeable fractions. Under anaerobic conditions, the relative percentage of all five metals including the summation of four fractions (the water-soluble and exchangeable, carbonate, oxides and organic fractions) constituted 45–60% of the total amount of iron, 33–50% for manganese, 33–63% for Zn, 63–74% for Cu and 19–43% for Cr. Both zinc and copper among water-soluble and exchangeable fraction were high at the end of incubation period, this accompanied by a significant decrease in the content of the organically bound fraction. In general, the reducing conditions were more favorable for metal bound to water soluble and exchangeable fraction.

Keywords: heavy metals; Aden Gulf; sediments; redox potential

1. Introduction

The distribution of geochemical forms of a metal into the different sedimentary phases show the important role of these forms in the cycling of metals between the water column and the sediment reservoir. Trace metal fractionation in the sediments is widely used for pollution studies in marine environments [1,2]. The bioavailability, speciation and transportation of heavy metals in the sediment system are very important tools to assess sediment pollution problems and seek remedial measures. Ramirez et al. [3] showed that the sites characterised by the highest metal concentrations in bioavailability phase had the lowest biodiversity. The bioavailability and toxicity can be ascertained by studying the distribution of heavy metals between the different phases. The fractions introduced by man's activity (including the adsorptive and exchangeable and binding

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ISSN 0275-7540 print/ISSN 1029-0370 online

DOI: 10.1080/02757540801919305
http://www.informaworld.com

to carbonates) are becoming more rapidly bioavailable; these are considered to be weakly bound and may equilibrate with the aqueous phase. The pH and redox potential have been recognised as critical parameters controlling the fate of pollutants in the environment. The Fe–Mn oxide and the organic matter have a scavenging effect and may provide a sink for heavy metals, the release of the metals from this matrix will most likely to be affected by the redox potential and pH [4]. Previous studies indicated that pH is an important factor in metals adsorption onto sediments or soils constituents. The pH of sediment solutions has a major impact on sediment's ability to retain heavy metals. Increasing solution pH leads to a rapid increase in net negative surface charge and thus increases the sediment or soil's affinity for metal ions [5,6]. The understanding of metal speciation and the complex interactions between metals, organics, and sorbent surfaces is important for predicting the fate and transport of metals in subsurface systems [6]. Exudation of organic compounds by microbial secretions, and plant and animal residues may influence on the solubility of metal ions and their uptake. These may be through their indirect effects on microbial activity, and direct effects through acidification, metal chelating and complexion properties for mobilisation of heavy metals, precipitation and oxidation-reduction reactions [6,7]. Burckhard et al. [8] showed that the organic acids may affect the behaviour and the interaction between heavy metals in soils. The objectives of this study were to investigate the chemical speciation of heavy metals under two different conditions (aerobic and anaerobic conditions).

2. Material and methods

2.1. *Sampling locations description*

Two sediment samples (S1 and S2) were collected from the Gulf of Aden. The region is characterised by human activities, Power and desalination plants, runoff, Industrial and municipal waste water was found at the two sites S1and S2. The geographic positions of the two sampling locations are 12°49′32″ N and 44 56′25″ E for S1 and 12°47′24″ N and 45°00′00″ E for S2.

2.2. *Sampling and pretreatment*

The sediments were collected using a self-gravity sampling implement consisting of a 60 cm plastic sampling tube. Upon retrieving the core in deck, the top sediment (10 cm) was taken and the wet sediment samples were refrigerated (−4°C) immediately to avoid changes in heavy metal distribution among different phases.

2.3. *Sequential extraction and analyses*

Twenty five grams of the two sediments were put into 250 ml glass bottles, to obtain flooded conditions, and 90 ml deionised distilled water (Milli-Q water) was added to the sediment samples. The bottles were closed with screw stoppers and were stirred by shaking on a rotary shaker at 200 rpm for 1 h to maintain homogeneous suspension, and then left to stand at room temperature. An aerobic (oxidised) condition was maintained by continuously passing air into the suspension using an air compressor. A reduced medium was maintained by passing nitrogen gas to replace the air in the flask. The redox potential (Eh) and pH were recorded at zero time and after three weeks (504 h). The pH and Eh of the suspension were measured by placing platinum or glass electrode and calomel electrode in the solution of each sample. Heavy metals were estimated following the procedure of Sakata [9] by Atomic Absorption Spectrophotometer (AAS) in an electrothermal atomisation mode using Perkin-Elmer 5100 PC, HGA 600 graphite furnace (GEM software). Fe,

Table 1. Extraction procedures for different fractions of heavy metals.

Fraction	Extraction reagent	Extraction conditions
Exchangeable	1 M $MgCl_2$, pH 7.0	Shaken at room temperature for 1 h with continuous agitation
Carbonate	I 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°C ± 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 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

Mn, Cu, Zn were determined by flame AAS in an acetylene air flame. Cr was determined by AAS in graphite furnace. A further set of samples were submitted to the sequential extraction techniques described by Tessier et al. [10]. Five steps of sequential extraction scheme (Table 1) used to the metals partitioning into water-soluble and exchangeable; carbonate fraction; Fe-Mn oxides fraction; organic fraction and residual fraction.

2.4. *Quality control studies*

The detection limits were calculated by six determinations in one batch of synthetic sea water (close or less than 1 µg/l). The precision was agreed to be within 10%. The variation coefficients were 1.3–6 % for Fe; 2.5–8.2% for Mn; 2.6–8.9% for Zn; 2.8–11.3% for Cu; and 2.4–9.4% for Cr. Natural sample was analysed in duplicate in each of six batches of samples after spiking by a known concentration from the standard reference material. The same natural sample was analysed without spiking. The percentages of recovery for spiked samples were used to determine the accuracy. The recoveries of metal spikes added to the sediments studied were 102% for Fe; 97% for Mn; 95% for Cu; 103% for Zn and 101% for Cr. The quality control studies for sequential extraction technique were calculated from the difference between the total concentrations of the metals and sum of the five fractions. In general, the recovery of the metals in the present study ranged between 89% and 117%. A recovery of 80–120% is common in a sequential extraction method.

3. Results and discussion

3.1. *The redox potential and pH*

The redox potential and pH values after the incubation period (three weeks) are shown in Figures 1 & 2. The results showed that the sediment suspensions under continuous oxygen aeration for 360 h increased the redox potential from 79 to 157 mV at sample S1 and from 135 to 188 mV at sample S2, while the pH value decreased from 8.63 to 8.04 at S1 and from 8.21 to 7.94 at S2.When the sediment suspension was aerated with nitrogen, the redox potential decreased from 77 to −133 mV at S1 and from 136 to −170 mV at S2. The pH value recorded wide variations during the incubation time; it decreased from 8.74 to 8.21 (S1) and from 7.69 to 6.23 (S2).

3.2. *Fractionation studies*

The results of heavy metals concentration in the sediments, which are subjected to both oxygen aeration and bubbled with nitrogen in different forms, are shown in Figures 3 and 4 and Tables 2

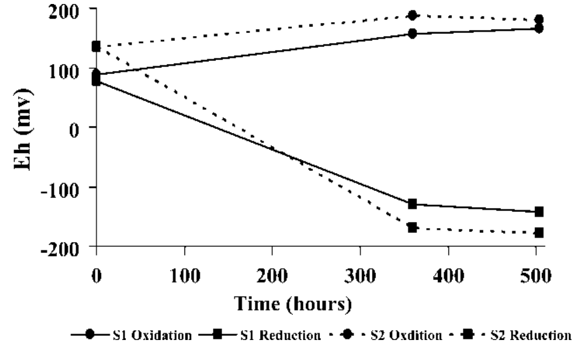

Figure 1. Changes of redox potential (Eh) of the sediments suspension incubated under aerobic and anaerobic conditions at sites (S1 and S2).

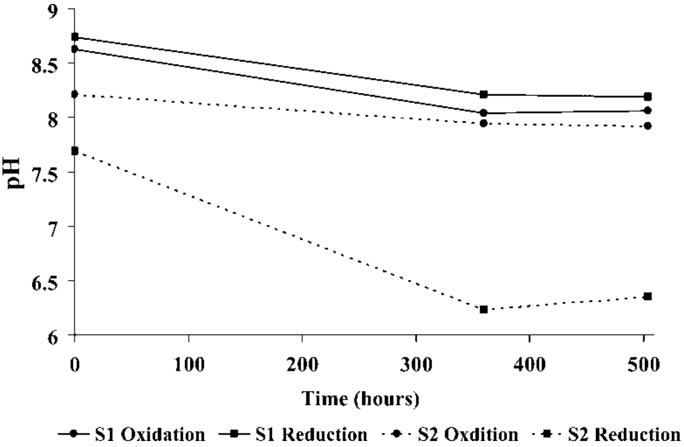

Figure 2. Changes of pH values of the sediments suspension incubated under aerobic and anaerobic conditions at sites (S1 and S2).

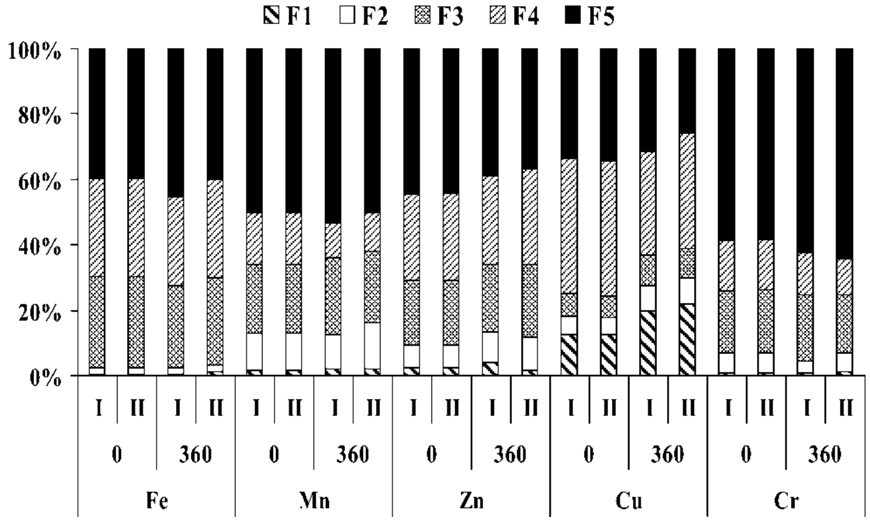

Figure 3. The relative percentage of heavy metal concentrations extracted by different reagents with time under aerobic (I) and anaerobic (II) conditions at site S1.

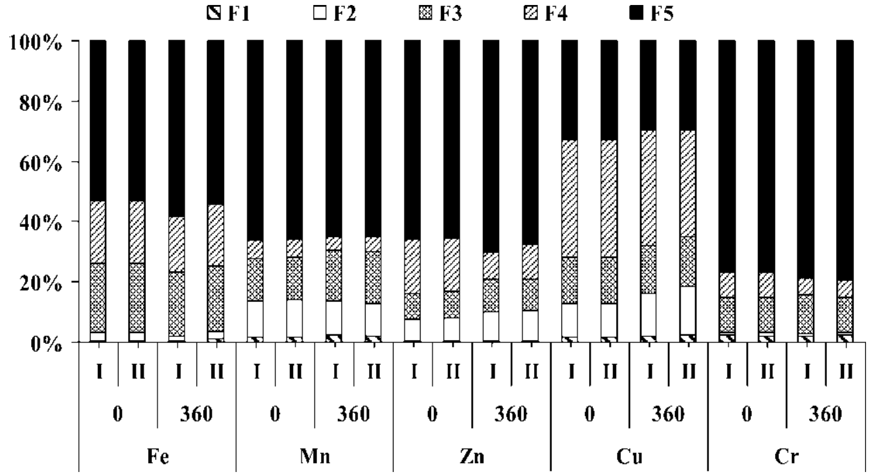

Figure 4. The relative percentage of heavy metal concentrations extracted by different reagents with time under aerobic (I) and anaerobic (II) conditions at site S2.

and 3. The concentration of heavy metals in the different forms varied with time incubation, after an incubation period (360 h), significant charges were occurred in the concentration of heavy metals associated with their different fractions. The changes in both redox potential (Eh) and pH value had marked effects on heavy metals transformation. The major mechanism of accumulation of heavy metals in sediments leads to the existence of five categories, viz., exchangeable, bound to carbonate, bound to reducible phases (iron and manganese), and bound to organic matter and residual. These categories have different behaviours with respect to remobilisation under changing environmental conditions. There are two basic approaches for fractionation in sediments. The theoretical one based upon thermodynamic calculations suffers from incomplete data [4]. The experimental determination implies a separation of the above said five different fractions by using a sequential extraction procedure [10].

3.2.1. *Water soluble and exchangeable fraction (F1)*

The metal concentrations at oxidised conditions bound to the water soluble and exchangeable fraction (F1) in the investigated sediments at zero time were 13.5 and 11.8 μg/g for Fe; 6.56 and

Table 2. Heavy metal concentrations (μg/g) extracted by different reagents with time under oxidation (I) and reduction conditions (II) at sample S1.

		F1		F2		F3		F4		F5		
Metal	Time (h)	I	II	I	II	I	II	I	II	I	II	Total
Fe	0	13.50	13.8	78.80	78.40	635.40	637.40	577.10	576.20	1464.00	1463.00	
	360	11.10	32.8	47.80	65.70	584.50	609.50	517.10	561.60	1609.00	1499.00	2769.00
Mn	0	6.56	6.46	55.51	55.91	63.99	63.85	27.32	27.61	300.00	299.00	
	360	8.71	8.84	52.56	48.50	75.89	78.71	20.15	22.30	296.00	295.00	443.31
Zn	0	1.67	1.61	6.52	6.90	8.22	8.19	16.72	16.87	62.00	61.00	
	360	2.73	1.04	8.84	9.45	9.84	10.08	8.43	10.93	65.00	64.00	90.57
Cu	0	2.94	2.87	5.17	5.21	6.97	6.91	17.91	17.93	15.00	15.00	
	360	4.98	5.55	6.12	7.07	7.13	7.24	16.72	15.54	13.00	13.00	46.23
Cr	0	1.68	1.66	3.10	3.13	34.21	34.19	25.02	25.20	229.00	229.00	
	360	1.70	2.52	2.33	2.53	37.67	35.04	17.0	16.80	234.00	236.00	285.70

Table 3. Heavy metal concentrations (μg/g) extracted by different reagents with time under oxidation (I) and reduction conditions (II) at sample S2.

		F1		F2		F3		F4		F5		
Metal	Time (h)	I	II	I	II	I	II	I	II	I	II	Total
Fe	0	11.80	11.50	57.85	57.55	766.00	764.00	822.00	825.00	1087.35	1086.95	
	360	10.73	29.57	55.79	51.74	690.00	734.00	749.00	815.00	1239.48	1094.69	2750.00
Mn	0	6.87	6.80	44.18	44.25	83.29	83.40	61.49	61.55	197.17	197.00	
	360	9.97	9.40	40.28	55.37	91.65	84.70	42.54	47.31	208.56	196.22	415.49
Zn	0	1.73	1.80	17.18	17.20	49.27	49.85	66.12	66.46	110.70	109.69	
	360	1.92	1.16	23.78	24.90	52.42	55.20	68.87	72.44	98.01	91.30	250.21
Cu	0	3.63	3.70	6.92	6.86	8.91	8.13	52.73	52.80	42.81	43.51	
	360	5.05	6.26	10.34	11.15	12.85	12.49	43.34	48.87	43.42	36.23	121.00
Cr	0	1.88	1.80	4.05	4.10	13.10	13.15	10.39	10.42	39.58	39.53	
	360	1.78	1.92	2.67	3.85	13.48	12.28	8.92	7.39	42.15	43.56	70.17

F1: Exchangeable fraction, F2: Carbonate fraction, F3: Oxides fraction, F4: Organic fraction, F5: Residual fraction.

6.87 μg/g for Mn; 1.67 and 1.73 μg/g for Zn; 2.94 and 3.63 μg/g for Cu and 1.68 and 1.88 μg/g for Cr for both S1 and S2, respectively. At oxidised status, the metal concentrations in the water soluble and exchangeable form of Fe, Mn, Zn and Cr revealed slight variation during the study period. The copper concentration bound to this fraction showed wide change, the Cu content increased from 2.94 to 4.98 μg/g at sample S1 and from 3.63 to 5.05 μg/g at sample S2 (after 360 h). At reducing medium (anaerobic condition), high change was observed in the Cu content, it changed from 2.87 to 5.55 and from 3.63 to 6.26 μg/g at the two samples S1 and S2, respectively. In general, large amounts of iron and manganese associated with the exchangeable and water soluble fractions increased with an increased incubation time. It seemed that the anaerobic conditions were more favorable for metal bound to water soluble and exchangeable fraction. Ford et al. [11] found at pH 5.0, the metal-solubility increased three to five fold when the redox potential was reduced from 325 to −100 mV. The fate and distribution of the heavy metals (iron, manganese, zinc and chromium) among the water-soluble and exchangeable fraction at the end of the incubation period were decreased or increased; these may be influenced by many factors, including the relative concentration of metals, differences in energies of adsorption on colloid surfaces and differences in the capacity of metals to form highly stable complexes with organic matter [12].

3.2.2. *Carbonate fraction (F2)*

This fraction shows the amount of each element that would be released into the environment if conditions became more acidic. It is the fraction with the most labile union to the sediment and therefore, the most dangerous for the environment. The results as shown in Tables 2 and 3 revealed increasing in the Cu and Zn concentrations bound to carbonate fraction (F2) at oxidised and reducing conditions at the two samples after incubation at 360 h, while the other metals (Fe, Mn, and Cr) decreased, the values at zero time (S2) were 57.85 and 57.55 μg/g for Fe; 44.18 and 44.25 μg/g for Mn; 17.18 and 17.2 μg/g for Zn; 6.92 and 6.86 μg/g for Cu and 4.05 and 4.1 μg/g for Cr. After 360 h, these values changed to reach 24 μg/g for Zn and 11 μg/g for Cu. On the other hand, a significant amount of Mn was found in the reducing condition at site S2 (55.37 μg/g). Weakly sorbed Mn retained on sediment surface by relatively weak electrostatic interactions may be released by ion-exchange processes and dissociation of Mn-carbonate phase [10]. The result indicates that considerable amount of Mn may be released into the environment if conditions become more acidic [13,14]. In addition, a considerable amount of Mn was detected in the reducible fraction, in which Mn exists as oxides and may be released if the sediment is subjected to more reducing conditions [15].

3.2.3. *Oxides fraction (F3)*

This fraction theoretically represents the contents of each metal bound to iron and manganese oxides that would be released if the sediment were subjected to more reductive conditions [15]. Manganese ions do not cause any dangerous effects on the biota in natural waters since different forms of Mn compounds exist in the water body due to the pH and redox potential conditions. In natural waters the amount of MnO_2 depends mainly on these factors. Manganese ions can be adsorbed and/or partially ion-exchanged on the surface of MnO_2 and they can be environmentally mobile in certain conditions. In water purification technology, MnO_2 is often used as an adsorbent. A thermodynamic affinity sequence of $Mn_2 > Cu_2 > Zn_2$ was established [16]. At $pH > 3$ the surface of the MnO_2 is negatively charged, and sorption of metal ions is preferred. Metal ions are adsorbed on the hydrous MnO_2 as free hydrated ions, and protons are released. The data of heavy metals content (for the two samples) at oxidised status bound to the oxides fraction (F3) at zero time were 633.4 and 766 μg/g for Fe; 64 and 93.29 μg/g for Mn; 8.22 and 49.27 μg/g for Zn; 6.97 and 8.91 μg/g Cu and 34.21 and 13.1 μg/g for Cr; these values showed slightly decreased after incubation 360 h except of Fe (Tables 2 and 3). The same trend of metals bound to carbonate form was observed at the reducing condition. It is obvious that the highest redox potential affected on the amount of iron and manganese in the oxides form. When the redox potential decreased to −133 mV at sample S1 and −170 mV at sample S2, it caused a marked transformation of the Fe-Mn oxide form to the water-soluble and exchangeable fractions. A small decrease in the pH value sufficed to convert the Mn-oxide form to the more exchangeable and water-soluble fractions, especially in reduced conditions. Although, manganese and other metals were solubilised at low pH and Eh, a large part of the solubilised iron and manganese did not remain water-soluble, but become associated with the exchangeable fraction. The results showed that the amount of iron, zinc, copper and chromium associated with oxides form was increased possibly affected with the decrease in the Eh and pH value. Also, these metal behaviours associated with the oxides fraction have the same trend as carbonate bound material and water-soluble and exchangeable fraction.

3.2.4. *The organic fraction (F4)*

This shows the amount of metal bound to the organic matter and sulfurs which would be released into the environment if conditions became oxidative. Such a change occurs during dredging [17]. The results of heavy metals bound to the organic fraction (F4) (Tables 2 and 3) at zero time for oxidation medium were 577 and 822 μg/g for Fe; 27.32 and 61.49 μg/g for Mn; 16.72 and 66.12 μg/g for Zn; 17.91 and 52.73 μg/g for Cu and 25.02 and 10.39 μg/g for Cr; these values of the metals revealed slightly decreased for Fe and Cr after incubation (360 h) and at reducing conditions.

The fluctuation and behaviour of the metals either under oxygen aeration or nitrogen bubbling may be due to the pH values for the two cases being nearly equal. The data revealed that the greater amount of manganese bound to organic fraction decreased through the incubation period. In contrast, the concentration of manganese associated with oxides increased. The results showed that the increase of zinc and copper among water-soluble and exchangeable fraction at the end of the incubation period were high, accompanied by a significant decrease in the content of the organically bound fraction. The amounts of iron, zinc and copper extracted in the organic form were recorded as being very high compared with those of manganese and chromium (Tables 2 and 3; Figures 3 and 4).This may be due to the decomposition of organic compounds produced in the sediment-water system, in that reducing status is brought about by microbial reduction. The microbiological processes have a great influence on the transformation of these metals. Chelating compounds produced in the sediment-water system may react with metal ions and alter the redox reaction of heavy metals in sediment.

The present study under both aerobic and anaerobic conditions showed that the relative percentage of metals associated with the organic fraction can be arranged in the following order:

$$\mathrm{Cu} > \mathrm{Fe} > \mathrm{Zn} > \mathrm{Cr} > \mathrm{Mn} \text{ at sample 1} \tag{S1}$$

$$\mathrm{Cu} > \mathrm{Fe} \sim \mathrm{Zn} > \mathrm{Cr} \sim \mathrm{Mn} \text{ at sample 2} \tag{S2}$$

Extractable Fe, Zn and Cu after about 360 h, which represents organic complexes formed under reduced condition, were 20.3%, 11.5% and 32.3% (S1) and 29.7%, 29.6% and 42.5% (S2), respectively. This appeared to vary directly with organic carbon content of the sediments (the content of organic carbon was 0.61% for S1 and 2.97% for S2). Shata et al. [18] showed that the metals bound to the organic fraction relative to the total content were 8.8% for Mn, 5.2% for Fe and 18.5% for Zn.

Under anaerobic conditions, the relative percentage of all five metals after incubation for about 360 h extracted from the two samples (S1 and S2) including the summation of four fractions (water-soluble + exchangeable + carbonate + oxides + organic fractions) constituted 45–60% of the total amount of iron, 33–50% for manganese 33–63% for zinc, 63–74% for Cu and 19–43% for Cr (Figures 3 and 4). The present study showed that under strongly reducing conditions (-130 to -170 mV) the levels of exchangeable Zinc were lower than under more oxidising conditions. This was in agreement with those reported by Okbah and Tayel [19]. The decrease in the exchangeable Zn fraction of the two samples (S1 and S2) may be due to its precipitation as Zn-carbonate [20] and increases in the acidified ammonium oxalate fraction caused a slight increase in the amount of Zn associated with the oxides fractions [21].

3.2.5. *The residual fraction (F5)*

In this fraction, the metals with the strongest association to the crystalline structures of the minerals were therefore the most difficult to separate from the sediments [22]. A large amount of Zn was concentrated in the residual fraction, the residual concentration of Zn in the sediments (S1 and S2) ranged between 60 and 110 μg/g, representing approximately 40–67% (Figures 3 and 4) of the total under oxidation and reduction conditions. This meant that large amounts of the Zn was in a stable form, and in natural circumstances, the Zn compounds could be found as solid species in the sediments, and the half of the Zn concentrated are found in the others fractions. In our study the residual concentration of Cu ranged between 28 and 36 μg/g for the two sites, representing about 33% of the total content. The residual Cr concentration of the two sediments (S1 and S2) in the Aden Gulf was between 39 μg/g (S2) and 229 μg/g (S1), these values represent from 80% to 60% for S1 and S2, respectively. The results of residual fractions of Fe and Mn are illustrated in Figures 3 and 4. A large amount of Fe and Mn was found in the residual form compared to the total concentration in aerobic and anaerobic conditions. The proportion of 50% for Fe and 70% for Mn was in the residual fraction. The distribution patterns of Fe at the two sites were similar.

4. Conclusion

In this study, we analysed heavy metal distribution and speciation in sediments collected from two sites in the Gulf of Aden under two different conditions after incubation for three weeks.

The metal speciation analysis provided information on their bioavailability and mobility, which is easier for those metals bound to labile phases.

The results obtained from the sediment speciation analysis in this study, enable us to explain the pattern of variance in two different conditions; oxidising and reducing conditions. Sites with the highest metal concentrations in phases 1 and 4 may have the lowest biodiversity.

Therefore it may be asserted that studies on metal speciation in sediments can be a useful means of understanding the responses of biological communities. The density of the population of living organisms fell when it was found in close contact with high bioavailability metal concentrations in a sedimentary environment.

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