Speciation and Mobility of Some Heavy Metals in the Coastal Sediments of Jeddah, Eastern Red Sea

صور الترابط و إنسيابية بعض العناصر الثقيلة فى الرواسب الساحلية لمدينة جدة- الساحل الشرقى للبحر الأحمر

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Abstract: Total and potentially mobile fractions of Fe, Mn, Cu, Zn and Pb were analyzed in 28 sediment samples collected from the coastal area of Jeddah. Sampling sites were selected to represent heavily sewage polluted areas and areas far from the effect of direct sewage dumping. Total concentrations reflected the degree of contamination and were particularly high in the confined environments. Concentrations in the mud fraction ($<63\mu m$) were 3 to 6 times higher than that in the sand fraction. The repartition of the elements between the exchangeable, reducible, oxidizable and residual fractions depends on the element nature and prevailing environmental conditions. Iron was mainly found in the residual fraction either as constituent of the detrital material and/or trapped in the form of insoluble sulphides. Dominance of the exchangeable fraction characterized the speciation of Mn. Mobilization of Mn under reducing conditions and its readsorption on the particle surface is a probable explanation. Cu and Zn appear to have comparable distribution between the different fractions, however, Cu seems preferentially associated with the oxidizable fractions while reducible Zn was slightly more important than the other forms. Pb was particularly distributed between the oxidizable and the exchangeable fraction. Residual Pb participation was very low and sometimes totally absent. The interest behind the use of speciation schemes is that it permits the distinction between the fraction of the element that could be released into the water when the physico-chemical conditions are modified and the part that is permanently or quasi permanently fixed in the sediments. Most of the Fe was found held in the residual unavailable form while most of Mn, Cu, Zn and Pb were distributed between the environmentally unstable exchangeable, oxidizable and reducible fractions. Therefore, these elements are supposed to have greater mobility and may, under particular conditions, greatly influence the environmental characteristics.

Keywords: Sediments, Heavy metals, Spectiation, Mobility, Red Sea, Jeddah.

المستخلص: قيست التركيزات الكلية وكذا الصور القابلة للإنسياب لعناصر الحديد و المنجنيز و النحاس و الزنك و الرصاص فى 28 عينة من رواسب المنطقة الساحلية لمدينة جدة. وقد تباينت أماكن جمع العينات ما بين مناطق شديدة التلوث بمخلفات الصرف الصحى و مناطق تكاد تكون خالية من التلوث. وقد تبين إرتفاع التركيزات الكلية فى المناطق الملوثة خاصة البيئة الشبه مغلقه منها، كما إتضح أن التركيزات فى الجزء الناعم من الرواسب تمثل 3 إلى 6 أمثال مثيلاتها فى الجزء الرملى. وقد إعتمد توزيع العناصر بين صور الترابط المختلفة وهى التبادلى والمختزل والمؤكسد والمتبقى على طبيعة العنصر والمواصفات السائدة فى الوسط. تميز عنصر الحديد بسيادة الصورة المتبقية الموجوده فى المواد المنقولة من الأرض أو فى صورة كبريتيدات صعبة الإستخلاص بينما تميز المنجنيز بإرتفاع تمثيل الجزء التبادلى وربما يعود هذا إلى إنسيابه تحت ظروف مختزله وإعادة إدمصاصه فى الأوساط المؤكسدة. وقد ظهر أن النحاس والزنك يتسمان بتوزيع متشابه غير أن هناك بعض التفوق لترابط النحاس بالمواد العضوية بينما يتفوق ترابط الزنك بأكاسيد الحديد و المنجنيز فى حين توزع الرصاص أساساً ما بين الصورة التبادلية و الصورة المؤكسدة.

وتتبع أهميةدراسة صور ترابط العناصر الثقيلة بالرواسب ف كونهاتميز بين الجزء من العنصر القابل للإنتقال بين الماء والرواسب والجزء الذيلايمكن أن ينساب من الرواسب. وقد وجد أن النسبة الكبرى من الحديد ترتبط بقوة مع الرواسب ولايمكنها الإنسياب الى الماء بينما كانت الغالبية للصور سهلة الحركة لعناصر المنجنيز - النحس - الزنك والرصاص. هذه العناصر يمكنها أن تؤثر على مواصفات الوسط إذا ما توفرت الظروف المواتية لانسيابها من الرواسب.

كلمات مدخلية: رواسب، عناصر ثقيلة، صور الترابط، إنسيابية، البحر الأحمر، جده.

Introduction

The eastern coast of the Red Sea is approximately 2000 Km long; about 90% belongs to the Kingdom of Saudi Arabia. Its coral reef community is one of the most diverse in the world.

The importance of the coral reef as suitable environment for feeding, breeding and as nursery ground for a vast variety of marine organisms has been recognized by several ecologists (Odum and Odum, 1955; Veron, 1986). Coral reefs are however, seriously endangered particularly in the

developing countries, due to intensive wastewater dumping in the coastal area.

The city of Jeddah is the most important urban agglomeration at the central part of the eastern Red Sea coast. Since the seventies the city has been suffering an immense economic and population growth. Three hundred thousand inhabitants in 1979, its population is approximately two million at present (no official figures are available). Industrial activity is also expanding and includes refineries, petrochemicals and foodstuff. Four wastewater treatment plants have been established and operated in the city. The most important is Al-Khumra station. Its effluent is situated south of the city and delivers mixed wastewater in the coastal area. Another site suffering from the impact of sewage discharge is the Al-Arbaeen Lagoon off the city center. This lagoon receives wastewater of domestic sewage from two discharge effluents.

Available data concerning heavy metal pollution in the Southern Corniche area and the Al-Arbaeen Lagoon demonstrate the association of high concentrations of heavy metals with the bottom sediments; however, their mode of association has never been considered. Despite the fact that the data on total concentrations are informative, the real environmental risk could not be assessed without investigating metal speciation. Sediment bound elements can be associated with several geochemical fractions. It is generally recognized that the environmental impact of trace metals depends to a significant extent on the host fraction and the way the trace metal is associated with it (Forstner and Wittman, 1983; Kirk, *et al.* 1985).

This study aims at assessing the mode of association of some environmentally important heavy metals with the bottom sediments in the coastal area of Jeddah taking in consideration the influence of human interference.

Study Area

The coastal area under investigation lies between $21°\ 22'$ and $21°\ 46'$ N and extends for about 45 km (Fig. 1). Four sites were selected to study the metal-sediment association mode. The sites are semi-closed areas, three of which are subjected to the impact of sewage discharge but to varying degrees while the forth site is relatively away from any massive sewage dumping.

Site I (Southern Corniche) is a shallow (2-3 m in depth) lagoon-like basin situated at about 20 km south of the city of Jeddah. Natural and artificial barriers limit water circulation particularly southwards. The lagoon receives about 100-

150×10^3 m^3 day-1 of treated and untreated sewage from Al-Khumra sewage treatment station. Pollutants are expected to accumulate in the area due to the restricted water exchange with the open seawater. Basaham, *et al.* (1998) and El Sayed (2002) found elevated concentrations of heavy metals and organic matter in the bottom sediments and suspended particulate matter.

Site II (Al-Arbaeen Lagoon) lies off the city center. Its surface area is about 290×10^3 m^2 and has an average depth of about 4 m. The lagoon is composed of two basins and communicates with the open sea through a relatively narrow channel. It receives wastewater of domestic sewage amounting to 60,000 m^3day-1. Description of the lagoon and its hydrography are given in El-Rayis and Moammar (1998). The interplay of sewage dumping and extended residence of water creates anoxic conditions and has resulted in heavy metal accumulation in the sediments (El-Rayis, 1990; Basaham, 1998)

Site III (Al-Frusiyah) is a semi-closed area of restricted circulation due to the presence of several reefal structures. The area is relatively shallow (maximum depth 10 m) and is bordered from the north by Al-Salam Lagoon and from the south by Al-Shabab Lagoon; both receive municipal wastewater and communicate freely with the area. This is felt through the presence of high concentrations of ammonium, nitrogen, low oxygen concentrations and the detection of hydrogen sulphide in bottom water.

Site IV (Sharm Obhur) is a narrow coastal inlet located about 35 km north of Jeddah. It extends 10 km inland and has an average width of about 200 m. Its depth increases from about 2 m at its head to 35 m at the sea connection. The border of the Sharm is becoming a residential area and land filling is increasingly affecting the morphology, bottom topography and bottom sediment characteristics. Sediment texture, mineralogy and matrix composition have been previously studied (El-Sabarouti, 1983; Basaham and El-Shater, 1994).

Sampling and Analytical Methods

A total of 28 sediment samples were collected from the study area (Fig.1). Samples were manually collected from the stations where water depth did not exceed 1m. In deeper waters, sediments were collected using a grab sampler. Sediments were immediately placed in labelled plastic bags and stored in an icebox and transported to the laboratory where they were spread over plastic sheets in a fuming cupboard and left to dry at room temperature.
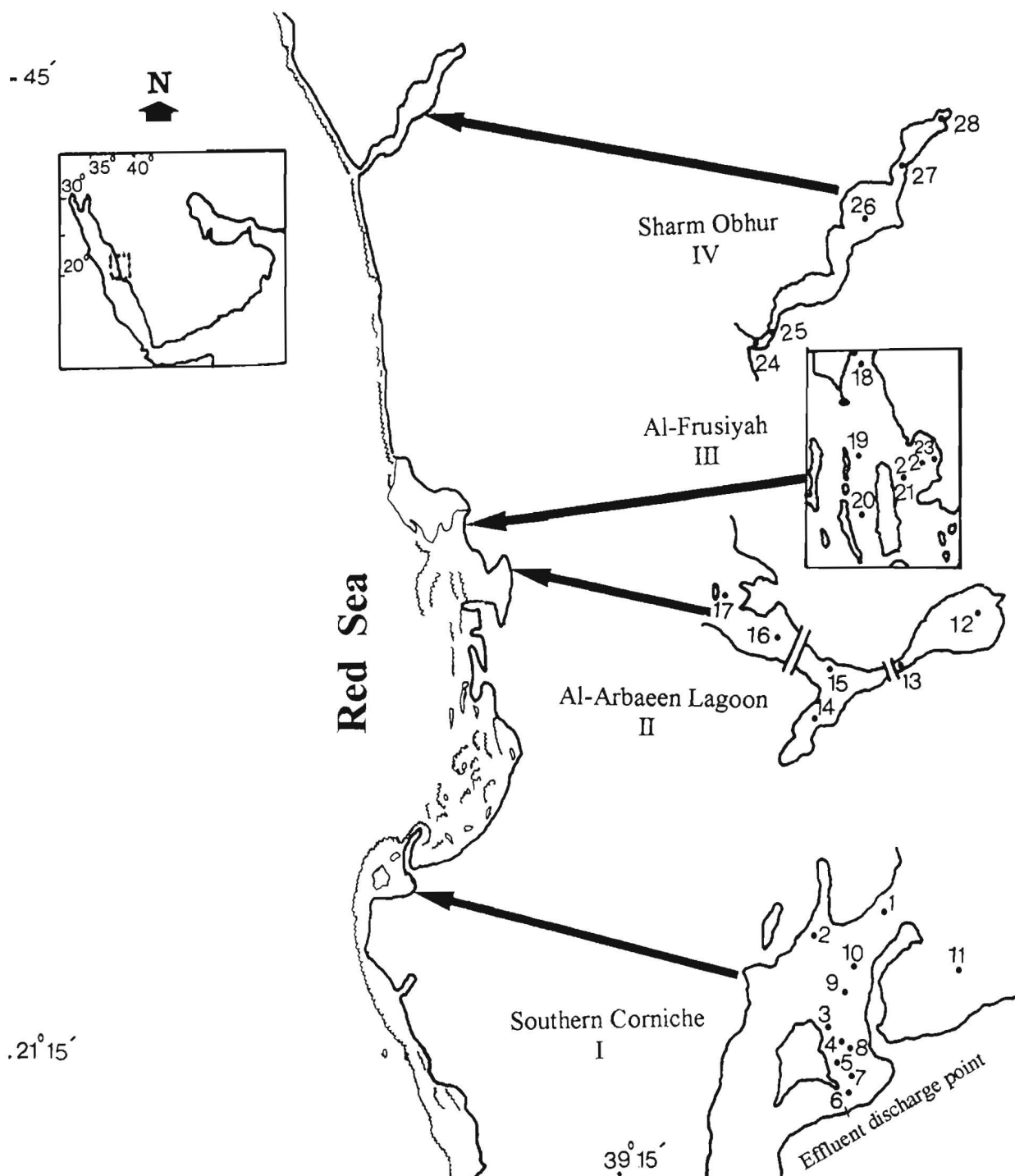
Fig. 1. Area of study and sampling locations.

Determination of the major sediment fractions, i.e, gravel, sand and mud was carried out using the standard wet sieving technique. Carbonate content was estimated using a calcimeter and organic carbon (OC) was determined using a modified sulfo-chromic wet oxidation method (Le Core, 1983).

It is widely accepted that most of the trace metal load in the sediments is associated with the fine-grained fraction, particularly the mud fraction (< 63 μm). This fact was confirmed during a previous study on the sediments of the Arabian Gulf (Basaham and El Sayed, 1998) and further to the examination of the sediments of this study.

Accordingly, representative sub samples were wet sieved and the less than 63 μm fraction was used for trace metal analysis.

Total metal concentrations were determined after a mineralization step consisting of heating 500mg of the powdered sample in concentrated nitric acid under reflux in Teflon cups at 140°C. The residue was taken in 10ml of 1M HCl. The leaching sequence used in this study for metal speciation in the mud fraction is presented in Figure (2).
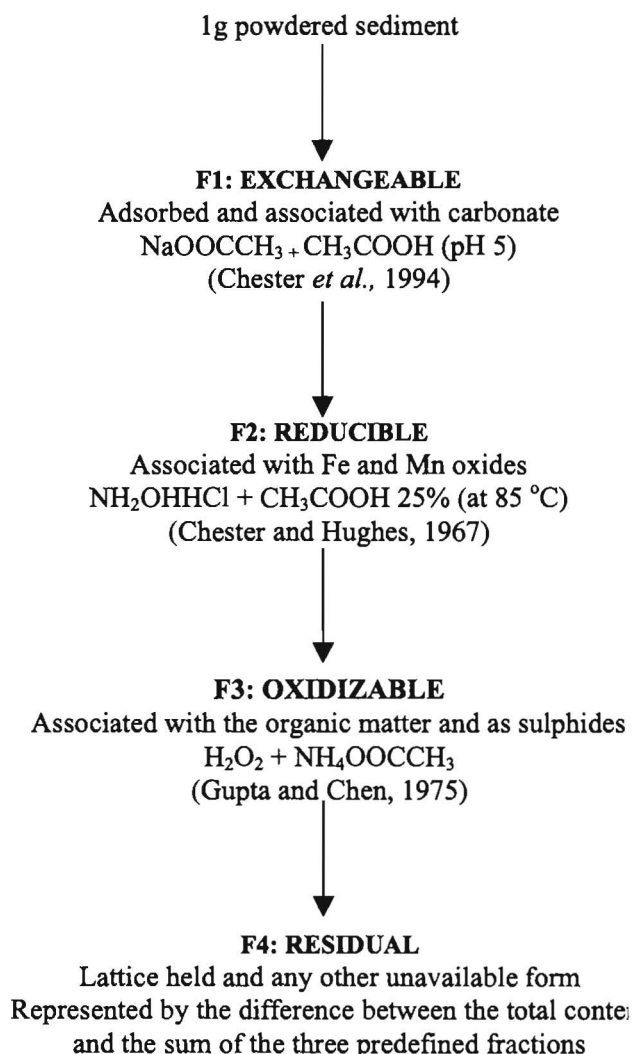
1g powdered sediment

↓

F1: EXCHANGEABLE
Adsorbed and associated with carbonate
$NaOOCCH_3 + CH_3COOH$ (pH 5)
(Chester *et al.*, 1994)

↓

F2: REDUCIBLE
Associated with Fe and Mn oxides
$NH_2OHHCl + CH_3COOH$ 25% (at 85 °C)
(Chester and Hughes, 1967)

↓

F3: OXIDIZABLE
Associated with the organic matter and as sulphides
$H_2O_2 + NH_4OOCCH_3$
(Gupta and Chen, 1975)

↓

F4: RESIDUAL
Lattice held and any other unavailable form
Represented by the difference between the total conter
and the sum of the three predefined fractions

Fig.2. Schematic representation of the sequential chemical extraction.

Accurately weighed 1g of the powdered sediment and the leaching solution were placed in a 50ml centrifuge tube and the sediment was maintained in suspension for the time defined by the method. The suspension was then centrifuged at 6000rpm for 10 min. To avoid matrix interference during measurement, the leachate was transferred to 25ml PTFE containers, heated to near dryness and the residue was dissolved in 3ml of concentrated HNO_3. The solution was then heated at 140°C until nearly dryness. The residue was then taken in 10ml of 1M HCl in graduated test tubes (polypropylene from Nalgen). Metal concentrations in the extracts were measured using an Atomic Absorption Spectrophotometer (Varian 250 SpectraA plus). Concentrations were calculated using working standard solutions, which were used for the calibration of the instrument.

Results and Discussion

Texture and matrix composition

Results of carbonate, OC and sediment types are presented in Table 1. Most of the samples are generally muddy-sand. The sand fraction averaged 56% and varied between 13 and 88%. Excluding the very polluted site II sediments are mainly composed of carbonate, which constituted between 11 - 88% of the mud fraction. Higher carbonate concentrations (17-96%) were measured in the bulk sediments, indicating the association of carbonate with the coarse sediments.

OC is one of the parameters used to identify environmental equilibrium rupture. OC concentrations in the study area (averages 0.7-7.84%) are generally higher than the concentrations reported for uncontaminated Red Sea sediments which range between 0.06-0.45 % (El-Sayed and Hosny, 1980; Basaham and El-Shater,1994; El-Sayed and Niaz, 1999). However, sites III and IV have values lower than 1 % and could be considered as receiving little organic matter disposal. On the contrary the impact of sewage discharge on the coastal area is clearly felt in the two other sites; site II being the most dramatically influenced due to its highly confined nature (Table 1 & Fig. 1). El Sayed and Niaz (1999) have estimated the OC build up in the Southern Corniche area (direct and potential) as equivalent to more than 13 tons day-1.

The relationship between OC content of the sediment and carbonate which is the major sediment constituent in the area is given in Figure 3. The negative correlation indicates the role that dilution plays on the carbonate component with regard to the organic carbon of the sediment.
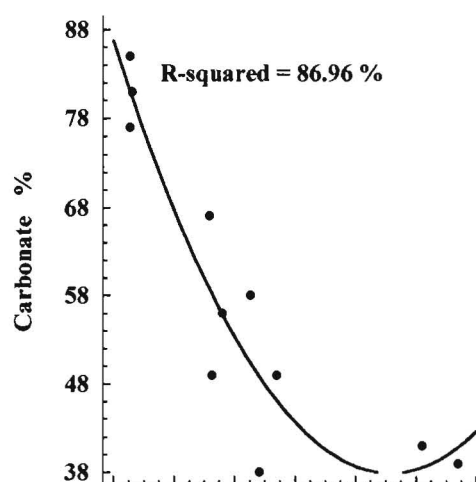

Fig.3. Relationship between carbonate and OC in the mud fraction (site I)

Table 1: Major sediment characteristics (%)

Sample No.	Gravel	Sand	Mud	CaCO$_3$ Mud fraction	O.C Mud fraction
1	0.10	20.80	79.10	81	0.61
2	0.40	50.10	49.50	85	0.54
3	16.50	80.50	3.00	56	3.60
4	--	--	--	39	11.40
5	1.90	59.50	38.60	67	3.18
6	8.60	67.80	23.60	49	3.24
7	--	--	--	41	10.20
8	31.00	61.50	7.50	38	4.83
9	8.80	82.00	9.20	58	4.53
10	40.80	48.40	10.80	49	5.40
11	11.90	61.50	26.60	77	0.54
12	--	--	--	36	4.50
13	--	--	--	28	4.47
14	--	--	--	--	18.23
15	--	--	--	4	6.97
16	--	--	--	36	8.04
17	--	--	--	40	4.87
18	--	--	--	68	0.50
19	--	--	--	88	0.90
20	--	--	--	68	0.60
21	--	--	--	72	1.00
22	--	--	--	80	0.70
23	--	--	--	32	0.80
24	7.66	67.62	24.32	74	0.61
25	3.40	88.39	8.21	55	0.88
26	0.25	13.21	86.54	11	0.79
27	0.54	67.12	32.34	43	0.78
28	2.11	23.06	74.83	29	0.44

Site I: samples 1-11; Site II: samples 12-17; Site III: samples 18-23; Site IV: samples 24-28
-- muddy samples

Total metal content

Influence of grain size on the concentration of heavy metals

It has been frequently reported (Martincic, *et al.* 1990, Basaham and El sayed, 1998; Basaham, *et al.* 1998) that several factors interfere severely and affect the total concentration of heavy metals in marine sediments. Grain size is one of these factors. The finer the sediments the higher is their capacity to retain and fix trace elements due to their greater specific surface area (Rabitti, *et al.* 1983; Donazzolo, *et al.* 1981).

To determine the impact of grain size on the total content of heavy metals, the sand and mud fractions of 13 sediment samples from sites I and IV were separated and their total metal contents were determined. Average concentrations of the different elements are presented in Table 2. It appears that the mud size fraction contains invariably higher concentrations. The ratio between the concentration in the two fractions ranged between 2.75 and 6.6; the highest value was that of Cu. The major part of

Table 2: Heavy metal concentrations (µg/g) and element1 mud/sandratios.

Element	Fe	Mn	Cu	Zn	Pb
Mud	8881	56	171	368	42
Sand	2605	12	31	80	15
Mud/Sand Site I	3.4	4.7	5.8	4.6	2.8
Mud/Sand Site II	2.75	3.4	6.6	4.4	----

The metal content is found in the mud fraction, particularly in the areas receiving sewage discharge ,confirming the capacity of the fine particles to fix dissolved species.

Distribution of heavy metals in the area: inter-site comparison

Total element concentrations in the mud fraction are given in Table 3. The examination of the results shows the wide disparity of the concentrations. The elements could be grouped in two associations according to their geochemical behavior. The first one is composed of Fe and Mn and the second consists of Cu, Zn and Pb. The first two elements are redox sensitive (Stumm and Morgan, 1981), which means that their distribution in the sediments will greatly depend on the oxidation-reduction potential of the environment beside the other influencing factors. Despite the absence of real proportionality, higher concentrations of Fe and Mn are associated with sediments having low carbonate content. The highest Fe concentrations are found at sites II and IV; the first one is the highly polluted Al-Arbaeen Lagoon while the second one is the remote less impacted Sharm Obhur. The massive discharge of sewage has created an excessively reducing environment at Al-Arbaeen Lagoon (El-Rayis and Moammar, 1998; Basaham, 1998). The iron associated with sewage is trapped as iron sulphide complexes (Fe $S(x)$); this assumption is supported by X-ray examination of the sediments (Basaham, 1998; Basaham, *et al.* 1998), which showed the presence of pyrite as one of the mineral constituents. The oxidation-reduction chemistry of Fe and Mn is comparable but differs in kinetics, therefore high Mn concentrations are also measured at the same site. At site IV conditions are different, as no important sewage dumping is taking place and no signs of anoxia are present. However, in the last few years filling operations are actively taking place and have brought large quantities of lithogenic material, rich in Fe and Mn compared to natural biogenic carbonate sediments. Recent sedimentological studies showed that sediment characteristics have significantly changed during the last five years (Rasul, N. KAU, pers. comm.). It is therefore clear that the elevated concentrations of iron and Mn at the two sites are due to different factors.

Table 3: Total metal concentrations in the mud fraction (ug/g)

Site No		Metal				
		Fe	Mn	Cu	Zn	Pb
Site I	Average	8882	59	179	368	42
	Range	1200 14700	14 92	10 648	17 1043	0 6 133
	SD	4546	27	179	314	48
Site II	Average	32350	241	491	696	140
	Range	24000 45300	116 372	62 1740	99 2524	15 480
	SD	7621	121	667	947	178
Site III	Average	2205	26	7	21	15
	Range	1300 3520	17 39	38235	14 32	44743
	SD	951	9	1	7	5
Site IV	Average	22300	253	34	62	11
	Range	12360 31320	97 372	21 51	50 102	43160
	SD	8309	124	13	23	7

The two other sites (I&III) have lower Fe and Mn concentrations; however, site I has been shown to be severely polluted due to sewage dumping (El Sayed and Niaz, 1999). The fact that site I has no elevated Fe and Mn concentrations despite sewage dumping is probably due to the absence of severely reducing conditions responsible for the generation and accumulation of hydrogen sulphide. Precipitation of metal sulphides is conditioned by the presence of excess H_2S. Lower concentrations at site III are explained by the highest carbonate content in the whole area.
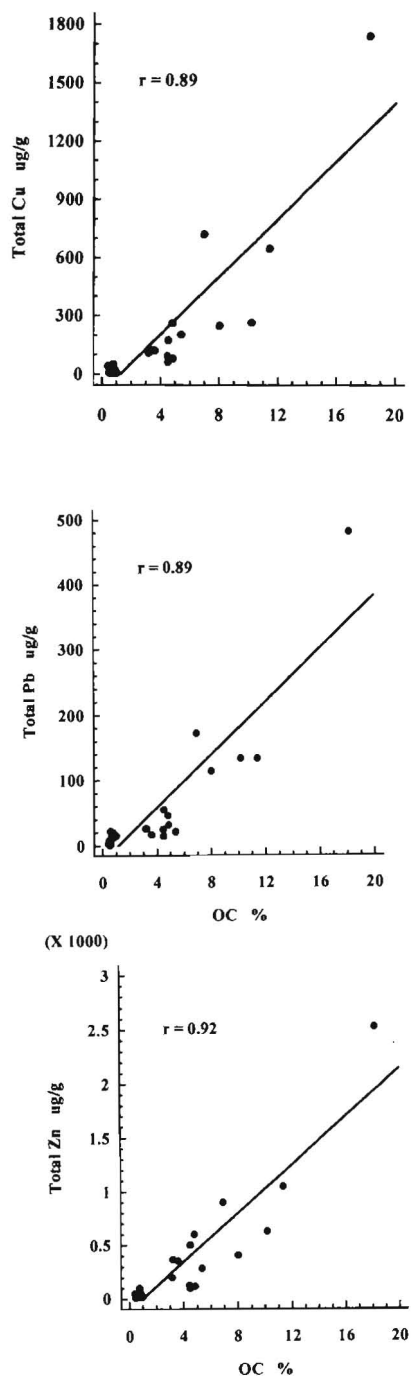

Fig. 4. Relationship between OC and total metal concentration for the whole area.

Fe and Al are frequently used as reference elements helping in neutralizing factors that may affect trace metal concentrations (Schropp and Windom, 1988; Loring, 1991; Din, 1992; Basaham and El Sayed, 1998). The metal /iron ratios (Table 4) clearly distinguish between the contaminated and uncontaminated sites. Sites I and II (contaminated) have lower Mn/Fe ratios (0.66-0.75). This could be explained as a result of Mn bleeding under reducing conditions, while iron will rapidly form insoluble $Fe(S)x$,. Using the metal/iron ratio, it seems that the sediments of the Southern Corniche are relatively more enriched in Cu and Zn than the Al-Arbaeen Lagoon. Sharm Obhur appears as the cleanest site since it has the lowest element/Fe ratio.

Elements of the second group, Cu, Zn and Pb are inter-correlated and their variability is controlled by OC fluctuations (Fig. 4).

Metal speciation

Iron

The geochemistry of Fe is greatly affected by redox conditions (Stumm and Morgan, 1981). In the oxic sediments iron is mainly present as the most stable oxide (FeIII), while in suboxic and anoxic environments iron oxide is used as electron acceptor in the oxidation of organic matter (Froelich *et al.*, 1979) and the liberated Fe^{2+} is swept out to the water column and/or re-trapped in the presence of excess H_2S as sulphide complexes.

The results of Fe speciation (Table 5a) indicate that in three of the sites (I, II & IV) residual iron is the major component of the element where it constitutes between 55 and 95% of the total concentration with averages ranging between 71 and 76%. This situation is similar to that recorded in the sediments of the Gulf of Aqaba (Abu-Hilal, 1993), in nearshore sediments (Rosental, *et al.*1986) and in the deep Atlantic sediments (Chester, *et al.* 1994). The lowest residual fraction is found in sediments having the highest carbonate concentration. The increase of the carbonate fraction means the decrease of the terrigenous component of the sediment. Regression analysis indicates that residual Fe correlates with its total content (r = 0.97). This means that the concentration of residual Fe is defined by its total concentration independently of the sediment matrix. Exchangeable iron was found in very low concentrations varying between an average of 14 µgg-1 at site III and 150 µgg-1 at site II.

Table 4: Average elmen/iron ratios in the sediments of the study area.

Element/Fe (x100)	Mn/Fe	Cu/Fe	Zn/Fe	Pb/Fe
Site I	0.66	2.01	4.15	0.47
Site II	0.75	1.52	2.15	0.43
Site III	1.18	0.32	0.93	0.70
Site IV	1.13	0.15	0.28	0.05

On a fraction basis, exchangeable iron represented between 0.10 and 0.21% at sites IV and I and between 0.49 and 0.69% at sites II and III. This result agrees with the finding of other authors (Kitano and Fujiyoshi, 1980; Van Valin and Morse, 1982).

Fe present in the reducible fraction alternates with the oxidizable fraction in occupying the second position after the residual fraction. At sites I and II reducible Fe comes in the second position averaging about 16 and 13% respectively. At sites III and IV the oxidizable fraction becomes the dominant one with an average of 31 and 21% respectively. Only at site I the oxidizable iron correlates with OC (r = 0.74). This relationship was expected at site II, highest in OC but it is probable that the presence of highly reducing conditions (Basaham, 1998) gives the advantage to the formation of iron sulphides, due to the presence of excess H_2S. Pyrite formation depends on the availability of dissolved sulphate and metabolisable OC beside the availability of reactive dissolved Fe (Goldhaber and Kaplan, 1974; Berner, 1984). Basaham (1998) studied the mineralogy of the sediments of Al-Arbaeen Lagoon and demonstrated the presence of pyrite as one of the mineral constituents. The technique we used to separate the oxidizable fraction is, most probably, unable to dissolve totally the sulphide fraction, particularly pyrite.

Manganese

Manganese is also a redox sensitive and very dynamic transition element. In oxic environments, the element is found as Mn(IV) while in the reducing environments its dominant oxidation state is Mn(II). The transformation is produced when Mn(IV) is used as electron acceptor in the oxidation of organic carbon (Froelich, *et al.*1979).

The great mobility of Mn is reflected in its distribution among the different geochemical fractions (Table 5b). The main feature of Mn speciation is the increasing importance of the exchangeable fraction, which varied between an average of 15±7% at site I and 32.7±4.5% at site III. Comparable proportions were extracted from reducing sediments (Van Valin and Morse, 1982) and polluted sediments (Nembrini, *et al.* 1982). Operationally, the exchangeable fractions represents the sum of adsorbed and carbonate bound fraction. However, the negative relationship between carbonate content and the exchangeable Mn concentrations at site I (r = - 0.89) demonstrates the low adsorbing capacity of the carbonate particles.

Reducible Mn showed limited variations and represented between 15 and 25% of its total content. Except at site II, the concentration of the reducible Mn co-varies with that of Fe (r = 0.95), which may result from the similarity of their redox chemistry.

The oxidizable fraction of Mn has approximately the same importance as the reducible fraction (Table 5b). The average values varied between about 15 and 20% but remarkable variations are recorded between the sampling stations at the individual sites. It is surprising to observe that the highest general average of oxidizable Mn (19.94%) was found at site III and not at the OC rich site II. This observation is similar to the situation recorded with oxidizable iron and may be interpreted on the same basis; Mn being found, at site II, mainly as sulphide that is hardly soluble in the extraction medium.

Residual manganese is the major fraction at only site I where it averages 51.03±10.75%; at all other stations with only few exceptional cases it represents less than 50%. The lowest residual fractions were successively recorded at sites II (35.9%) and III (22.4%). It is to be noted that the sites where the residual fraction is the highest are those suffering active filling with land derived material. This detrital material may contain significant proportions of residual Mn. The same sites have been shown to be rich in residual Fe. Residual iron and Mn are well correlated (r = 0.80) in the sediments of the entire area.

Copper

Cu is a micronutrient and its depletion in the surface waters has been attributed to its biological incorporation and scavenging by mineral and organic particles in the water column (Bruland, 1983). The characteristic feature of the speciation of

Table 5a: Distribution of Fe between the different geochemical fractions

Site No .	ug/g				Fraction %			
	1	2	3	4	1	2	3	4
Site I								
Average	13.0	1478	751	6640	0.2	16 2	9 2	74.4
Range	7 - 27	151 - 3275	14 - 1626	984 - 11599	0 1 - 0 7	7 7 - 35.1	0.1 - 21.8	58.8 - 84.5
Site II								
Average	150	4070	3099	25031	0.5	13 2	10 1	76.2
Range	12 - 449	1054 -12353	1222 - 7008	17684 - 42944	0 1 - 1 6	2 3 - 38.1	2.7 - 20.1	55 - 94.8
Site III								
Average	14 .0	502	671	1019	0.7	25 1	31 3	42.9
Range	5 - 29	369 - 648	408 1095	308 - 1914	0.2 - 1.7	17 - 40.4	22.3 - 37	23.7 - 59.8
Site IV								
Average	25.2	1679	4827	15768	0.1	7 6	21.1	71.3
Range	5 - 59	864 - 2259	486 -9960	9761 - 26977	0.03 - 0.2	7 - 8.8	2.2 - 36.8	54.2 - 90.8

1= Exchangeable   2 = Reducible   3 = Oxidizable   4 = Residual

Table 5b: Distribution of Mn between the diffrent geochemical fractions

Site No.	ug/g				Fraction %			
	1	2	3	4	1	2	3	4
Site I								
Average	8	9	10	32	15	17	17	51
Range	4 - 20	3 - 14	1 - 20	5 - 55	9 - 31	8 - 27	6 - 33	27 - 61
Site II								
Average	74	32	32	103	31	16	18	35
Range	30 - 151	17 - 44	11 - 53	21 - 225	22 - 45	6 - 27	3 - 41	16 - 65
Site III								
Average	9	6	5	6	33	25	20	22
Range	5 - 15	4 - 9	3 - 9	2 - 12	26 - 39	16 - 39	14 - 25	14 - 30
Site IV								
Average	48	39	40	126	19	17	16	48
Range	22 - 103	21 - 56	7 - 83	47 - 207	10 - 29	12 - 23	3 - 25	34 - 56

1= Exchangeable   2 = Reducible   3 = Oxidizable   4 = Residual

Table 5d: Distribution of Zn between the diffrent geochemical fractions

Site No.	ug/g				Fraction %			
	1	2	3	4	1	2	3	4
Site I								
Average	117	136	68	47	36	35	13	16
Range	7 - 225	5 - 353	2 - 450	3 - 163	22 - 46	22 - 56	4 - 43	2 - 38
Site II								
Average	260	144	229	63	33	28	16	23
Range	12 - 808	23 - 403	5 - 1287	13 - 165	12 - 55	16 - 41	3 - 51	1 - 53
Site III								
Average	6	8	6	3	30	38	27	5
Range	5 - 7	6 - 11	3 - 13	n.d - 4	20 - 42	27 - 54	13 - 41	n.d - 15
Site IV								
Average	6	17	14	25	9	29	22	40
Range	3 - 12	10 - 24	3 - 24	12 - 47	5 - 18	20 - 42	7 - 48	23 - 68

n.d not detectable

1= Exchangeable 2 = Reducible 3 = Oxidizable 4 = Residual

Table 5e: Distribution of Pb between the diffrent geochemical fractions

Site No.	ug/g				Fraction %			
	1	2	3	4	1	2	3	4
Site I								
Average	8	21	8	4	18	47	32	3
Range	n.d - 17	n.d - 69	1 - 41	n.d - 41	n.d - 35	n.d - 68	6 - 100	n.d - 31
Site II								
Average	26	64	16	33	20	53	18	9
Range	1 - 84	6 - 157	2 - 59	n.d - 179	6 - 38	33 - 73	6 - 50	n.d - 37
Site III								
Average	6	7	2	1	41	46	9	4
Range	3 - 7	5 - 11	n.d - 3	n.d - 2	32 - 52	31 - 63	n.d - 14	n.d - 9
Site IV								
Average	4	5	2	2	23	53	15	9
Range	n.d - 7	2 - 7	1 - 2	n.d - 3	n.d - 44	32 - 82	12 - 21	n.d - 20

n.d not detectable

1= Exchangeable 2 = Reducible 3 = Oxidizable 4 = Residual

copper is the dominance of the oxidizable fraction, which varied between an average of 32% at site IV and 63% at site III (Table 5c). Several studies have shown the dominance of the organic fraction in Cu speciation and agree with our results (Rapin, *et al.* 1983; Rosental, *et al.* 1986; Mat, *et al.*1994)

Excepting at site III where total Cu conçentration is very low and its variability is very limited, a clear correlation was found between OC and oxidizable copper (Table 6).

Table 6: Linear regression of oxidizable Cu on organic carbon

Site	Linear regreation equation	r
I	Oxidizable Cu = 3.69 + 21.53 * OC	0.94
II	Oxidizable Cu = - 441.72 + 88.85 * OC	0.98
IV	Oxidizable Cu = - 4.94 + 20.77 *OC	0.88

The regression equations provide interesting information on the capacity of organic matter as a host for copper. When excluding the three stations directly impacted by sewage dumping at site I, the capacity of copper retention by OC at sites I & IV, represented by Cu concentration at 100% OC, are comparable and amounts to about 2100 µgg-1. Sedimentary OC in both sites is mainly of in-situ biological origin but the productivity is greatly enhanced at site I. The situation is different at site II because of the dumping of great quantities of organic matter and the confined nature of the area. Anoxia is dominating in the whole water column excepting the thin surface layer (few centimetres) and light penetration is very limited. Therefore, organic matter is supposed to be of a different nature. OC at this site has copper retention capacity of ~ 9000 µgg-1, more than four times that recorded in the previous areas. This difference could hardly be explained by the difference of the total Cu/OC ratio. The Cu/OC ratio is almost the same at sites I & IV but is only slightly higher at site II. It should be noted that this retention capacity is only an apparent or conditional measure of the complexing capacity of the organic matter and does not have any empirical implications. The regression equations reveal also that copper concentration in the non-organic matrix (OC = 0) at site II is very high and approximates ten times that of the sediments at the other sites.

The exchangeable and the reducible fractions of Cu have equal importance in its speciation scheme

each represents about 10% excepting at site IV where the reducible fraction represents 20%. The exchangeable Cu at site I varies inversely with the carbonate content but co-varies with the reducible fraction and seems to be adsorbed on the Mn oxide. The lowest reducible fraction (7.79%) was found in sediments having the highest organic content. Probably, reducing conditions are favourable for the transfer of this fraction into the oxidizable fraction. Residual Cu varied between 11 and 48% with the highest values measured at sites II and IV where carbonate content is the lowest.

Zinc

Zinc has some common features with Cu. It is a micronutrient and has a nutrient-like behavior in oceanic water. It has also a great affinity to organic matter and forms with it highly stable complexes (Ivring and Williams, 1953). The speciation of Zn is distinguished by the dominance of the exchangeable and reducible fractions, which shared almost equal parts in the whole area averaging 27 and 32% respectively excepting at site IV where the reducible fraction ranked as first in position (Table 5d). Ranked in the second position are the oxidizable and residual fractions, both having a general average of about 20% of the total.

Exchangeable Zn averaged 35.8 and 33% at sites I&II respectively. It is seemingly associated with a mineral phase other than calcium carbonate since the two variables vary inversely (r = -0.94). The most favourable sites for the adsorption of Zn seems to be the Fe and Mn oxide coating as could be seen from the good agreement between the exchangeable Zn and the reducible Fe (= 0.59) and Mn (r = 0.85). At sites III and IV exchangeable Zn represents 30 and 9% respectively. Its distribution seems to follow the same trend, in association with Cu.

Zn associated with the reducible fraction is the most important species. Its average value varied between a maximum of 38% at site III and a minimum of 28% at site IV. Values between 30 and 40% are frequently recorded. The behavior of reducible Zn at sites I and II resembled that of Cu and is characterized by its negative correlation with the carbonate content (r = -0.85 and -0.72 respectively) and its positive correlation with the reducible Fe (r = 0.97 and 0.96 respectively). It has been frequently shown that hydrous Fe and Mn oxides are strong scavenging agents for numerous heavy metal ions (Feely, *et al.* 1983, Rosental, *et al.* 1986).

Zn in the oxidizable fraction has lesser importance than its corresponding Cu fraction. The highest average (~ 30%) is found in the sediments of site III and the lowest in the sediments of site I. In almost the whole area, concentration of Zn in the oxidizable fraction correlates positively with OC (r = 0.79) and co-varies with oxidizable Cu (r = 0.97). The capacity of the organic matter for the retention of Zn as detected from the regression of oxidizable Zn on the OC (Table 7) is clearly lower than that measured for Cu, which agrees with the order of the stability constants of the organo-metallic complexes (Ivring and Williams, 1953). Zn in the non-organic phase (OC = 0) at site II is also several times higher than the other sites, reflecting the degree of contamination of this area.

Table 7: Linear regression of oxidizable Zn on organic carbon

Site	Linear regreation equation	r
I	Oxidizable Zn = - 52.63 + 27.54 * OC	0.77
II	Oxidizable Zn = - 511.38 + 94.39 * OC	0.96
IV	Oxidizable Zn = - 16.0384 + 42.28 * OC	075

Residual Zn constituted varying proportions of the total element concentration going from a minimum average of 5% to a maximum of 40%. As is the case with Cu, the two sites (II & IV) having the highest proportions are those suffering solid material dumping either with sewage input or with filling process. As one might expect, residual Zn should be associated with non-carbonate detrital material as indicated by its inverse relationship with the carbonate content (r = -0.49).

Lead

Pb concentrations varied widely in the study area; from 1 to about 500 ?gg^{-1}. Pb speciation is characterized by the dominance of the potentially mobile species (Table 5e). In the entire area 65% of the samples had undetectable concentrations in the residual fraction. At site I exchangeable Pb is absent from stations far from the sewage effluent and represented an average of 18% in the contaminated sediments. At site II, exchangeable Pb varied between 6 and 38% and averaged 20%. Comparable participation (23%) and concentrations are measured at site IV. At site III exchangeable Pb represented 41%; however, concentrations were lower than at site II.

The reducible Pb appears as the major fraction of sedimentary Pb. On the average it constitutes 47, 53, 46 and 53% of the total element at sites I, II, III and IV respectively. Generally the highest concentrations are measured at sites I and II averaging 21 and 64 µgg-1 respectively, while at sites III and IV concentrations averaged 6.9 and 4.7 µgg-1 respectively.

According to the importance of its participation in the total Pb pool, the oxidizable Pb is ranked in the third position. Concentrations varied widely but the highest were recorded at the most polluted sites (I&II). Generally oxidizable Pb correlates with OC and the oxidizable fraction of Fe, Mn and Cu. (r = 0.86, 0.97, 0.95 and 0.99 respectively). The residual Pb occupies the last position in importance; it averaged 3 - 4% at sites I and III and increased to 9% at the other two sites. This distribution pattern may result from the impact of the environmental conditions. It is expected that at site II, due to highly reducing conditions, residual Pb would be in the form of insoluble sulphides or in association with insoluble Fe sulphides (Waldichuk, 1985), while at site IV it would rather be incorporated in land derived material held in inert positions. Speciation of Pb in our study area agrees with the results of Prohic and Kniewald (1987) for the sediments of the Karka River estuary; however, in the sediments of the Tees estuary, Jones and Turki (1997) have shown that exchangeable Pb was insignificant.

Mobility of the Elements

The interest behind the use of speciation schemes is that it permits the distinction between the fraction of the element that could be released into the water when the physico-chemical conditions are modified and the part that is permanently or quasi-permanently fixed in the sediments. The first fraction is of the greatest interest because it constitutes the part which participates in the biogeochemical cycle of the element. This participation may have diverse effects on the aquatic life depending on the nature of the element (essential-toxic). Therefore, globally, speciation schemes permit the division of sedimentary elements into "potentially mobile" and "immobile" fractions.

In our speciation scheme, the first three fractions (exchangeable, reducible and oxidizable) could be considered as potentially mobile; however, mobilizing conditions must be totally different. For example, increase of acidity will liberate the exchangeable fraction while development of reducing conditions will result in mobilizing oxides of iron and manganese as well as attached elements.

Table 8: Relative mobility of elements

Element	Fe		Mn		Cu		Zn		Pb	
Site	Mobile	Immobile	Mobile	Immobile	Mobile	Immobile	Mobile	Immobile	Mobile	Immobile
Site I	26	74	49	51	75	26	84	16	97	3
Site II	24	76	64	36	52	48	77	23	91	9
Site III	57	43	78	22	89	11	95	5	96	4
Site IV	29	71	52	48	59	41	60	40	91	9
Average	33	68	59	41	70	30	78	22	94	6

The distinction of the metal content into mobile and immobile fractions is represented in Table 8. Fe has the weakest mobility within the elements. Its mobile fraction averaged 32.6%. Formation of insoluble sulphides and increase of detrital fraction are supposed to be the reason for the increase of the immobile fraction. The mobility of Mn is remarkably higher than that of iron; about 59% of the total element is in the mobile fraction. Cu is more mobile than Mn; about 70% of the total element is associated with the mobile fraction. This high mobility is related to the tendency of Cu to be associated with the organic matter. Zn has slightly higher mobility than copper; its average mobile fraction constituted 78% of the total element and is almost equally distributed between the exchangeable, reducible and oxidizable fractions. Pb is the highest in mobility since its potentially mobile fraction represents more than 90% of the total element burden. The mobility of Pb is particularly attributed to the important participation of the exchangeable and reducible fractions.

Conclusion

Concentrations of heavy metals in the sediments of the coastal area of Jeddah have been greatly enhanced in areas suffering sewage disposal, particularly when water circulation is limited. Element concentrations in the mud fraction (< 63(m) were found to be 3 to 6 times higher than that in the sand fraction.

Most of the Fe is held in the residual unavailable form while most of the Mn, Cu, Zn and Pb is distributed between the environmentally unstable exchangeable, oxidizable and reducible fractions. Therefore, these elements are supposed to have greater mobility and may, under particular conditions, greatly influence the environmental characteristics.

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