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TRACE METALS IN FISH, MUSSELS, SHRIMPAND SEDIMENT FROM RED SEA COAST OF YEMEN

By

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ABSTRACT

After the reported death of different fish species from AlHodeydah, samples were collected from different sites along the Yemen Red Sea coast to study the concentrations of trace metals in the muscles of consumable fishes. The concentration of (Cd, Co, Cr, Cu, Fe, Hg, Mn., Ni, Pb and Zn) was studies on the Indian halibut (Psettodes erumei). Threadfin bream (Nimepterus japonicus), Skip jack (Katsuwonus pelamis), Grnts (Pomadasys opercularis), Talang queenfish (chorynemus lysan), Golden toothless trevally.

Shrimp (Penaens semicnlcatus) (Gnathodon speciosus) and Giant trevally,(Caranx ignobrilis) and the snail (Strombus tricornis) were collected from Al-Salif and analysed as well as intertidal surface sediments from the same sites.

The results show a dgree of some trace metal pollution in Ras-Kathnib and Al-Salif sediments of Cd, Cu, Fe, Mn, Zn and Pb. At the other sites concentration of trace metals are relative low and manily attributed to natural rather than anthropogenic origin.

The concentration of Cd, Cr, Mn, Ni, Pb and Zn in some fishes from Al-Salif and Al-Hodiedah was higher than the other sites, which was mainly due to the activities in both sites;Both the shrimp and the snail shows higher concentrations of most metals compared to the fish from the same site.

INTRODUCTION

Under natural conditions, the most important inputs of metals to coastal regions are the mechanical and chemical weathering of rocks (Bryan, 1984). Heavy minerals are usually common and represent 50% or more of the beach deposits in some places along the Red Sea coast of Yemen (DouAbul and Haddad ,1996). These beach deposits are mainly derived from mountainous region, which drain from the Yemen Highlands to the sea through numerous wadis.

The marine environment may also be polluted with effluent containing trace elements from both anthropogenic and natural processes. Such input could result from treated and /or untreated municipal and industrial wastes, agricultural runoff, and input from the atmosphere (Abaychi & DouAbul, 1985), and may quantitatively and qualitatively alter the natural biochemical cycle (Grimanis *et. at.*, 1978). However, fish , living in polluted waters may accumulate toxic trace elements via their food chains. The heavy metals have an effect on the physiology and metabolism of fish. Heba 1992 found that the trace metals have an effect on the growth and protein turnover of fishes from tropical and temperate areas. In his study he found that the tanks treated with heavy metal have less growth rate and protein turnover with compared with untreated ones .

Marine pollution of the Red Sea had recently drawn the attention of national and international agencies as well as public awareness, because of the enormous increment of pollutant particularly oil and trace metal;The increase of sewage and industrial effluent discharged into the coastal area have, seriously endangered the Red Sea ecosystem (Behairy & Saad, 1984).

Limited investigation dealing with presence of varoius pollutants have been carried out in this area (Al-Shiwafi & DouAbul, 1996 DouAbul & Heba, 1996, Rushdi *et al.*, 1991) as well as the visual inspection by some ecologists (TMRU. 1985).

The Red Sea is considered to be of special interest to ecologist, biologist, and marine geologists because of its unique oceanographic feature. It is a semi-enclosed water body, of relatively shallow and irregular continental shelf and is one of the marine ecosystem whose coastal water offer a suitable location for investigation of trace metal pollution.

Whilst attention is often focused upon the threat of oil pollution, which can put the entire coastline at risk, localized non-oil pollution source are already causing greater impact, which has received little scientific attention. Among the most dangerous pollutants are heavy metals, which are introduced into the marine environment by waste and sewage products. It is difficult to evaluate inputs of heavy metals since there are some entering the ocean a higher rates from natural activities than from humans. It is also a fact that some of the knowledge we have about the situation in the natural ecosystems concerning metals and metalloids, mainly from work in the temperate areas of the world, it seems reasonable to suppose that effect might be enhanced in the tropical area (Bryan,1984).

In Yemen, the marine and coastal areas, are of the major economic importance. Marine resources are exploited for local consumption and export. The report of Haskoning (1991) suggested that the main impacts presently affecting the marine environment of Yemen are pollution and over-exploitation of certain natural resources.

Whereas oil pollution of coastal zone of Yemen seems to be widespread, contamination of seawater by domestic and industrial waste water, is limited to urban areas. Discharge of waste water containing heavy metals or other toxic pollutants may locally deteriorate seawater quality along the Yemen coast (Haskoning,1991).

The primary purpose of this investigation is to monitor existing levels of potentially hazardous trace elements in the Red Sea coast of Yemen.

METHODOLOGY

The study was carried out on a coastal area of AL-Hodeydah city during 1994, sites were chosen according to the suitability of getting the fishes, and to the importance of the site itself. The first site was infront of the Power Station at Ras-Kathnib (Fig .1). The second was further north at Al-Salif port. To the south of Al-Hodeydah city another site, Al-Taif, a remot fishermen village was chosen. Fish samples were taken as well from fishermen fishing off Al-Hodeydah coasts. After collection, the fish samples were wrapped in a plastic bags, stored in a cool box, and frozen till return to the city center (2 hours in average).

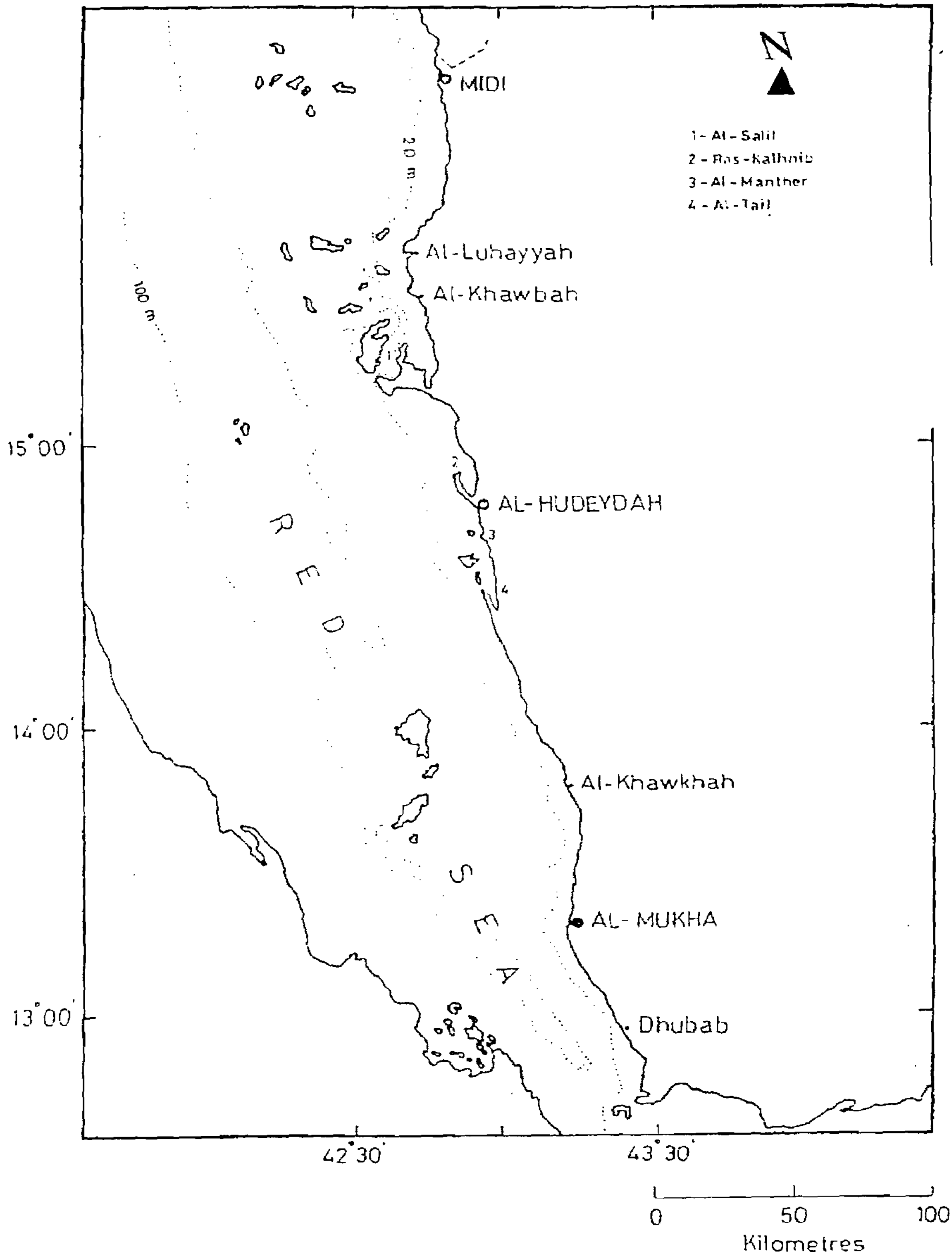

Fig. 1 Map shows the survived coast around AL-Hodeydah

Composite samples of fish, having similar size (length and weight) were chosen for each species. Sub-samples of each of the following species ; Indian halibut (*Psettodes erumei,* Threadfin bream *Nimepterus,* skip jack *japonicus katsuwonuc pelamis,* Grnts *Pomadasys opercularis.* Talang queenfish *Chorynemus lvsan.* Golden toothless trevally *Gnathanodon speciosus. and* Giant trevally *Caranx ignobilis)* were dissected according to the procedure described by (ROPME manual, 1983).

Shrimp *Penaeus semiculcatus.* was taken from Al-Salif, where a composite sample of the same length and weight were used as well for the metal analysis. The integumett (Exoskeleton) and the digestive tracts were removed, and a homogenized sample was used for the metal analysis. In addition the snail *Strombus tricornis* was collected from Al-Salif as well, the whole samples were used for analysis after the removing of the shells, and the whole body was washed with distilled water to remove any traces of sand, and then a known wet weight of the composite were used for the chemical analysis.

Homogenized, exactly weigh air dried subsamples of sediment were sieved and the fraction less than <63mm was used for digestion, preparation and analysis of surface sediment (ROPME, 1983) procedures was followed. Composite samples of fish, of the shrimps and the snails having similar size (length and weight)were determined separately before the soft parts pooled. Sub sample muscles of each of the species were grined on a pre-cleaned agate mortar after mixing with anhydrous sodium sulphate. The digestion was carried out according to the procedure described by (ROPME, 1983).

Blank and spiked samples were used for both sediment and organisms. Metal concentration of Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb and Zn were determined using standard conditions recommended by the manufacture of AAS (Perkin-Elmer 2800). Reagent blank was also included with each set of analysis. Standard addition method were used for the calculation of concentration for each metal analysed. Three replicates of each sample were analyzed, and blank values were negligible for all element studied.

RESULTS & DISCUSSION

The Red Sea being a semi enclosed ecosystem is particularly vulnerable to pollutants from its surrounding countries. Knowing and understanding the potential mineral wealth of deep water sedimentary area, which may be exploited in the future. Then it could contribute tremendously to the contamination of the area, by metal and metalloids (Karbe ***et al***, 1981) concentrations of some metals are reported near some industrial areas of the Red Sea such as ports and desalination plants (Dicks,1987). It is well established that aquatic sediments are the final accumulation site of water-borne constitutes derived from natural source (Living organisms and their detritus) *in situ* and surroundings, and artificial (domestic, urban-industrial and agricultural wastes). The aquatic sediments can thus provide not only a historic record of sedimentary environment, but also reserve the feature of average sedimentary environmental constituents.

Molluscs have been used for monitoring contaminants in the environment (Farrington ***et al***, 1983) These organisms which concentrate pollutants from the marine environment, yet do not readily metabolize contaminant such as petroleum hydrocarbons (Farrington & Quinn, 1973). The concentration of a contaminant in a muscle is the difference between uptake and excretion of that contaminate. Thus, the contaminants found in muscles reflect the current contaminant burden of an ecosystem (Jackson ***et al***. 1994). Based upon the foregoing fact that the snail *Strombes tricornis* were collected from the Red Sea coast (Fig.1) in order to correlate the distribution pattern of trace metal found in them with that of fish, consequently it will be possible to pinpoint the origin of contaminations (i.e. whether it is local or transported).

Recent comprehensive work on trace metal in fish from the Red Sea coast of Yemen revealed rather low concentration (DouAbul & Heba, 1996). However the results found in this investigation can be shown in (Tabels 1&2)

However, some of the trace metals found in this Study will be discussed separately for their importance as health hazards to human. These are as follows:

<u>Cadmium</u>: In the Red Sea (Karbe ***et al***, 1981a) measured the Cd from the near-bottom waters to be (0.005-013 ppb). The highest concentrations seems to be in the vicinity of hot brines, which could explain the concentrations of Cd in shrimp (0.6 to 7.9 ppm) from (Karbe ***et al***, 1981b).

Cadmium concentrations in sediment from sites round Al.Hodeydah did not show significant differences (Table 1).The concentration ranged between (3.05-3.38 ppm), the highest concentration was found in Ras-Kathnib sediments, these some what high concentrations are attributed to the mineralogy of the area, and to lesser extent to pollution. The Cd concentrations of the fish muscles from this study are elevated (2.4-3.6 ppm.)when compared with those from the Omani waters (0.04-0.13ppm.) from the work of Burns *et. al.* (1982). The Cd concentration in the shrimp *Penaeus semiculcatus* collected from Al-Salif, did not show much differences in concentration from other fish species from the same site or those from other sites.

Shrimp species collected from (35-220m depth) from central Red Sea by Karbe and Schnier (1981) showed a Cd concentration range (0.6-7.9 ppm.), which is almost double the concentration found in our shrimps from the coastal area Table (2). These differences could be due first to the different concentration of Cd between the relatively shallower coastal area and those from deeper waters where the Cd expected to be higher, and second due to the different lipid content in animals from different species, age and other physiological factors, which' lead to a modification of concentration calculated per unit weight of tissue.

Although the sample size of this initial study is limited for the snail *S.tricornis* collected from Al-Salif only, the analysis of this sample gave some idea about the trace metal content in this species. We can say that the Cd content (3.6 ppm) is similar to background level reported for other related species from other parts of the world (Bryan, 1984). Chan *et al*, (1974) suggested that the consumption of the locally caught fish and shellfish from waters .having> 50 ppb Cd may cause health problems in the long run. For this reason fish and other consumed, food from the sea should be regularly monitored for their heavy metal content in general and Cd in particular.

<u>Zinc</u>: Zinc seems to be highly *abundant in Red Sea water, its* concentration ranges between (0.03-12.3 ppb) from Karbe and Schnier (1981), than Cd, Cu, and Pb from water taken in different depths along the Red Sea axial. Zinc in sediments from this study seems to be higher than those found in the sediments from Oman (Burns, *et al*, 1982). Ras-Kathnib and Al-Salif sediment showed the highest Zn concentrations (Table 1), these differences compared to the other sites could be attributed to an anthropogenic sources, since contaminations from

Table (1): Concentrations of metals in sediments from a range of contaminated and un contaminated areas (ppm dry weight). Compiled from sources indicated in the footnote,and the results of this study.

Location	Cd	Co	Cr	Cu	Fe	Hg	Mn	Ni	Pb	Zn
Gulf of Bothnia (industialized)[1] (mean)	4.1	25	-	33	7.5%	2.8	6410	70	67	129
Long Island sound (max.)	4.2	14.8	276	269	-	2.2	1218	42	210	291
New Bedford Harbor (industrialized)(max.)	76	-	2300	7250	1.4%	3.8	180	550	560	2300
Cannel Estuary (polluted)	1.1	10	16	24	1440	-	346	17	147	183
Cannel Estuary (polluted)	<0.4	5.6	19	72	9000	-	281	11	31	65
Oman (Raysut)[2] (outside harbor)	4.20	-	23.2	5.4	0.28	0.024	35	21	56	16
Ras-Kathnib	3.38	7.4	16.0	38.5	4236	-	65	11.2	8.6	138
AL-Salife	3.15	5.5	15.9	27.8	3078	-	48	9.3	5.12	122.5
AL-Manther	3.25	5.5	18.15	39.3	3284	-	32	14.7	8.7	112.2
AL-Taif	3.05	7.1	24.5	24.8	3187	-	20.7	11.4	8.5	88.6

[1]**Bryan (1984) - see ref.**

[2]**Burns,et.al. (1982) - see ref.**

Table 2: Metal concentrations (ppm dry weight) in arrange of fish species, shrimps and snails (compiled from the sources indicated) and from this study.

Species	Cd	Co	Cr	Cu	Fe	Mn	Ni	Pb	Zn	Locality
Pseudopleuronectes Americanus (flounder) Muscle	<0.4	-	<1.2	4.4	-	1.2	2	<1.2	20.8	New York Bight [1]
Flat fish	0.02-0.11	-	-	0.34-0.96	4.4-27.2	0.2-1.2	0.22-1.6	0.35-0.72	2.8-23.2	Poland
Morone saxatilis (stripped.bass)	0.12	-	-	1.40	-	-	4	2.0	15.2	Chesapeake Bay
Makaira indica (black marline)	3.60	-	-	1.60	-	-	-	2.4	34.4	NE Australia
Epinephelus tauvina (Salala)	0.05	-	3.30	0.65	19	0.27	1.9	0.21	13.6	Oman [2]
Crangon crangon (shrimp)	1.20	-	2.80	92	-	-	-	12.8	88	England & Wales
Shrimp (Penaeus)	0.6-7.9	0.13-2.5	0.03-17.9	29-171	50-3400	-	-	-	52-118	Red Sea [2]
Psettodes erumei	2.50	1.22	2.90	1.50	7.6	0.19	1.69	1.7	49.2	AL-Sallfe
Psettodes erumei	2.70	1.15	2.80	0.65	8.9	0.13	1.8	1.95	44.18	AL-Hodeydah
Psettodes erumei	3.50	1.24	2.70	1.37	7.9	0.28	1.97	1.43	44.09	AL-Taif
Nimepterus iaponicus	2.40	1.15	1.10	1.42	9.6	0.4	2.29	1.8	48.09	AL-Salife
Katsuwonus pelamis	2.56	1.16	1.50	1.36	10.2	0.17	2.49	2.1	46.24	AL-Salife
Pomadasvs opercularis	2.80	1.08	2.40	2.96	13	3.16	1.98	3.8	52.18	AL-Hodeydah
Chathanodon lvsan	2.56	1.58	2.10	2.21	20.1	1.24	1.6	2.1	81.03	AL-Hodeydah
Gnathanodon speciosus	2.57	1.29	2.70	1.77	19.4	0.34	1.19	1.6	43.38	Ras-Kathnib
Giant trevally	2.90	1.06	0.91	1.47	17.5	4.77	2.36	2.5	37.61	AL-Taif
Pomadasvs opercularis	2.65	1.28	2.70	1.58	14.4	0.17	1.9	1.4	55.57	AL-Taif
Penaeus semiculcatus	2.40	1.33	1.20	5.93	7.30	-	3.85	1.06	123.86	AL-Salife
Strombus tricornis	3.60	3.04	3.50	32.62	178	66.4	5.98	3.7	155.8	AL-Salife

[1]Bryan (1984) - see ref. [2]Burns,et.al. (1982) - see ref.

ships is most obvious in dock and harbours, where lead, Zinc and Chromium are used in preservative paints (Bellinger and Benham, 1978).

In our study no significant differences could be found in Zinc concentrations between different fish species (Table 2). The shrimp *P.semiculcatus* have higher Zn (123.86 ppm). Compared to the fish (Table2) but did not show differences compared to those from (Karbe and Shnier 1981) study. The snail *Stricornis* have higher Zn compared to the fish but did not show differences compared to those from (Karbe and Shnier 1981) study. The snail *S.tricornis*_had the highest concentrations compared to the other species (Table 2).

Lead: The major source of lead to the marine environment, is almost certainly the atmosphere. Much of the atmospheric lead emanates from its use in lead alkyl "antiknock" additives in petrol (gasoline) and its impact on concentrations in coastal waters appear to be very significant (Fowler, 1985). In coastal zones adjacent to populated regions, waters are highly contaminated with Pb. No data for the Red Sea waters could be traced, while Pb in the Omani and the Arabian Gulf waters have concentrations in the range of (0.05-0. 12 ppb) from Fowler (1985).

Lead in the sediment from the four sites round Al-Hodeydah did not show significant differences in concentrations (Table 1), and were very low (5.12- 8.6 ppm) compared to sediment from Al-Aqaba (80-825 ppm).Fowler (1985) gave the Pb concentration from the Arabian Gulf sediment (0.7 - 75 ppm). The lower concentration in our samples might be attributed through other reasons to the lower populations and industrial activities.

Levels of Pb in fish muscles are generally low. Fish species from Al--Hodeydah and Al-Salif (e.g *K.pelamis* and *P.opercularis)* have almost higher Pb concentrations as (Table 2) shows. These high concentrations could be due to the higher activity in both of these sites. but it could be also due to the age differences, feeding and other factors.

The shrimp *P. semiculcatus* did not show much difference of the lead burden compared to that of fish species, while the snail S. *tricornis* has higher concentration (Table 2). This could be due to the direct contact with the sediment, and may as well be to the sediment in gut content, since the whole body was used for the digestion, and the animals were not purged of food material before analysis.

There is no evidence to suggest that lead in food stuffs of marine origin poses any special problems to man although, the recent introduction of limits for fish (8 ppm. Dry weight) and shellfish of (40 ppm. Dry weight) in England and Wales is evidence of some anaxiety (Bryan, 1984).

Copper: Martin *et al*, (1977) stated that the use of sea water for cooling has through corrosion sometimes lead to local pollution problems, particularly with Copper. Another source of this metal is effluent from desalination installations. The elevated Cu level in Ras-Kathnib is due mainly to the site proximity to Electricity Power Plant, while the high concentration in the Al-Manther sediment could not be expected from anthropogenic source, since this site is a remot fishermen village, but it is situated as (Fig. 1) shows in a semi-closed area (Khor Gulaifiqua), the coast is covered by fine sediment and the restricted water exchange with the open sea might affect to some extent the rate of deposition of metals and the exchange with the overlying waters.

Fish from this study, like the flat fish *(Psettodes erumei)*from different sites did not show any elevated Cu concentrations(Table 2), while fish *(P.opercularis* and *C.lysan)* from Al-Hodeydah had high concentrations. The shrimp *P.semiculcatus* showed a lower concentration (5.93ppm) of Cu compared to the shrimp from Karbe *et. al*. (1981) study where the Cu concentration was (29-171 ppm). These differences could, be attributed to higher Cu concentration in deeper water close to the highpothermal vents compared to the surface waters. The snail *S.tricornis* had relatively high Cu concentration.

Chromium:The higher levels of chromium in sediments from Al-Manther and Al-Taif, where the coast is composed mostly of fine grained fraction (like AlSalif and Ras-Kathnib), could be attributed to the mineralogy of the site.

Chromium and Manganese concentrations in our fish and shellfish samples were close to those found in fish from Salala in Oman (Bums *et el*, 1982) and those from England and Wales (Bryan, 1984).

No significant differences noticed in the content between different fish species. Ni shows some elevations in fish from Al-Salif and Al-Taif only. The snail showed higher concentration of all the mentioned metals, it is difficult to draw any broad conclusions regarding trends of trace metal levels on the Yemen coasts of the Red Sea, since no comparable data available for this particular region. Considering this fact, we feel that the data presented here can serve as a baseline for further in depth studies. Furthermore, the levels of the investigated trace metals lay within the range of values reported for other regions of the world. It can gathered from (Table 2), that the level of almost all of the investigated metals were very low indeed to create a threat to marine organisms in general and fish in particular.

Cadmium and Zinc are relatively high compared to those found in other coastal areas from the Arabian Sea and the Arabian Gulf (Fowler,1985), which probably arise from the upwelling that brings deep, presumably Cd-rich, waters into the coast. As well the proximity to high density population centers and/or areas of port activities might be responsible. For example, Cd, Co, Cu, Pb and Zn, from Ras-Kathnib sediments suggest a local anthropogenic input, however further sampling is necessary to confirm this possibility, since some other pristine areas like Al-Taif and Al-Manther shows even higher concentrations. This could be due to differences in mineralogy and organic matter content of the sediments.

Although this study is the first in the Red Sea Coast of Yemen, the data are necessary requirement to control the change of the levels of these elements owing to pollution. Thus trace metal results in this study are important, owing to the lack of information in this area. However, these levels might provide a bases-line for future trace metals studies in Yemen. A more extensive program is needed to investigate the trace metal concentration in this area, taking into account clean and polluted coastal area, inshore, offshore open Ocean and deep waters.

In conclusion , this investigation showed that the concentration of the trace metals in some fishes from Al-Hodydah and Al-Salif were relative higher when compared to the other sites. This might be due to the activities in both sites. Also, it showed that both the shrimp and snail have higher concentration of trace-metal when compared with fish species.

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