

*Full Length Research Paper*

# Assessment of Some Heavy Metals Pollution in Mollusca from Hadramout Coast, Yemen

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Hadhramout is considered as the industrial and commercial center for fishing in Yemen. Accordingly, Yemen food security depends highly on maritime products of Hadhramout. Consequently, any severe contamination caused by industrial activities would have a direct or an indirect negative impact on the sea life and marine environment. Twenty Mollusca samples were collected from five sampling locations (Rassharma, Burum, AL-Mukalla, AL-Sheherand Arryidah) at Hadhramout coastal area (Yemen). The samples were collected on a seasonal basis from Augusts of 2013 to May 2014. The results showed that the concentrations of heavy metals (Ni, Co, Mn, Cd, Fe, Cu, Zn, Cr and Pb) in Mollusca were in the range of 1.67-19.17, 1.67-6.67, 2.5-13.33, 0.83-15.8, 40-458.3, 5-108.3, 21.5-118.3, 0.83-8.3 and 1.67-6.67 µg/g, respectively. The present study showed significant seasonal variations of these elements and showed that the metal concentrations in Mollusca are several times higher than those in water and lower than those in sediments. The highest concentration of these elements were recorded in the Mollusca of Burum, Al-Mukalla, Al-Shaher, Arryidah and Ras-Sharma, compared to WHO. According to WHO, the concentrations of Fe, Cr and Zn in Mollusca were below the permissible levels except for Al-Mukalla and Al-Shaher, while Mn, Cd, Cu and Pb were higher than the permissible level WHO except for Ras-Sharma.

**Keywords:** Mollusca, heavy metals, Seasonal variations, Hadhramout coast of Yemen.

## INTRODUCTION

Environmental pollution by heavy metals is an increasing problem worldwide. Because of the accumulation effect of some heavy metals, especially through the food chain, their bioavailability needs to be monitored. The investigation of metal concentrations in living organisms may provide information about bioavailability and, the level of environmental pollution by specific metals.

Marine pollution of the Gulf of Aden had recently drawn the attention of national and international agencies as well as public awareness of the enormous increment of pollutants particularly oil and metals. The increase of sewage and industrial effluents discharged

into the Gulf of Aden has seriously threatened the ecosystem.

Limited investigation dealing with the presence of various pollutants has been carried out in this area (Heba et al., 2003; Heba and Al-Mudaffer, 2000). There are different types of impacts on the coastal and marine environment of Yemen (Al-Shwafi, 2003; Al-Shwafi et al., 2005; Bawazir and Abu Al-Fatooh, 2001; Dou Abul et al., 1997; Rushdi et al., 1994). These impacts are mainly caused by human and developmental activities (Rushdi et al., 1994). These activities introduce pollutants to the marine environments and cause the destruction of some special habitats. The most widely recognized issue is the oil-related pollution, where considerable attention has been focused (Rushdi et al., 1994; Dou Abul et al., 1997). However, the pollutions of other areas include the impact of growing industrial and domestic effluents,

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unplanned coastal development as well as various miscellaneous human activities such as fishing, hunting and tourism (Rushdi et al., 1991). However, the potential threat remains strong, either from shipping accident or problems from oil transfer points along the coast (Al-Shawafi et al., 2009). In fact, the waters off Yemen are now threatened by several kinds of pollution from passing ships and local shore facilities (Al-Shawafi and Rushdi, 2008).

Some organisms can accumulate high concentrations of heavy metals. They may also represent moving time-averaged values for the relative biological availability of pollutants at each site. Mollusks are being an important group of organisms that have been studied for their potentialities as an indicator organism (Al-Saad and DouAbul, 1987). Mollusks are most frequently used as bio monitors for heavy metals, chemical substances and other contaminants in sea water and associated sediments. (Ali and Baharoon, 2002).

## MATERIALS AND METHODS

### Study area

Hadhrumout governorate is situated between the latitudes of 14° 30' and 14° 56' N, and longitudes 49° 07' and 50° 21' E. Its coastline occupies about 750 km of the Yemeni coasts. The study area is located in Hadhrumout Governorate and includes five sites namely; Burum, Al Mukalla, AL-Sheher, Arryidah and Ras- Sharma background (protected area).

Hadhrumout coast (Figure 1), complementary considered as part of the Gulf of Aden, occupies nearly one-third of the south Yemeni coast length with an estimated area of the continental shelf of about 70,000 km<sup>2</sup> (up to a depth 200 m). As estimated, the Hadhrumout coast is a productive area (EEZ) of about 13500 km<sup>2</sup> (approximately 20%).

The coastal strip of the province of Hadhrumout consists of a series of sandy beaches punctuated at intervals by configurations of rock protruding and mostly extends into the shallow water. The slope of sea bottom here abrupt, in terms of distance between the beach and the continental shelf, relatively narrow with an average of 15 kilometers, except in the northeast of the coast where it can be up to 60 km in width. The depth of the Gulf in the coast of Hadhrumout as average about 1750 meters in the midst of the Gulf with higher depth up to 5370 meters. There are some sandy beaches with a background consisting of rocky heights, such as the shores of east Bir Ali, east Maifa Hajar, behinds Mukalla and Sharma.

This coastline consists of successive environments, which is almost identical to a significant degree, such as

sandy beaches, narrow coastal plains, rocky heights, sand dunes, proximity to the beach bottoms with a shallow rocky-sandy foundations and deep rocky bottoms. There are a lot of areas of environmental concern along the coast, from which the coast of Bir Ali and its islands and coral formations with elevated bioenergy; the coast of Broom distinguished by transition from a moderately high bioenergy from the Ras-El-Kalp coast to the high energy that extends along the east Broom area, Halla and behind of Mukalla areas. Hadhrumout coast is also characterized by wide sandy bays, which can be prolonged to the dry sandy beaches of a depth of over 100 meters; but it often limited between the tide curve and the depth of 30 meters.

### Sample collection and analysis

Different indicators samples for this study were taken from the locations that have been selected along the Hadhrumout coast, focusing on five main locations representing western border - east Burum and eastern Arryidah region and what's between them representative of the cape of Mukalla, Sheher and Ras-Sharma (Figure 1). Each location consists of three sub-stations located in order to ensure the inclusion of the largest area of the region.

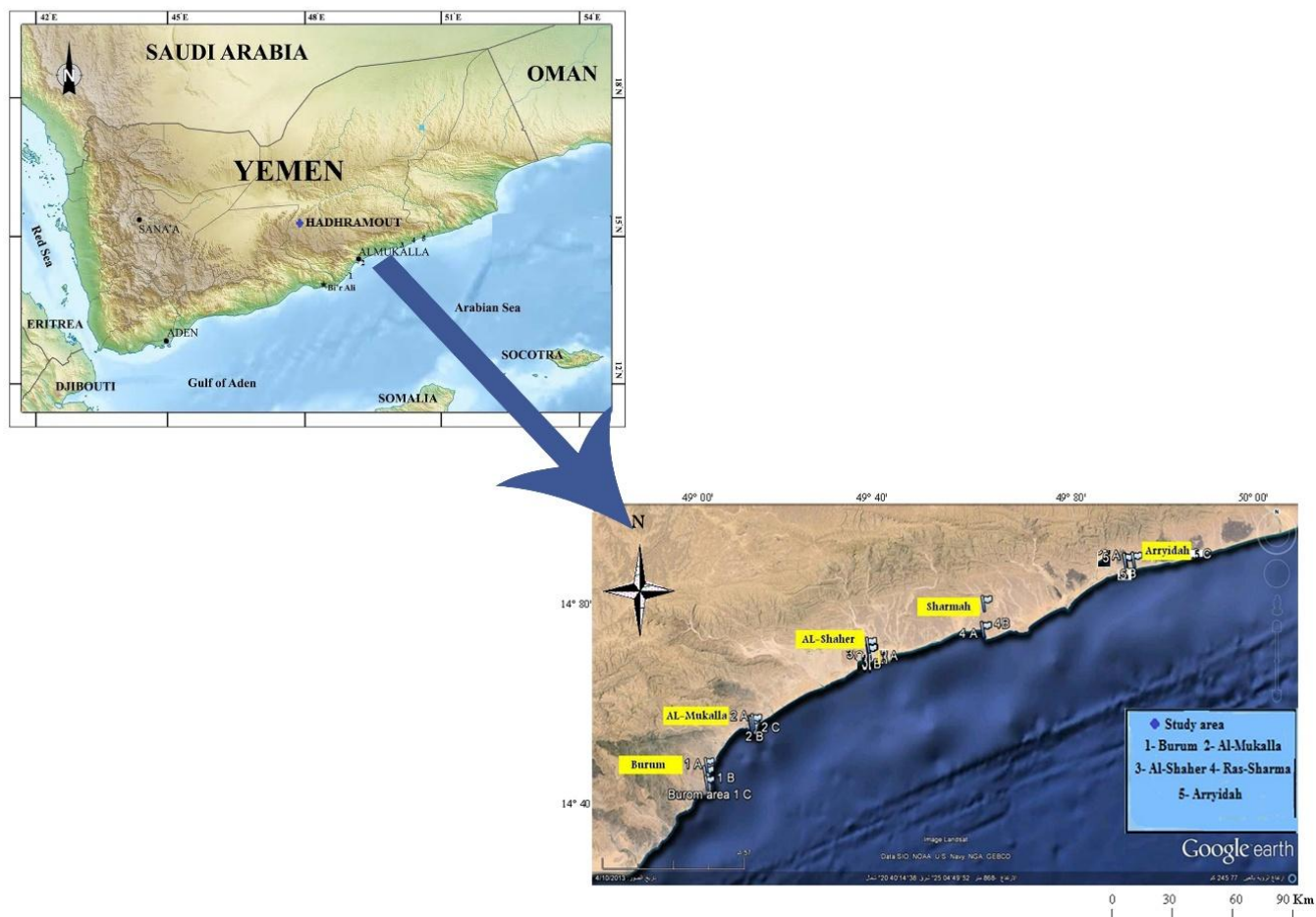
Sampling stations are shown in table (1) the study area extends from the Burum area in the west (14° 35' N and 48° 59' 537"E) to Arryidah in the east (14° 89' N and 49°15' E) in addition to Ras Sharma as background (protected area). In general, these coasts are irregular in form, but dominated by sandy bays of varying size and separated by promontories of limestone or igneous rocks sometimes of substantial height such as Burum area and Al-Mukalla.

### Water sampling

Twenty seawater samples were collected from the five sampling sites at Hadhrumout coastal area, Gulf of Aden from August 2013 to May 2014. Water samples were collected at 1m depth in pre-cleaned plastic bottles (1L) and preserved in an icebox for further analyses.

### Mollusca sampling

Mollusca samples were collected from the Hadhrumout Governorate/Yemen from August 2013 to May 2014 once a month. Digital GPS Navigator was used to fix the locations of these samples. Samples represent four time periods: seasonal monsoons, summer and winter, and the inter seasonal periods. August 2013 is



**Figure 1.** Map of the Hadhramout governorate, showing study area location

representative of the summit of summer monsoons. November 2013 represents the period between summer and winter monsoons. February 2014 represents the winter monsoons and May 2014 represents a post-winter monsoon and prior to summer monsoon.

Inter-tidal and sub-tidal Mollusca were collected from the five sampling sites at Hadhramout coastal area Gulf of Aden. About 200 specimens of Mollusca were collected from five sampling sites by hand (twisted from the rocky substrate) or using a hammer and a paint scraper. Mollusca was protected from the contamination effect by keeping glass wares sealed in the containers (Ice freezer) and immediately transported to the laboratory and kept frozen until processing to reduce the time of atmospheric contact.

### Analysis of heavy metals

Water samples were digested as follows, the sample, 100 ml was transferred into a beaker and 4ml

concentrated  $\text{HNO}_3$ , 10 ml HCL and 3ml  $\text{H}_2\text{O}_2$  were added. The beaker with the content was placed on a hot plate and evaporated down to about 10 ml. The beaker wall and watch glass were washed with distilled water and the sample was filtered to remove any insoluble materials that could clog the atomizer. The volume was adjusted to 100  $\text{cm}^3$  with distilled water (EPA, 2007) Determination of heavy metals in the seawater samples was done using Atomic Absorption Spectrophotometer (AAS) Unicam model Solaar 929.

Mollusca samples were analyzed using the method described according to (ROMPE, 1983). Original sediments samples were spilt and washed to remove the dissolved salts using distilled water (DW). This step were repeated several times to ensure the complete removal of dissolved salts. Mollusca samples were dried in an oven at  $40^\circ\text{C}$  for 12 hours, homogenized in an agate mortar. Gloves were used in all handling stages to avoid contamination. Dry fine powder of Mollusca was homogenized in its container. For a pre digestion, 3 grams of each sample were placed in a beaker, where

1.5 ml of concentrated Perchloric acid and 4.5 ml of concentrated Nitric acid were added. The beaker was placed in a water bath set at 70° C for 2 hours until the solution is clear. Before re-heating the beaker on a hot plate at 70° C to reduce the solution to 1-2 ml, about 2-3 ml of deionized water were added. The final volume of the solution was adjusted to 50 ml for analysis of heavy metals (Ni, Co, Mn, Cd, Fe, Cu, Zn, Cr and Pb) in resulting solutions. Atomic Absorption Spectrophotometer (AAS) was used for analysis. Table 1

## RESULTS AND DISCUSSION

### The concentrations of heavy metals in seawater

Heavy metals may enter the water from different sources, including; sewage, industrial, agriculture domestic effluents and urban runoff. Heavy metals (Ni, Co, Mn, Cd, Fe, Cu, Zn and Pb) are common pollutants, which are widely distributed in the aquatic environment.

The heavy metal concentrations in seawater from the five locations in the investigated area are illustrated in tables (2, 3, 4 and 5).

Trace metals were measured to assess the status of contamination in Hadhramout coastal area, Gulf of Aden. Concentrations of Ni, Co, Mn, Cd, Fe, Cu, Zn and Pb in seawater were in the range of 0.8 to 1.9, 0.5 to 1.2, 0.10 to 0.34, 0.1 to 0.2, 0.6 to 2.1, 0.3 to 0.8, 0.03 to 0.48, 0.5 to 1.9mg/L, respectively. In this survey, high concentrations of parameters were recorded in the seawater of Burum area, AL-Mukalla area, AL-Shaher and Arryidah area, compared with EPA (2001)

The results of the present study revealed that the different physicochemical parameters of water at the investigated locations, the concentrations of Cu, Zn and Mn in water were below the permissible levels, according to the EPA (2001), while Ni, Co, Cd, Fe and Pb were higher than the permissible levels.

### The concentrations of heavy metals in Mollusca

Contamination of aquatic environment with toxic elements is increasing due to progressive industrialization. The accumulation of heavy metals in Mollusca of aquatic organisms is affected by physical and chemical factors such as temperature, water hardness, pH and salinity (Karakoc, 1999). In the present study, the Mollusca has different amount of heavy metals from the different sites. However, these differences were found to be statistically non-significant ( $P < 0.05$ ). Concentrations of heavy metals in Mollusca are given in tables (6-9).

The highest values for metals were recorded at Al-Mukalla, Al-Sheher, Burum, and Al-Arryida, while the

lowest ones were recorded in Mollusca samples at relatively pristine region in Ras-Sharma, which is located at the extreme eastern part of the study area. The concentration of metals in Mollusca increased in the study area. This could be attributed to the increase of industrial and human activities in the study area. The metals levels in marine organisms of this study were compared with the reported studies from other regions around the world as given in table 10.

On the other hand, the variations in metals concentration at a given area may often be due to seasonal changes of the organisms' tissues weight rather than to any variation in the absolute metal content of the organism and these seasonal variations may be due to the fluctuation of the amount of agricultural drainage water, sewage effluents and industrial wastes discharged into the seawater.

The results of the present study revealed that heavy metals in Mollusca at the investigated locations were below the permissible levels for Fe and Zn according to the WHO (1989) except AL-Mukalla and AL-Shaher. While Mn, Cd, Cu and Pb were higher than the permissible level by WHO (1989) except Ras-Sharma.

### *Nickel*

Nickel occurs naturally in the earth's crust and is ubiquitous in air, water, soil and the biosphere. The average concentration of nickel in the earth's crust is 0.008%. Nickel also exists as a number of compounds. Nickel compounds that are soluble in water include nickel chloride and nickel sulfate; insoluble nickel compounds include nickel oxide, nickel sulfide and nickel sub-sulfide. Nickel carbonyl is a highly toxic, volatile liquid that has specialised industrial uses (PHE, 2009).

The present results showed that the nickel concentration in Mollusca is 1.67 µg/g during winter at Ras-Sharma and Arryidah to 19.17 µg/g during autumn at Al-Mukalla. The highest concentration of nickel was detected in Mollusca at Al-Mukalla, which receive increasing quantities of municipal and industrial wastewaters from many outlets as well as from fishermen and cargo boats. The concentrations of nickel in this study were higher than other studies (Ali, 1997; de Mora et al., 2004; Al-Alimi, 2008).

### *Cobalt*

Cobalt is an essential element for the growth of many marine algal species, including diatoms, chrysophytes, and dinoflagellates. Cobalt has also been shown to enhance growth of some plants at low concentrations. At higher concentrations, cobalt is toxic to humans,

**Table 1.** Locations of seawater sampling in the study Area

Location	Station	Latitudes	Longitudes
RasSharmah	1	14 ° 49' 356" N	50 ° 01' 996" E
	2	14 ° 49' 289" N	50 ° 02' 163" E
	3	14 ° 49' 316" N	50 ° 02' 358" E
Burum	4	14 ° 20' 985" N	48 ° 59' 023" E
	5	14 ° 20' 954" N	48 ° 59' 135" E
	6	14 ° 20' 928" N	48 ° 59' 238" E
AL-Mukalla	7	14 ° 31' 198" N	49 ° 09' 986" E
	8	14 ° 30' 999" N	49 ° 10' 145" E
	9	14 ° 30' 720" N	49 ° 09' 615" E
AL-Shaher	10	14 ° 44' 960" N	49 ° 35' 877" E
	11	14 ° 44' 994" N	49 ° 35' 983" E
	12	14 ° 44' 931" N	49 ° 35' 779" E
Arryidah	13	15 ° 02' 735" N	50 ° 33' 397" E
	14	15 ° 02' 714" N	50 ° 33' 612" E
	15	15 ° 02' 689" N	50 ° 33' 827" E

**Table 2.** Average concentration of total metals ( $\mu\text{g/g}$ ) in collected Mollusca samples from each sampling site during August

Location stations	Ni	Co	Mn	Cd	Fe	Cu	Zn	Cr	Pb
Rassharma	0.80	0.40	0.10	0.10	0.50	0.50	0.29	< 0.10	0.70
Burum	1.50	0.50	0.20	0.20	1.20	0.80	0.41	< 0.10	0.90
AL-Mukalla	1.90	0.70	0.30	0.20	0.90	0.70	0.40	< 0.10	1.10
AL-Shaher	1.50	0.70	0.20	0.20	0.80	0.80	0.33	< 0.10	0.80
Arryidah	1.20	0.60	0.10	0.20	0.70	0.60	0.40	< 0.10	0.80
Minimum	0.80	0.40	0.10	0.20	0.50	0.50	0.29	< 0.10	0.70
Maximum	1.90	0.70	0.30	0.20	1.20	0.80	0.40	< 0.10	1.10
Average	1.30	0.57	0.20	0.20	0.70	0.60	0.36	< 0.10	0.87

**Table 3.** Average concentration of total metals ( $\mu\text{g/g}$ ) in collected Mollusca samples from each sampling site during November

Location	Ni	Co	Mn	Cd	Fe	Cu	Zn	Cr	Pb
Rassharma	1.50	0.80	0.10	0.10	1.50	0.60	0.38	< 0.10	0.80
Burum	1.80	1.20	0.20	0.10	1.80	0.70	0.44	< 0.10	0.90
AL-Mukalla	1.70	1.20	0.20	0.20	2.10	0.80	0.48	< 0.10	1.10
AL-Shaher	1.90	1.10	0.20	0.20	1.90	0.70	0.41	< 0.10	0.80
Arryidah	1.60	1.10	0.20	0.10	1.70	0.70	0.40	< 0.10	0.80
Minimum	1.58	0.80	0.10	0.10	1.50	0.60	0.38	< 0.10	0.80
Maximum	1.90	1.20	0.20	0.20	2.10	0.80	0.48	< 0.10	1.10
Average	1.60	1.03	0.15	0.15	1.77	0.73	0.42	< 0.10	0.90

**Table 4.** Average concentration of total metals ( $\mu\text{g/g}$ ) in collected Mollusca samples from each sampling site during February

Location	Ni	Co	Mn	Cd	Fe	Cu	Zn	Cr	Pb
Rassharma	0.60	0.40	0.10	0.10	0.50	0.30	0.20	< 0.10	0.40
Burum	0.90	0.50	0.20	0.20	1.20	0.50	0.33	< 0.10	0.60
AL-Mukalla	0.90	0.60	0.20	0.20	0.90	0.50	0.40	< 0.10	0.50
AL-Shaher	0.90	0.70	0.20	0.20	0.88	0.40	0.30	< 0.10	0.50
Arryidah	0.80	0.60	0.10	0.10	0.70	0.40	0.30	< 0.10	0.50
Minimum	0.60	0.4	0.10	0.10	0.50	0.30	0.20	< 0.10	0.40
Maximum	0.90	0.70	0.20	0.20	1.20	0.50	0.40	< 0.10	0.50
Average	0.77	0.53	0.15	0.51	0.70	0.40	0.30	< 0.10	0.47

**Table 5.** Average concentration of total metals ( $\mu\text{g/g}$ ) in collected seawater samples from each sampling site during May

Location	Ni	Co	Mn	Cd	Fe	Cu	Zn	Cr	Pb
Rassharma	0.70	0.40	0.10	0.10	0.10	0.30	0.11	< 0.10	0.40
Burum	0.90	0.50	0.20	0.10	0.60	0.50	0.15	< 0.10	0.50
AL-Mukalla	0.90	0.70	0.30	0.20	0.70	0.40	0.15	< 0.10	0.60
AL-Shaher	1.00	0.70	0.20	0.20	0.70	0.40	0.16	< 0.10	0.80
Arryidah	1.00	0.60	0.20	0.10	0.60	0.30	0.13	< 0.10	0.50
Minimum	0.70	0.40	0.10	0.10	0.10	0.30	0.11	< 0.10	0.40
Maximum	1.00	0.70	0.30	0.20	0.70	0.40	0.15	< 0.10	0.60
Average	0.87	0.57	0.20	0.10	0.47	0.33	0.13	< 0.10	0.50

**Table 6.** Average concentration of total metals ( $\mu\text{g/g}$ ) in collected Mollusca samples from each sampling site during August

Location	Ni	Co	Mn	Cd	Fe	Cu	Zn	Cr	Pb
Rassharma	4.17	1.67	1.67	0.83	30.00	0.30	0.11	<b>1.67</b>	<b>1.67</b>
Burum	7.50	5.83	2.50	1.67	47.50	54.17	<b>39.17</b>	2.50	5.00
AL-Mukalla	14.17	3.33	4.17	2.50	87.50	49.17	118.33	8.30	2.50
AL-Shaher	6.67	6.67	3.33	2.50	238.33	52.50	48.33	6.67	2.50
Arryidah	5.83	2.50	2.50	1.67	55.83	20.00	30.83	1.67	2.50
Minimum	4.17	1.67	1.67	0.83	30.00	4.17	10.83	1.67	1.67
Maximum	14.17	6.67	4.17	2.50	238.30	54.17	118.30	8.30	5.00
Average	8.00	4.04	2.86	1.79	103.90	34.05	53.81	4.39	2.98

**Table 7.** Average concentration of total metals ( $\mu\text{g/g}$ ) in collected Mollusca samples from each sampling site during November

Location stations	Ni	Co	Mn	Cd	Fe	Cu	Zn	Cr	Pb
Rassharma	3.33	1.67	2.50	0.83	40.00	14.17	22.33	0.83	2.50
Burum	6.67	5.00	4.17	5.70	91.67	78.33	26.67	2.50	6.67
AL-Mukalla	19.17	4.17	4.17	3.33	225.00	70.00	63.75	3.33	2.50
AL-Shaher	6.67	5.00	4.17	4.17	458.33	70.00	58.17	1.67	6.07
Arryidah	3.33	1.67	3.33	0.83	40.00	20.00	26.67	0.83	2.50
Minimum	3.33	1.67	2.50	0.83	40.00	14.17	22.33	0.83	2.50
Maximum	19.17	5.00	4.17	5.70	458.30	78.33	63.75	3.33	6.67
Average	8.81	3.45	3.57	3.06	193.3	49.29	40.52	1.90	4.20

**Table 8.** Average concentration of total metals ( $\mu\text{g/g}$ ) in collected Mollusca samples from each sampling site during February

Location stations	Ni	Co	Mn	Cd	Fe	Cu	Zn	Cr	Pb
Rassharma	1.67	1.67	1.67	3.33	35.00	11.67	49.5	0.83	1.67
Burum	6.67	2.50	2.50	10.00	78.33	108.30	53.67	1.67	3.33
AL-Mukalla	3.33	2.50	6.67	7.50	183.33	27.50	77.50	6.67	2.50
AL-Shaher	10.83	4.17	13.33	6.67	333.33	77.50	59.42	1.67	2.50
Arryidah	1.67	1.67	2.50	5.83	56.67	13.33	56.83	1.67	1.67
Minimum	1.67	1.67	1.67	3.33	35.00	11.67	49.50	0.83	1.67
Maximum	10.83	4.17	13.33	10.00	333.30	108.30	77.50	6.67	3.33
Average	5.24	2.62	5.95	6.67	150.70	51.18	60.56	2.86	2.38

**Table 9.** Average concentration of total metals ( $\mu\text{g/g}$ ) in collected Mollusca samples from each sampling site during May

Location stations	Ni	Co	Mn	Cd	Fe	Cu	Zn	Cr	Pb
Rassharma	4.17	1.67	1.67	3.33	29.17	4.18	21.17	1.67	1.67
Burum	8.33	3.33	4.17	15.83	200.00	21.67	34.33	2.50	3.33
AL-Mukalla	6.67	2.50	4.17	15.00	425.00	7.50	45.17	4.17	2.50
AL-Shaher	7.50	2.50	5.83	7.50	333.33	13.33	56.08	1.67	2.50
Arryidah	5.00	1.67	2.50	5.83	133.33	5.00	21.50	1.67	2.50
Minimum	4.17	1.67	1.67	3.33	29.17	4.18	21.17	1.67	1.67
Maximum	8.33	3.33	5.83	15.83	425.00	21.67	56.08	4.17	3.33
Average	6.31	2.38	3.69	9.52	225.00	11.07	36.50	2.50	2.50

**Table 10.** Comparison with the of metals in marine organism collected from different regions of the world

Ecosystem	Concentration( $\mu\text{g/g}$ )							Reference
	Cr	Cd	Zn	Cu	Pb	Mn	Ni	
Alexandria, Egypt	-	23.2	61.2	338.4	38.3	-----	-----	Ghazaly(1988)
Gulf of Aden, Yemen*	3.64	1.1	73.9	11.3	2.4	16	2.31	Ali, 1997
Arabian Gulf	-----	0.90-2.40	8.7-333.8	1.41-1.63	5.90-7.60	-----	-----	Hashim et al., 1994
Malaysia	-----	0.51-1.22	75.14-128.9	6.31-20.1	2.0-8.76	-----	-----	Yap et al., 2002
China	0.08-8.15	0.01-2.38	0.08-231.0	3.95-11.13	0.99-2.93	-----	2.75-4.78	Feng et al., 2004
Gulf of Aden, Yemen**	-----	4-27	62-170	10-24	2.5-4	2-35	-----	Sokolowski et al., 2004
Oman	0.5-3.8	9-21.9	391-1614	60.9-276	0.4-0.7	3.4-7.1	0.8-3.1	de Mora et al., 2004
Aden, Yemen	-	0.6-1.9	10.2-120.3	2.1-25.3	9.8-23.7	-	-	Heba et al., 2003
Gulf of Aden, Yemen	0.55-2.13	0.1-3.63	2.38-30	3.75-67.13	2.6-12.6	2.9-33.8	0.5-2.5	AL-Alimi., 2008
China	-	0.03	32.10	--	-	-	-	Wang et al., 2010
India	-	0.04	12.76	-	-	-	-	Aktaret al. 2011
Gulf of Aden, Yemen	-	0.01	-	-	0.098	-	-	Al-Hudaifi, 2015
Gulf of Aden, Yemen	0.83-8.3	0.83-15.83	21.5-118.3	5-108.3	1.67-6.67	2.5-13.33	1.67-19.17	Present study

terrestrial and aquatic animals and plants (Bruland *et al.*, 1991).

In the present study, the concentration of cobalt in Mollusca was ranged between 1.67 µg/g during autumn, winter and spring at Ras-Sharma and Arryidah to 6.67 µg/g during summer at Al-Shaher. The highest concentration of cobalt were detected in Mollusca of Al-Shaher during summer that were related to the increased metabolism due to high temperature and where there is much industrial and anthropogenic activity. In general, the concentration of cobalt in all locations was high compared to Ras-Sharma (protected area); the suggested reason for this increase is due to the increase of sewage and industrial discharge in this location.

### **Manganese**

Manganese (Mn) is essential for aquatic organisms, where it is present below limited concentration due to its role in physiological metalloenzymes, in bone structure and for normal functioning of the nervous system (WHO, 1996). In the present study the concentration of manganese ranged between 2.5-13.33 µg/g. The concentration of Mn in Mollusca of all locations was higher than the permissible level (1 µg/g) of Mn as stated by WHO (1989). Distribution of Mn in Mollusca of the studied area is shown in (Figure 2).

The highest concentration of manganese was detected in Mollusca of Al-Shaher during winter season, which receives effluents from human activities and the accumulated concentrations of Mn in Mollusca to be sensitive to environmental conditions, including level of metal exposure, and thus seem to reflect ambient metal availability in the ecosystem quite efficiently.

### **Cadmium**

Cadmium is another heavy metal of concern, because it can cause kidney and bone damage to people who suffer long-term chronic exposure to it. Sources of cadmium into the environment from human activities are mainly from the mining, extraction, and processing of Copper, Lead, and Zinc. Other sources can include solid waste incineration, reprocessing of galvanized metal, and sewage sludge. Cadmium can also be found in some batteries, fertilizers, tires, and many industrial processes.

The concentration of Cd in Mollusca of the present study was higher than the permissible level (1 µg/g) of Cd as stated by WHO except in Mollusca collected from Ras-Sharma during August and November. Distribution of Cd in Mollusca of the study area is shown in (Figure 3). Cadmium is accumulated at higher level at Burum

during spring due to the effect of the waste discharge of Burum city.

### **Iron**

Natural sources of Fe includes, storm dust fall, erosion or crustily weathering dead decomposition of biota in the water, whereas the anthropogenic sources include sewage waste, industrial effluents, automobile effluent, petroleum and fertilizer industry effluents, automobile serve station waste oil discharge, shipwrecks and dumping of water materials (FAO, 1994).

In the present study, values of iron varies between 29.17 during spring at Ras-Sharma and 458 µg/g during autumn at Al-Shaher. The concentrations of Fe in Mollusca at AL-Shaher and AL-Mukalla were more than the permissible limit for Fe (100 ug/g) by WHO (1989). The highest concentration of iron was detected in Mollusca of (Al-Shaher) in autumn, which suggests that it's input from activities (Agricultural runoff and untreated sewage inputs from densely populated urban areas small shipping activities are intense. Activities of fishery and fish processing are common in the city that lacks efficient services of a sewerage system, including collection, sewers and treatment plants.) that take place on this shore (Figure 4).

### **Copper**

Copper (Cu) is essential for a good health, but a very high intake can cause adverse health problems. It is an essential component of numerous oxidation reduction enzymes (cytochrom oxidase, uricase and tyrosine) (Beveridge and McAndrew, 2000). In the present study concentration of Cu in Mollusca ranged between 4.17 during summer at Ras-Sharma and 108 ug/g during winter at Burum. The concentrations of Cu in Mollusca of Burum and AL-Mukalla and Al-Shaher during summer, autumn and winter are still higher than the permissible level for Cu (30 µg/g) as recommended by WHO (1989). The highest concentration of copper was detected in Mollusca of (Burum) in winter, where anthropogenic input is present (domestic sewage, leaching from ship antifouling paints and the runoff). Distribution of Cu in Mollusca of the study area is shown in (Figure 5).

### **Zinc**

Zinc is an essential trace element in living organisms, being involved in nucleic acid synthesis and occurs in many enzymes. Zinc and its compounds are extensively used in commerce and in medicine. The most common sources are galvanized ironwork, zinc chloride used in



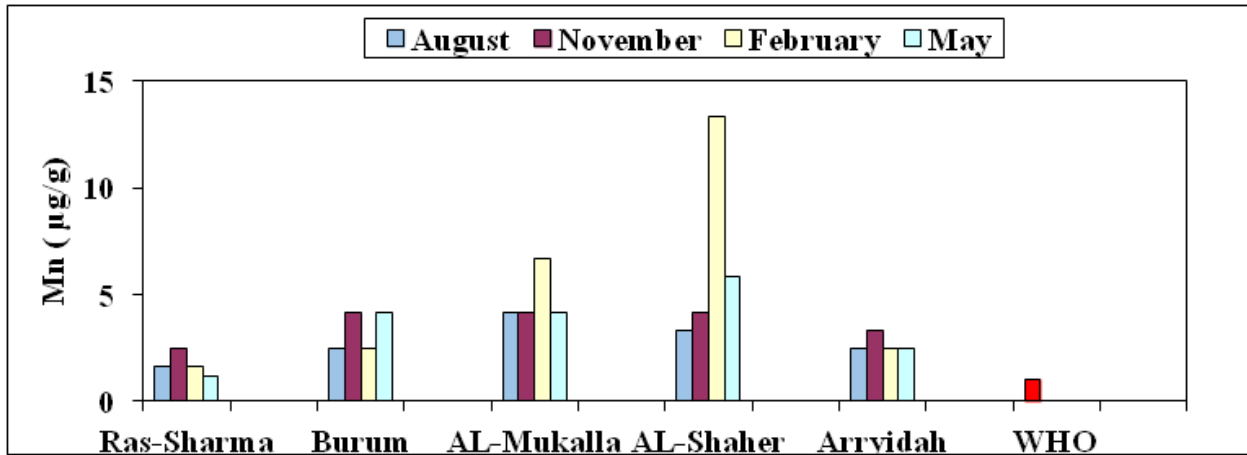


Figure 2. Manganese concentration in Mollusca samples compared with international standard recorded during the study period

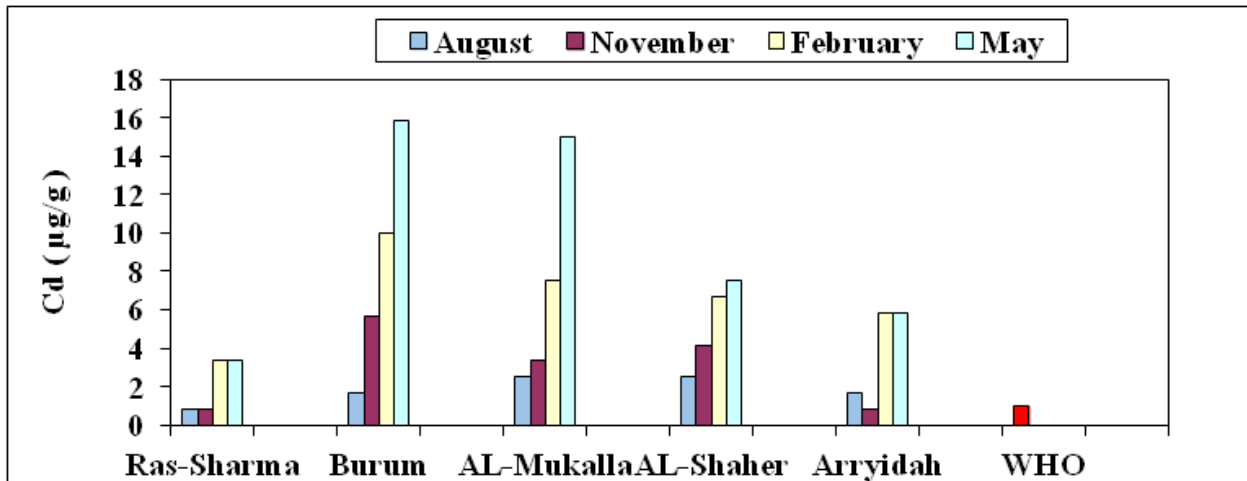


Figure 3. Cadmium concentration in Mollusca samples compared with international standard recorded during the study period.

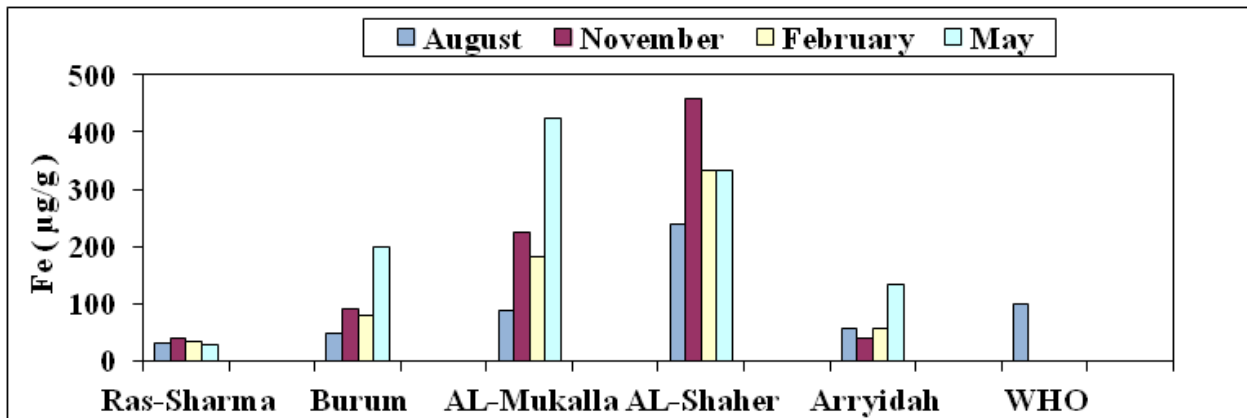
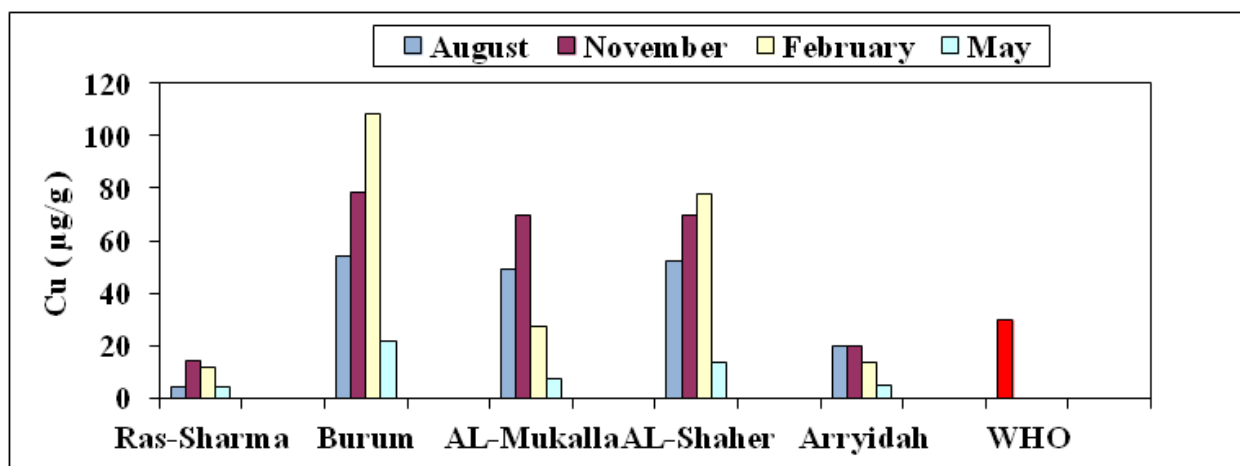


Figure 4. Iron concentration in Mollusca samples compared with international standard recorded during the study period



**Figure 5.** Copper concentration in Mollusca samples compared with international standard recorded during the study period

plumbing and paints containing zinc. It is soluble in water and illness may be caused by drinking water containing zinc (Tafa and Assefa, 2014). Zinc wastes can have a direct toxicity to aquatic life, and fisheries can be affected by either zinc alone or more often together with copper and other metals (Alabaster and Lloyd, 1982).

Zinc (Zn) is readily accumulated by aquatic biota, but mechanisms are presented for its elimination. Zn concentrations are the highest in the lowest trophic levels, but can exceed 100 times their normal levels in polluted areas (Ketchum, 1980).

In the present study, concentration of zinc in Mollusca between 10.83 during summer at Ras-Sharma and 118.3 µg/g during summer at Al-Mukalla. The highest concentration of zinc (Figure 6) was detected in Mollusca of AL-Mukalla. This site is in the vicinity of ports busy with navigational activities and cargo handling particularly petroleum and petroleum products. The results of the present studies are in agreement with those obtained by Szefer *et al.* (1999); Sokolowski *et al.* (2004). According to world permissible levels of heavy metals values in aquatic organisms, the maximum allowable value of Zn concentration must not exceed 100 µg/g. The Zn concentration in Mollusca at AL-Mukalla during August was higher than the allowable permissible limit by WHO (1989).

### Chromium

Chromium is a metal that rarely occurs in nature. The main mineral containing this element is chromate  $\text{FeCr}_2\text{O}_4$ , which contains up to 70% of pure  $\text{Cr}_2\text{O}_3$ . Its higher content in the environment is caused by human activity. The risk of global pollution of the natural environment by chromium does not yet exist, although its local emissions into the atmosphere, waters and soils

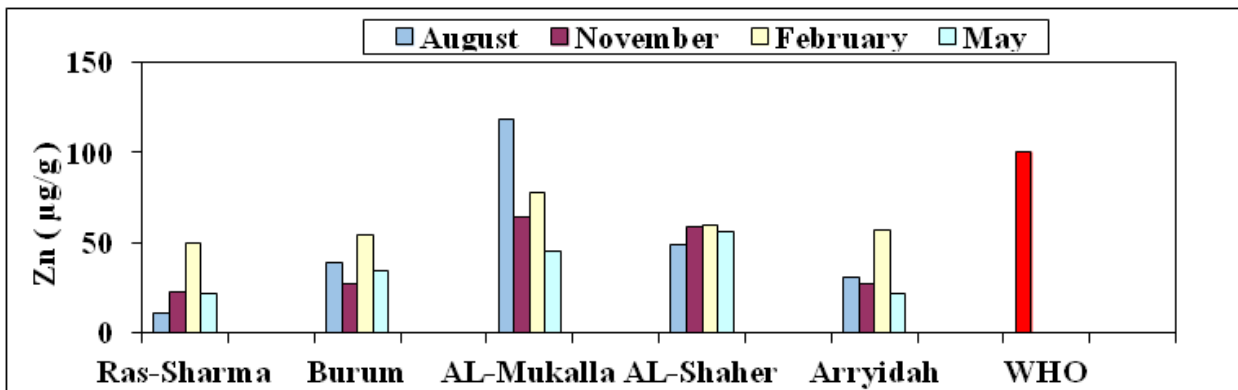
may cause its excessive inclusion in biochemical circulation, thus posing a danger to man and animals. Chromium (in small quantities) is an element significant to the life of plants and animals. High concentrations of Cr are harmful. Chromium, with an oxidation number of six, is more dangerous to living organisms than trivalent chromium, due to its greater ability to diffuse through cell tissue (Baralkiewicz and Siepak, 1999).

In the present study, values of Chromium in Mollusca ranged from 0.83 µg/g during autumn and winter at Ras-Sharma to 8.3 µg/g during summer at Al-Mukalla. The increase in chromium level is due to the discharge of industrial, sewage and agricultural wastes in the investigated areas.

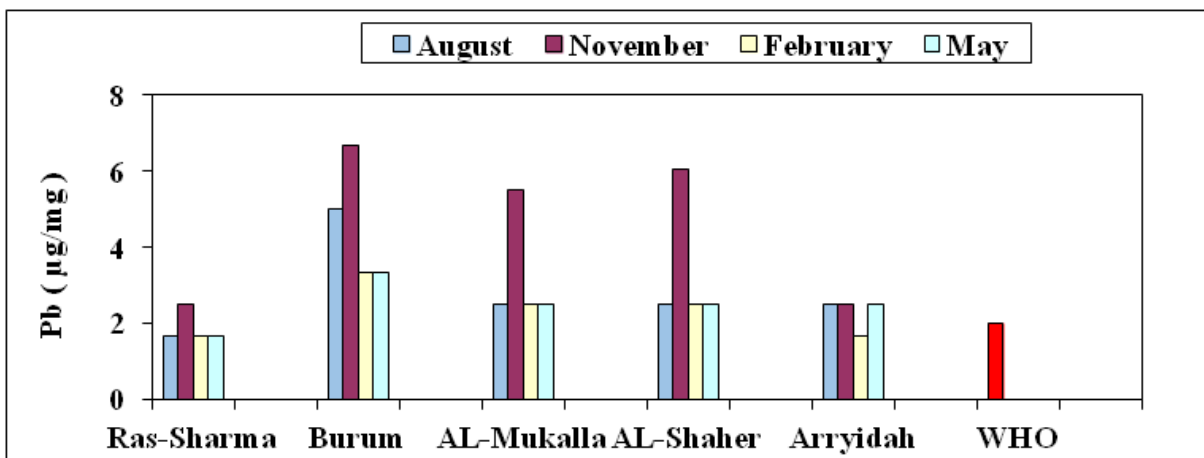
In the current study, the concentrations of Chromium were considered high when compared with other studies on the Gulf of Aden (Ali, 1997; Al-Alimi, 2008), also the concentration of Cr was higher than the results of other studies of de mora *et al.* (2004); in Oman and the study of Feng *et al.* (2004) in China.

### Lead

Lead (Pb) is toxic, even at low concentration, it is considered to be one of the most dangerous elements in ecology and aquatic ecosystem. Lead is an easy contaminant of water sediment and marine organism from different sources of pollution e.g. sewage, agricultural and industrial effluents. Lead had no function in the biochemical process in marine organism. It causes death of marine organism due to suffocation. Uptake of lead by hydrophytes is depended on exposure time, aqueous concentrations, pH, temperature, salinity, diet and other parameters such as internal ion regulatory capacity and metabolism of species under consideration (Sorensen 1991).



**Figure 6.** Zinc concentration in Mollusca samples compared with international standard recorded during the study period.



**Figure 7.** Lead concentration in Mollusca samples compared with international standard recorded during the study period.

In the current study, the concentration of Pb in Mollusca ranged from 1.67 during summer, winter and spring at Ras-Sharma to 6.67 g/g during autumn at Burum, locations Burum, Al-Mukalla and Al-Shaher recorded the highest values of Pb. The possible sources of Pb could be attributed to the different industrial wastes and from water pipes, lead acid batteries, solder, alloys, cable sheathing, pigments, rust inhibitors and plastic stabilizers (WHO 2004; Akan et al., 2010). Pb concentration at Mollusca in the present study exceeds the permissible levels of Pb (2.0 µg/g) stated by WHO (1989) except in Arryidah during February and Ras-Sharma. (Figure 7).

**CONCLUSIONS**

The highest concentration of most metals in Mollusca were recorded at Al-Mukalla, while the lowest concentration were recorded at Ras-Sharma. Al-Mukalla

is the capital of Hadramout Governorate. Now this coastal area receives significant amounts of sewage and industrial effluents from harbor activities, fish-processing and canning factories, electrical power plants, and petroleum-tank stations. Industrial activity and human activity in Hadhramout coastal has a negative impact to water quality, because heavy metals from water can be poisonous to organism and can lead to a decrease in the productivity in marine fisheries, marine culture, and also in biodiversity.

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