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Abstract

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 direct or indirect negative impact on the sea life and marine environment.

Seawater samples were collected from Hadhramout Governorate coastal area Yemen. Five sampling locations were selected to conduct the present study. The samples were taken on a seasonal basis from Augusts of 2013 until May 2014.

Twenty seawater samples were collected from the five areas (Ras sharma, Burum, AL-Mukalla, AL-Sheher and Arryidah) at Hadhramout coastal area.

Trace metals were measured to assess the status of contamination in the study area. Concentrations of Ni, Co, Mn, Cd, Fe, Cu, Zn and Pb in seawater were in the range of 0.8 to 1.9 mg/L, 0.5 to 1.2mg/L, 0.10 to 0.34mg/L, 0.1 to 0.2mg/L, 0.6 to 2.1mg/L, 0.3 to 0.8mg/L, 0.03mg/L to 0.48mg/L, 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, comparing with EPA.

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 while Ni, Co, Cd, Fe and Pb were higher than the permissible level.

Key words: Seawater, Trace metals, seasonal, Hadhramout Governorate coastal area.

Introduction

Pollution of the aquatic environment by inorganic chemicals has been considered a major threat to the aquatic organisms including fishes. The agricultural drainage water containing pesticides, fertilizers, and effluents of industrial activities and runoffs in addition to sewage effluents supply the water bodies and sediment with huge quantities of inorganic anions and heavy metals [17]. The most anthropogenic sources of metals are industrial, petroleum contamination and sewage disposal [11].

Heavy metals are among the most common environmental pollutants, and their occurrence in waters and biota indicate the presence of natural or anthropogenic sources. The main natural sources of metals in waters are chemical weathering of minerals and soil leaching. The anthropogenic sources are associated mainly with industrial and domestic effluents, urban storm, water runoff, landfill, mining of coal and ore, atmospheric sources and inputs rural areas [12]. Water pollution by trace metals is an important factor in both geochemical cycling of metals and in environmental health [12]. The existence of heavy metals in aquatic environments has led to serious concerns about their influence on plant and animal life. The nutritional requirements of elements (Cu, Zn etc.) differ substantially between species or elements, and optimum ranges of concentrations are generally narrow. Given elements (Pb, Cd etc.) exhibit extreme toxicity even at trace levels [16].

Toxic levels of heavy metals in waters may impose serious threat to aquatic species as well as humans. The concentrations of heavy metals in natural water bodies are often elevated due to anthropogenic interferences. Investigations on heavy metals in natural waters have received considerable attention as they provide a coded history of lake's environment. It has also been established that the damage to aquatic ecosystem owing to heavy metals is mainly a function of bio-available metal fraction rather than the total amount of metal present in waters or in sediments. Hence, to assess the extent of pollution hazard and to understand the dynamics of heavy metals in natural water bodies, the intensities of different chemical fractions of heavy metals in sediments have to be looked into besides the total amount of metals in waters and sediments [18].

Uptake and accumulation of metals from the surrounding water by absorption and diffusion across the body surfaces and ingestion of food and particulates pose a major problem with respect to their effects on biota and humans, as

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they are bioconcentrated up the food chain. The ability of some marine organisms to accumulate heavy metals to very high tissue and body concentrations (e.g. by factors of 10 to 10) renders them very useful as bioindicators. Interest in such organisms for assessment and monitoring of marine pollution is growing worldwide, and cosmopolitan biomonitors frequently include benthic invertebrates and seaweeds. Uptake of predominantly soluble forms of metals (e.g. Cu, Zn, and Cd) by organisms occurs mainly from the water phase and is proportional to the metal ion activity in the water. Some of the disadvantages associated with measurement of dissolved concentrations (e.g. variation over time, tidal cycle, dilution due to run-off, cost, bioavailbility) are overcome by the analysis of sediments.

Hadhramout coast receives several types of pollutants from different sources and the accumulation of chemical pollutants (salts, heavy metals, pesticides and other pollutants) are expected to increase annually in water, sediments and fish flesh and consequently have adverse impact on their quality.

Levels of heavy metals in water samples have been widely reported in the literature [1, 2, 3, 4, 5, 6, 7, and 15]. The water quality of Hadhramout coast are believed to be gradually deteriorating particularly in the industrialized and densely populated area. Therefore, the aim of the present study was to determine physico-chemical parameters of water and levels of some trace metals (Ni, Co, Mn, Cd, Fe, Cu, Zn and Pb) in water. Also, to compare between such levels and the world standard allowable limits.

Materials and Methods:

Study area:

Hadhramout 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 750km of the Yemeni coasts. The study area is located in Hadhramout Governorate and includes five sites namely, Burum, Al Mukalla, AL-Sheher, Arryidah and Ras- Sharma.

The study area extends from Burum area in the west (14º 35' N and 48° 59′ 537″E) to Arryidah in the east (14º 89' N and 49º15' E) in addition to Ras Sharmah as background (protect area). In general, these coasts are irregular in form, but dominated by sandy bays of varying size separated by promontories of limestone or igneous rocks sometimes of substantial height such as Burum area and Al-Mukalla.

Sampling:

Seawater samples were collected from the target points. Locations of these samples were carefully fixed by digital GPS Navigator (Model: KGP-913) (table (1) and Figure (1).

Twenty surface seawater samples were collected from the five sampling sites at Hadhramout coastal area Gulf of Aden during August 2013 to May 2014. These seawater samples were drown to pre-cleaned plastic bottles (1 L) and preserved in an icebox for further analyses.

The samples were digested as follows. The sample, 100 ml was transferred into a beaker and 4ml concentrated HNO_3, 10 ml HCL and 3ml H_2O_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 cm^3 with distilled water [9]. Determination of heavy metals in the seawater samples was done using Atomic Absorption Spectrophotometer (AAS) Unicam model Solaar 929.

Table (1): Locations of seawater sampling points in the study Area

Location	point	Latitudes	Longitudes
Ras Sharmah	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◦ º31 198″ N	49◦ 09′ 986″ E
	8	14◦ 30′ 999″ N	49◦ º10′ 145″ E
	9	14◦ º30 ′ 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

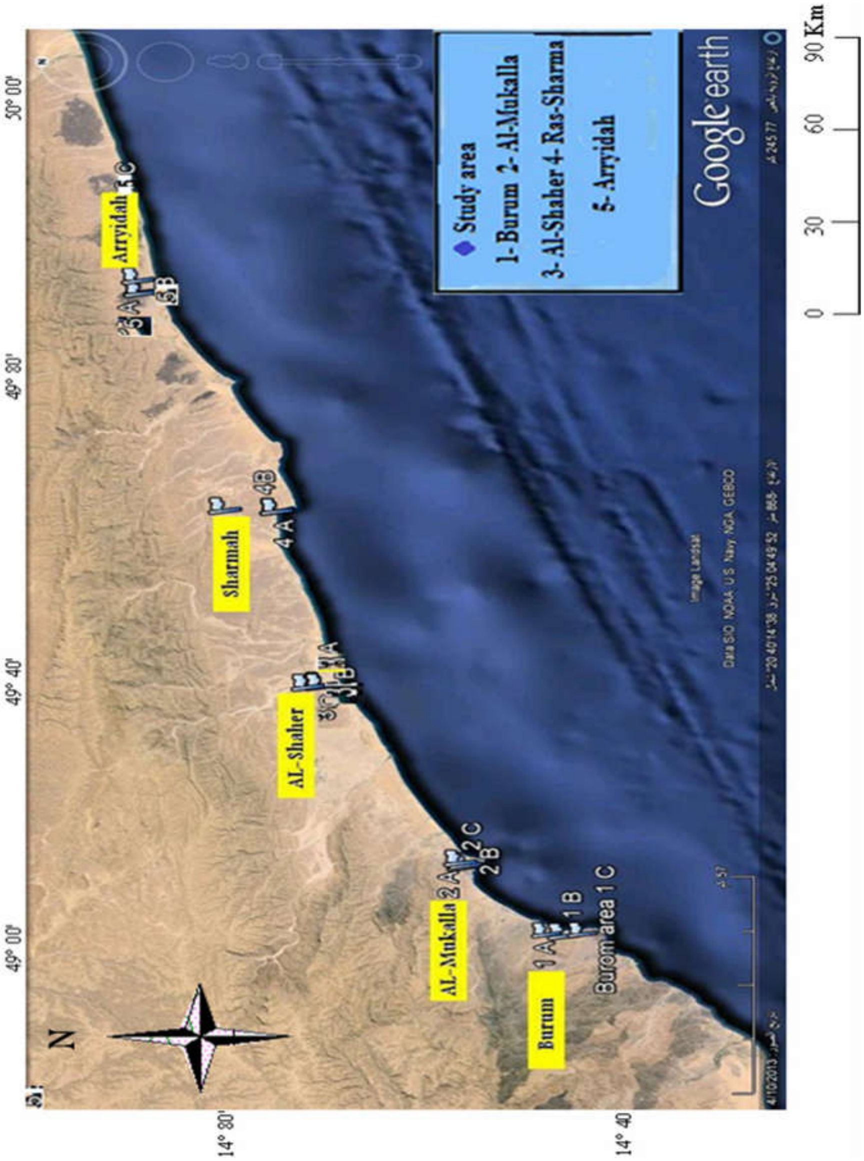

Figure. (1): position of seawater sampling points in the study area (source: Google Earth)

Results and Discussion:
Assessment of aquatic pollution depends on physico-chemical monitoring to identify and quantify toxicants and to provide data for regulatory purposes, and to compare to allowable concentration for particular recipient water [13]. The concept that water quality criteria are the basis for any kind of water pollution control policy is certainly valid [10].
Heavy metals may enter the water from different sources including in sewage, industrial, agriculture domestic effluent and urban runoff. Heavy metals (Ni, Co, Mn, Fe, Cd, Cu, Zn and Pb) are common pollutants, which are widely distributed in aquatic environment. The concentrations of the selected metals are listed in Tables (1, 2, 3 and 4).

Nickel*:*
The concentration of nickel in surface water of the studied area ranged between 0.6 mg/L to 1.9 mg/L. Its highest values were recorded at AL-Mukalla during August and AL-Shaher during November and the lowest values were registered in Ras-Sharma during February. The highest concentration of nickel were detected in seawater surface of the studied area in AL-Mukalla and AL-Shaher. This could be attributed to the discharge of industrial effluents and domestic sewage in these two cities. The petroleum related activities also bring Nickel and contaminate the environment. The concentration of nickel in water at all location was higher than the permissible levels (0.07 mg/L) recommended by EPA (2001) Figure (2).

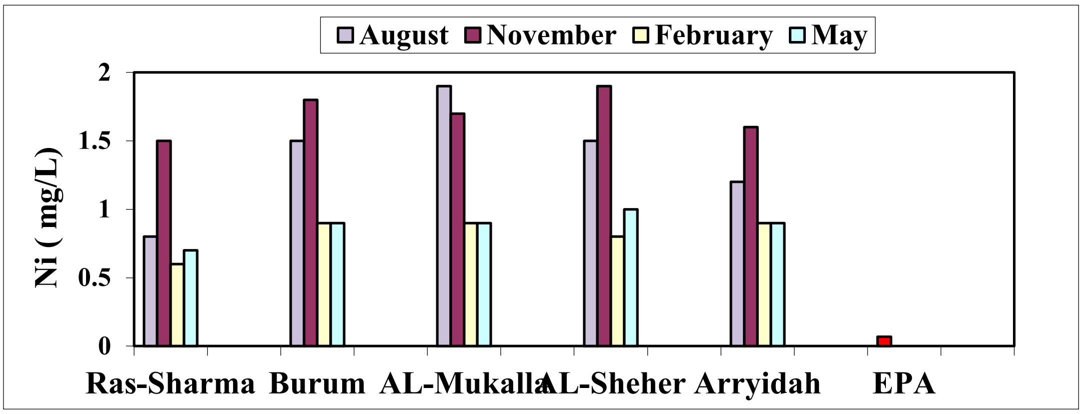

Figure (2): Nickel concentration in surface seawater samples compared with international standard recorded during the study period

Cobalt:
The concentration of cobalt in water of the studied area ranged between 0.4 mg/L to 1.2 mg/L. Its highest values were recorded at AL-Mukalla during November and the lowest values were registered at Ras-Sharma during August, February and May. The highest concentration of cobalt were detected in water surface of Al-Mukalla during November. It is exhibited that untreated effluents from AL-Mukalla fish canning factory and petroleum products storage tanks are contributing to cobalt high concentration in the area. The concentration of cobalt in water at AL-Mukalla, Al-Shaher and arryidah location was higher than the permissible levels (0.5mg/L) recommended by EPA [8]. Figure (3).

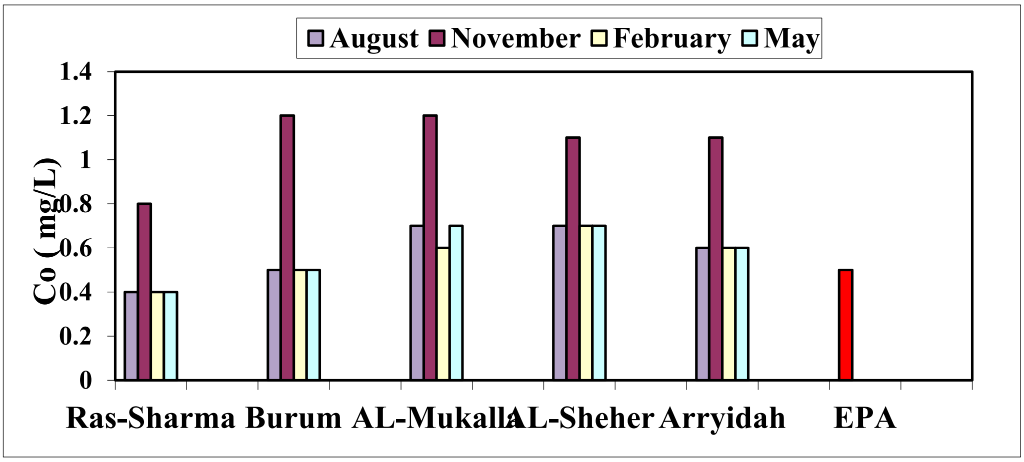

Figure (3): Cobalt concentration in surface seawater samples compared with international standard recorded during the study period

Manganese:

Manganese (Mn) concentrations varied between 0.1 mg/L to 0.3 mg/L. The maximum value was recorded at AL-Mukalla and Al-Shaher during August and the minimum are occurred at Ras-Sharma during the study period. It lies within the permissible level (0.3 mg/L) according to the limit stated by EPA (2001). Figure (4).

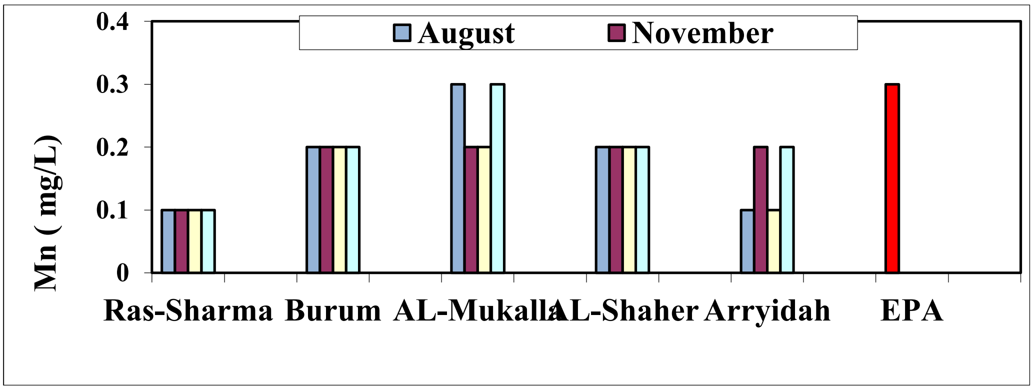

Figure (4): Manganese concentration in surface seawater samples compared with international standard recorded during the study period

Cadmium:

Cadmium concentration in water of studied area ranged between 0.1 mg/L to 0.2 mg/L. The maximum value was recorded at AL-Mukalla and Al-Shaher during the study period and the minimum are occurred at Ras-Sharma during the study period. The high concentration of Cadmium observed at AL-Mukalla and Al-Shaher, these high concentration might be caused by fluvial input from the coastal plain and mineral weathering in the coastal area, however the lowest concentration in Arryidah in surface, this may be attributed to the removing of this metal by many ways such as adsorption on particulate matter, precipitation or removed by marine organisms. The concentration of cadmium in water at all location was higher than the permissible levels (0.05 mg/L) recommended by EPA [8]. Figure (5).

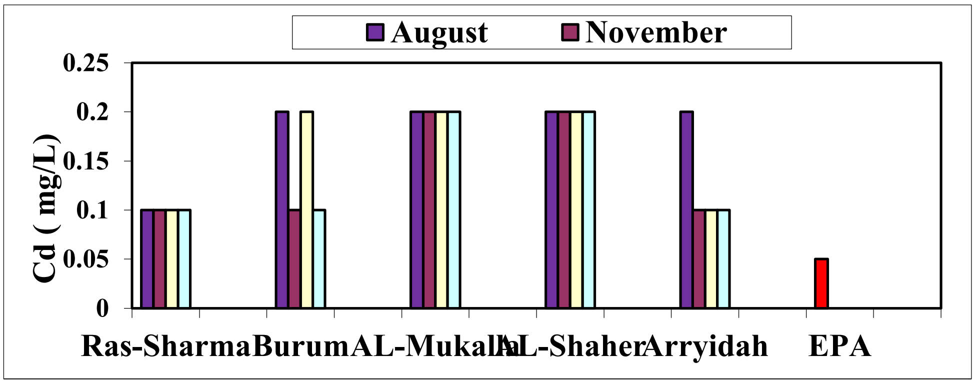

Figure (5): Cadmium concentration in surface seawater samples compared with international standard recorded during the study period.

Iron:

The present study indicated that the concentration of iron in water in the studied area ranged between 0.1 mg/L to 2.1 mg/L. The maximum value was recorded at AL-Mukalla during November and the minimum are occurred at Ras-Sharma during May. The increase in iron in water is mainly due to liberation of iron as ferrous ions from sediments and industrial wastes effluent from Talkha fertilizer factory and re-cooling water in electrical station opposite to this area. However, the minimum values may be due to oxidation of Fe2+ to Fe3+ which precipitate as Fe $(OH)_3$ to the sediment of the oxygenated water.

The concentration of iron in water at AL-Mukalla, Burum, Al-Shaher and arryidah location was higher than the permissible levels (0.3 mg/L) recommended by EPA [8]. Figure (6).

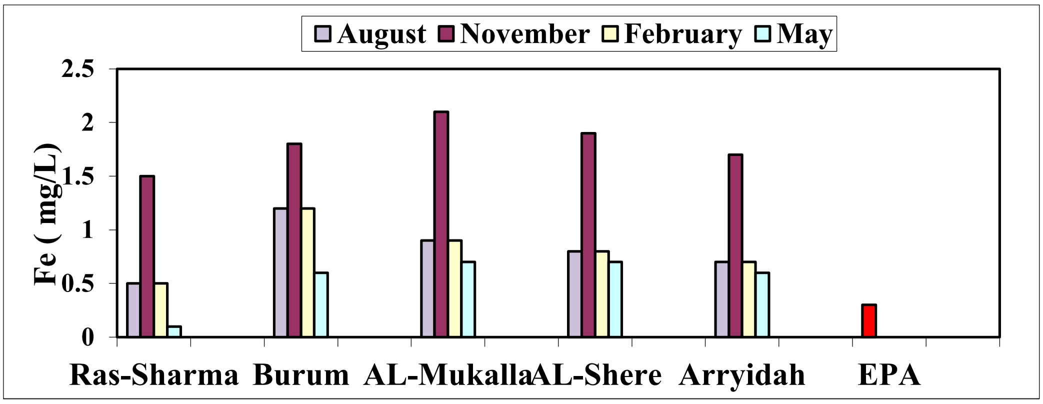

Figure (6): Iron concentration in surface seawater samples compared with international standard recorded during the study period.

Copper:

The concentration of copper in water of the studied area ranged between 0.3 mg/L to 0.8 mg/L. Its highest values were recorded at AL-Mukalla, Burum and AL-Shaher during August and November and the lowest values were Ras-Sharma during February and May. The decrease of Cu concentration in water is mainly due to its tendency to form complex with organic legends and humic matter, which leads to decreasing in the preparation of free ions in water where 90 % of Cu in water was complexes by dissolved organic materials and suspended matter [14]. The concentration of copper in water of studied locations is still below the permissible level (1.0 mg/L) recommended by EPA [8]. Figure (7).

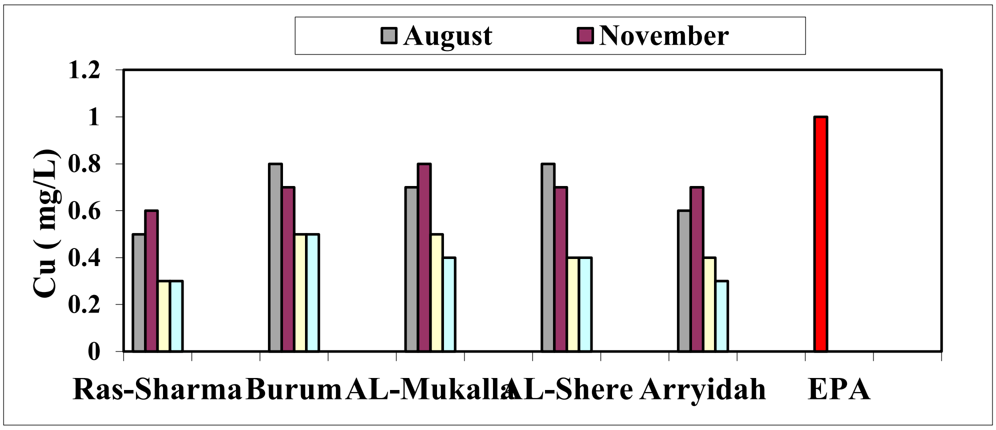

Figure (7): Copper concentration in surface seawater samples compared with international standard recorded during the study period

Zinc:

Zinc (Zn) concentration in water of the studied area ranged between 0.11 mg/L to 0.48 mg/L. Its highest values were recorded in AL-Mukalla during November and the lowest values were Ras-Sharma during May. The high concentration of Zinc observed at AL-Mukalla is from the domestic sewage, municipal waste, atmospheric deposition of fly ash, anthropogenic sources and dredging and dumping of sediments. The concentration of Zn in the studied area lies within the permissive limit (5 mg/L) as stated by EPA [8]. Figure (8).

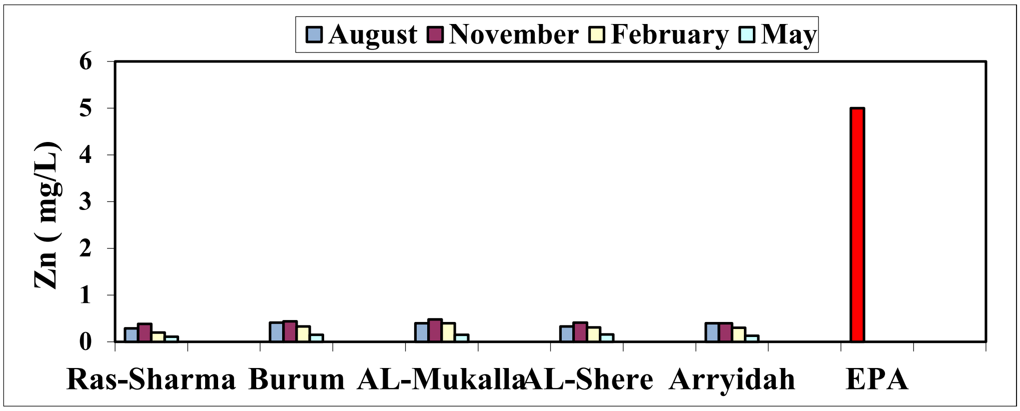

Figure (8): Zinc concentration in surface seawater samples compared with international standard recorded during the study period.

Lead:

The present study revealed that the concentration of lead in seawater of the studied area ranged between 0.4 mg/L to 1.1 mg/L. Its highest values were recorded in AL-Mukalla during Augusts and November and the lowest values were in Ras-Sharma during February and May. The highest concentration of lead was detected in seawater of Al-Mukalla and could be attributed to the spill of leaded petrol from fishing boats. Dust, which holds a huge amount of lead from the combustion of petrol in automobile cars. EPA [8] stated that the maximum Pb concentration in water is 0.05 mg/L. Figure (9).

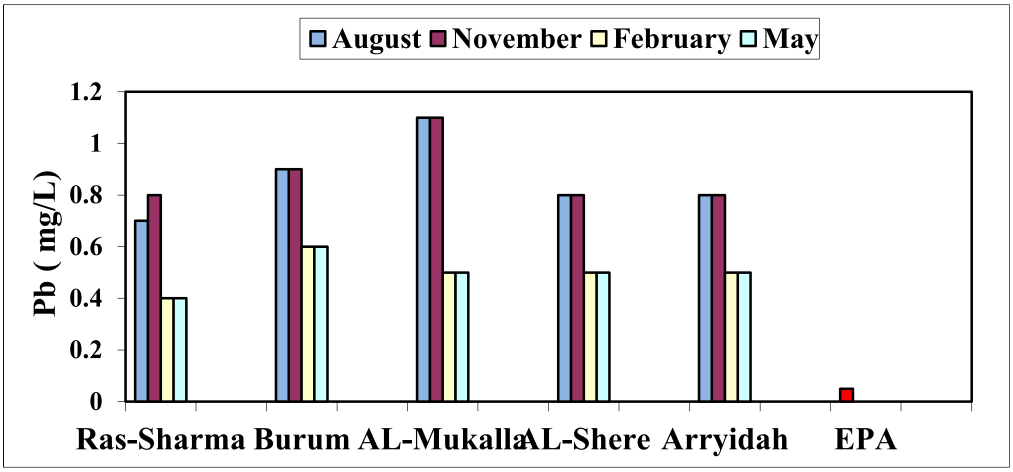

Figure (9): Lead concentration in surface seawater samples compared with international standard recorded during the study period

Table (2): Results of the concentration of total metals (mg/ L) in collecteseawater samples from study locations during August

Location	Ni	Co	Mn	Cd	Fe	Cu	Zn	Pb
Ras sharma	0.80	0.40	0.10	0.10	0.50	0.50	0.29	0.70
Burum	1.50	0.50	0.20	0.20	1.20	0.80	0.41	0.90
AL-Mukalla	1.90	0.70	0.30	0.20	0.90	0.70	0.40	1.10
AL-Shaher	1.50	0.70	0.20	0.20	0.80	0.80	0.33	0.80
Arryidah	1.20	0.60	0.10	0.20	0.70	0.60	0.40	0.80
Minimum	0.80	0.40	0.10	0.20	0.50	0.50	0.29	0.70
Maximum	1.90	0.70	0.30	0.20	1.20	0.80	0.40	1.10
Average	1.30	0.57	0.20	0.20	0.70	0.60	0.36	0.87
EPA	0.07	0.5	0.3	0.05	0.3	1	5	0.05

Table (3): Results of the concentration of total metals (mg/ L) in collected seawater samples from study locations during November

Location	Ni	Co	Mn	Cd	Fe	Cu	Zn	Pb
Ras sharma	1.50	0.80	0.10	0.10	1.50	0.60	0.38	0.80
Burum	1.80	1.20	0.20	0.10	1.80	0.70	0.44	0.90
AL-Mukalla	1.70	1.20	0.20	0.20	2.10	0.80	0.48	1.10
AL-Shaher	1.90	1.10	0.20	0.20	1.90	0.70	0.41	0.80
Arryidah	1.60	1.10	0.20	0.10	1.70	0.70	0.40	0.80
Minimum	1.50	0.80	0.10	0.10	1.50	0.60	0.38	0.80
Maximum	1.90	1.20	0.20	0.20	2.10	0.80	0.48	1.10
Average	1.60	1.03	0.15	0.15	1.77	0.73	0.42	0.90
EPA	0.07	0.5	0.3	0.05	0.3	1	5	0.05

Table (4): Results of the concentration of total metals (mg/ L) in collected seawater samples from study locations during February

Location	Ni	Co	Mn	Cd	Fe	Cu	Zn	Pb
Ras sharma	0.60	0.40	0.10	0.10	0.50	0.30	0.20	0.40
Burum	0.90	0.50	0.20	0.20	1.20	0.50	0.33	0.60
AL-Mukalla	0.90	0.60	0.20	0.20	0.90	0.50	0.40	0.50
AL-Shaher	0.90	0.70	0.20	0.20	0.88	0.40	0.30	0.50
Arryidah	0.80	0.60	0.10	0.10	0.70	0.40	0.30	0.50
Minimum	0.60	0.4	0.10	0.10	0.50	0.30	0.20	0.40
Maximum	0.90	0.70	0.20	0.20	1.20	0.50	0.40	0.50
Average	0.77	0.53	0.15	0.51	0.70	0.40	0.30	0.47
EPA	0.07	0.5	0.3	0.05	0.3	1	5	0.05

Table (5): Results of the concentration of total metals (mg/ L) in collected seawater samples from study locations during May

Location	Ni	Co	Mn	Cd	Fe	Cu	Zn	Pb
Ras sharma	0.70	0.40	0.10	0.10	0.10	0.30	0.11	0.40
Burum	0.90	0.50	0.20	0.10	0.60	0.50	0.15	0.50
AL-Mukalla	0.90	0.70	0.30	0.20	0.70	0.40	0.15	0.60
AL-Shaher	1.00	0.70	0.20	0.20	0.70	0.40	0.16	0.60
Arryidah	1.00	0.60	0.20	0.10	0.60	0.30	0.13	0.50
Minimum	0.70	0.40	0.10	0.10	0.10	0.30	0.11	0.40
Maximum	1.00	0.70	0.30	0.20	0.70	0.40	0.15	0.60
Average	0.87	0.57	0.20	0.10	0.47	0.33	0.13	0.50
EPA	0.07	0.5	0.3	0.05	0.3	1	5	0.05

Conclusions:

The heavy metals levels at Hadhramout coastal water are higher than the limit permissible by EPA, except Cu, Zn and Mn. Spatial distribution of heavy metals in seawater indicates that there is the highest concentration of heavy metals which has been found at Al-Mukalla, this might be related to the different activities of Al-Mukalla harbor, activities of fishery and fish processing, Hadhramout hotel and untreated sewage. Industrial activity and human activity in Hadhramout coastal has a negative impact on 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.

Recommendations:

1- Enforcing and implementing the existing laws, regulation to protect the marine environment.
2- Upgrading of wastewater treatment plants.
3- Continuous evaluation of short and long term impacts of major pollutants on the coastal systems.

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تقييم التلوث بالمعادن الثقيلة لمياه البحر لساحل حضرموت ـــ اليمن

نبيل عبده الشوافي　　محمد عبدالله الوصابي
هشام محمد ناجي　　ندى شيخ مول الدويلة

الملخص

تعد محافظة حضرموت أحد المراكز الصناعية والتجارية للأسماك، وبناء عليه فإن الأمن الغذائي في المنطقة يعتمد بدرجة كبيرة على الإنتاج البحري ومن ثم فإن أي تلوث مباشر أو غير مباشر سواء الناجم عن الأنشطة الصناعية أو الزراعية يكون له أثر سلبي في البيئة البحرية للمنطقة الذي يؤثر تبعا في الصناعة والامن الغذائي ونشاط السكان . أجريت هذه الدراسة في خمس مناطق (رأس شرمة (منطقة محمية)، بروم، المكلا، الشحر، الريدة) من ساحل حضرموت لتقويم درجة التلوث بها، حيث تم تقدير بعض المعادن الثقيلة (النيكل، الكوبلت، المنجنيز، الكادميوم، الحديد، النحاس، الزنك، الكروم، الرصاص) في مياه هذه المناطق بمعدل مرة واحدة كل ثلاثة أشهر اعتبارا من أغسطس لعام 2013 إلى مايو 2014. بينت نتائج الدراسة الحالية بأن تراكيز المعادن الثقيلة في المياه كانت على النحو الآتي: النيكل (0.6- 1.9 ملجم/لتر) ، الكوبلت (1.2-0.4 ملجم/لتر) ، المنجنيز (0.34-0.1 ملجم/لتر) ، الكادميوم (0.2 – 0.1 ملجم/لتر) ، الحديد (2.1 -0.1 ملجم/لتر) ، النحاس (0.8 – 0.3 ملجم/لتر) ، الزنك (0.48 – 0.11 ملجم/لتر) ، الرصاص(1.9 – 0.4 ملجم/لتر) .أظهرت النتائج أن تراكيز المعادن الثقيلة كانت أعلى بشكل ملحوظ خلال موسم الصيف في المياه لمعظم العينات في جميع المواقع خلال فترة الدراسة وذلك بسبب كثرة استخدام المياه في فصل الصيف الحار مما ينتج عنه ازدياد في مياه الصرف الصحي، وكذلك بسبب ارتفاع معدل المتغيرات البيئية في فصل الصيف وبمقارنة نتائج المياه بالدراسات السابقة المحلية والدولية وكذلك المعايير الدولية فقد أظهرت وجود تراكيز عالية أو مساوية للمعادن في جميع مناطق الدراسة. وقد تم شرح الأسباب لهذه التغيرات والتي لها علاقة بالتلوث النفطي بالإضافة إلى التلوث الناجم عن مخلفات الأنشطة البشرية، وكانت أعلى التراكيز تتركز في مدينة المكلا وذلك بسبب الأنشطة الصناعية الموجودة فيها) الميناء، مصنع تعليب الأسماك) إلى جانب أنها منطقة حضرية مزدحمة بالسكان (مياه الصرف الصحي). وهذا يزكي أهمية المزيد من الدراسات في تلك المناطق .

الكلمات المفتاحية: ماء البحر، المعادن الثقيلة، التغيرات الموسمية، ساحل حضرموت