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Oil Contamination in Algae from Gulf of Aden Coast of Yemen

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□ ABSTRACT □

The contamination of algae by oil is posing a great threat to public health and marine life, wherever there is oil pollution. Fifteen different species of algae were studied from Gulf of Aden of Yemen. The extract of algae were examined for the content of oil. They were estimated by GC/MS and quantification was achieved by standard hydrocarbons. It was observed that algae extract contained oil. In the algae range of these oil was found to be from ND ng g^{-1} to 4.5 ng $g^{-1.}$ These algae were found to be contaminated and it is urgently needed to control the source of contamination.

Key words: Oil, contamination, Gulf of Aden, Chlorophyta, Phyaophyta and Rhodophyta marine algae

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التلوث النفطي في طحالب ساحل خليج عدن – اليمن

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□ الملخّص □

يشكل تلوث الطحالب بالنفط خطرا عظيما على الصحة العامة والحياة البحرية. وفي هذا البحث تمت دراسة خمسة عشر نوع مختلفة من الطحالب. لقد تم تعيين تراكيز النفط في هذه الطحالب بواسطة جهاز GC/MS، وعرفت تراكيزها بواسطة محاليل هيدروكربونه قياسية. وفي هذه الدراسة لوحظ احتواء الطحالب على النفط. ففي الطحالب المأخوذة من ساحل خليج عدن اليمني كانت التراكيز في الحدود ما بين صفر و 4.5 نانو جرام/ جرام

ولقد أثبتت هذه الدراسة أن الطحالب المدروسة تحتوي على كميات متباينة من النفط وأن هناك حاجة ملحة لمراقبة هذه التراكيز وضبط مصادر هذه الملوثات.

الكلمات المفتاحية: تلوث نفطي – خليج عدن – طحالب الخضراء – البنية – والحمراء البحرية.

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Introduction:

The Gulf of Aden is a highly productive fishery area due to the upwelling processes. The high primary productivity, due in part, to the upwelled nutrient, supports a feed web, which ultimately sustains the fish community. The seasonally of the monsoon winds drive the upwelling and, it turn, cause a seasonal periodicity throughout the food web. However, there are different types of impacts on the coastal and marine environment of Yemen. These impacts are mainly caused by human and developmental activities, which introduce pollutants to the marine environment and cause the detraction of some special habitats. The most widely recognized issue is that of oil-related pollution, where considerable attention has been focused. However, other areas of concern include the impact of growing industrial and domestic effluents, unplanned coastal development as well as various miscellaneous anthropogenic activities such as fishing, hunting and tourism.

The climate in this area is regulated by two monsoons, the North East monsoon in the winter (December to march), and the South West monsoon in the summer (June to August). The air temperature ranged from 24.0 ^{0}C in the winter to 34.0 ^{0}C in the summer, the relative humidity is high throughout the year (average 70.5%).

The mean surface seawater temperature changes from 26.0 ^{0}C in the winter to about 32.0 ^{0}C in May (Al-Shwafi, 2008).

The coral habitats around the coast of Aden, are very sensitive bio-indicator of environmental and climate change. They are scattered with different genera around the area. No rivers flow into the coastal waters, so the out flow to the sea from the single available wadi in the area is very rare.

There is, however outflow from two 50 to 70 km East of Aden are reach the sea from time to time (approximately twice a year), following heavy rain over the mountains (flash flood). These wadis are wadi Bana and wadi Hussan.

Marine resources in the area substantial and very important to the local community (local fishermen) and to the national economy.

Coral reefs, Seagrass beds, Salt marches, wetlands, roks, commercial fish and shrimps are common around the coastline and also significant. Habitats provide important nursery grounds for commercial fish and other shellfish species.

Many bird species use the Aden wetlands as a stopping point and feeding area NAP, 2003, Al-Shwafi, 2007).

Surface water transport in summer is directed south by the prevailing northern winds for about 4 months, it is velocity of 12-50 cm sec^{-1} (Al-Shwafi, 1997) while in winter the flow is reversed, pushing water into the Red Sea from the Gulf of Aden, the net value of the latter movement is greater than summer overflow.

The second variations in sea level of the Red Sea suggest that a significant water exchange through Bab Al-Mandab, and this may introduce nutrients from Indian Ocean to the Red Sea. These processes may partly explain the relatively long southern Red Sea pelagic fishery (Laith, *et., al.*,2002).

Objectives:

The aim of the study was to perform a baseline study on the state of contamination on marine algae of Aden City.

The objectives of the present study were to:

1- Make an assessment of the status of some critical marine algae along Aden City Coastline a result of oil contamination including the degree of damage caused by oil and thus recommend urgent protection;

2- Shed some light on the sub-lethal effects of the most prominent contaminants upon the marine resources in the area, as well as it's possible implications with human health who consumes them;

3-Collect and review relevant existing study in a manner to serve as a baseline data for further follow-up study in the region.

Material and Methods:

Fifteen species of algae "Chlorophyta: (*Halimeda tuna, Rhizoclonium kochiamum,Caldophora koiei, Enteromorpha compressa, Caulerpa racemosa*

Phaophyta: (*Padina boryana, Turbinaria elatensis, Sargassum binderi, Cystoseira myrica, Sargassum boveanum* and Rhodophyta (*Hypnea cornuta, Champia parvula, Galaxaura marginate, Laurencia paniculata, Gracilaria foliifere* " were collected from the Gulf of Aden coast of Yemen during winter 2005. The samples were taken from the algae flesh for the determination of petroleum hydrocarbon concentrations.

Materials:

All solvents were redistilled in an all- glass distillation apparatus equipped

With a 150-cm vacuum-jacketed fractionation column filled with 3mm diameter glass helices. Blanks of 1000- fold concentrates were determined by gas chromatography with flame ionization detection. The gas chromatograph was a Hewlet packard HP5980-GC with split/ splitless injector furnished with a 25m x 0.3mm fused silica capillary with a chemically bonded gum phase SE54. Water used for cleaning the adsorption resin and sample work- up was purified with a Millipore milli-Q system. Sodium chloride and sodium sulfate were Kiln fired at 450^0 C overnight and cooled in a greasless desiccator. Silica gel used for column chromatography was solvent extracted with n-hexane in a glass cartridge inserted into an extraction apparatus, as described by Ehrhardt (1987). After extraction, the Silica gel was first dried in the same cartridge by passing ultra pure nitrogen through it and was then activated by heating the cartridge in an electric tube oven to 200^0 C for 6 h with the stream of nitrogen reduced to a few ml per minute.

Methods:

The extraction method is that of Wade *et al*., (1988). A total of 10g of wet tissues was Soxhlet- extracted with methylene chloride and concentrated in Kuderna-Danish tubes.The extracts were fractionated by alumina: silica gel (80-100 mesh) chromatography. The extracts were sequentially eluted from the column with 50 ml of pentane (aliphatic fraction) and 200 of 1:1 pentane- dichloromethane (aromatic fraction) and concentrated for instrumental analysis.

Aliphatic hydrocarbons (n-C_{13}-n-C_{34}), pristane, and phytane were analyzed by gas chromatography (HP-5980) in the splitless mode with flame ionization detection (FID). A 30m x 0.32mm i.d. fused- silica column with DB-5 bonded phase (J&W Scientific, INC.) provided component separations. The FID was calibrated at five concentrations, and deuterated *n*-alkanes were used as surrogates and internal standards. Aromatic hydrocarbons were quantified by gas chromatography with mass spectrometric detection (HP-5890-GC and HP-5970-MSD). The samples were injected in the splitless mode onto a 30m x 0.25 mm (0.32µm film thickness) DB-5 fused silica capillary column

(J &W Scientific Inc.) at an initial temperature of 60^0 C and temperature programmed at 12^0 C/min to 300^0 C and held at the final temperature for 6 min. The mass spectral data were acquired, and the molecular ions for each of the PAH analyte were used for quantification. The GC/MS was calibrated by the injection of standards at five concentrations. Analyte identification were based on the retention time of the quantitation ion for each Analyte and a series of confirmation ion. Deurated aromatic compounds were used for surrogate and internal standards.

Result and discussion:

Oil contamination residues in marine algae from Gulf of Aden coast were found to vary considerably (Tables 1-3):

Table (1) : Concentration of Oil in Chlorophyta algae

No.	Name of Algae	Concentration ng /g
1	*Halimeda tuna*	3.1
2	*Rhizoclonium kochiamum*	ND
3	*Caldophora koiei*	4.3
4	*Enteromorpha compressa*	2.1
5	*Caulerpa racemosa*	0.9
Mean		2.08
Range		4.3-ND

Table (2) : Concentration of Oil in Phaophyta algae

No.	Name of Algae	Concentration ng /g
1	*Padina boryana*	3.5
2	*Turbinaria elatensis*	0.4
3	*Sargassum binderi*	4.5
4	*Cystoseira myrica*	2.6
5	*Sargassum boveanum*	0.7
Mean		2.34
Range		4.5-04

Table (3): Concentration of Oil in Rhodophyta algae

No.	Name of Algae	Concentration ng / g
1	*Hypnea cornuta*	2.8
2	*Champia parvula*	0.2
3	*Galaxaura marginate*	1.3
4	*Laurencia paniculata*	2.5
5	*Gracilaria foliifere*	0.9
Mean		1.54
Range		2.8-0.2

From Table,1 and Figure,1: the oil contamination in Chlorophta algae ranged from ND at *Rhizoclonium kochiamum* to 4.3 ng g^{-1} at *Caldophora koiei* with mean 2.08 ng g^{-1}, Table, 2 and Figure 2: the oil contamination in Phaophyta algae ranged from 0.4 ng g^{-1} at *Turbinaria elatensis* to 4.5 ng g^{-1} at *Sargassum binderi* with mean 2.34 ng g^{-1} , and Table,3 and Figure3: the oil contamination in Rhodophyta algae ranged from 0.2 at *Champia parvula* to 2.8 ng g^{-1} at *Hypnea cornuta* with mean 1.54 ng g^{-1}.

The sources discharges of oil or hydrocarbons products are common. Refinery, and refinery harbour at little Aden, bunkering berths in the harbour and the ship fuel supply pipeline from the refinery to the south of the harbuor, are shore oil facilities.

Oily water resulting from the refining process is separated, and its effluent water discharged into the sea south to the refinery.

The bunkering operation facilities cause a degree of harbour pollution due to oil leaking from the ground from damage to storage tanks in 1986, it leaks from the pipes carrying supplies to the bunking berths (MSRRC, 1996).

One bunker barge sank in 1995, causing considerable localized oil pollution in the Tawahi area (Facey, 1996).

The process of handling the loading and unloading operations of the crude and refined oil in the harbour seems to be quite efficient and leads to almost no leakage of oil at all. In may 2002, and due to lack of care, two tons of crude oil accidentally spilled to the sea during loading operations on the refinery harbour at little Aden (Al Burika). This oil was in some extent cleaned with chemicals by the oil pollution control boat, which belongs to the Public Corporation for the Maritime Affairs. But, a quantity of this spilled oil washed by tide to the shore and some were remains on the seawater.

Land-based sources of oil include operational and accidental discharges and emission from oil exploration refining and storage facilities, urban industrial and agricultural run off transport and inappropriate disposal of used lubricating oils (DouAbul, A.A.Z. and Al-Shwafi, N.A .1998).

Yemeni officials have repeatedly reported severe oil pollution in the region. Currently 100 million tons of oil transit the Red Sea annually (SAP, 2001). An example of a chronic oil pollution sources on the Yemen Coast is the authorized discharge of ballast water effluent of the SAFER supertanker storage at Ras Isa. Similar problems occur in the Gulf of Aden with vessels deballasting at the Aden refinery (Al-Shwafi,N.A. and DouAbul,A.A.Z.,1996) . However, the problem of passing vessels deballasting in the Gulf of Aden or the Red Sea appears to be the great cause of oil pollution in Republic of Yemen waters (Ba-Iss, A. A. and Al-Shwafi,N.A 2005). This effluent to some degree. Contaminated with oil, the value of the mixed oil, were below the normally allowed values for the refineries on different parts of the world (Al-Shwafi, *et al*., 2005).

Conclusion and recommendation:

The extract of algae species was obtained. Fifteen species were selected from Gulf of Aden coast of Yemen. Although the algae were found to be contaminated but their comparative oil was different. These results are summarized in Figure 1 to 3 and Table 1 to 3. The algae obtained contained different amount of oil. It is suggested that immediate steps should be taken to control or stop this contamination of oil in marine organisms.

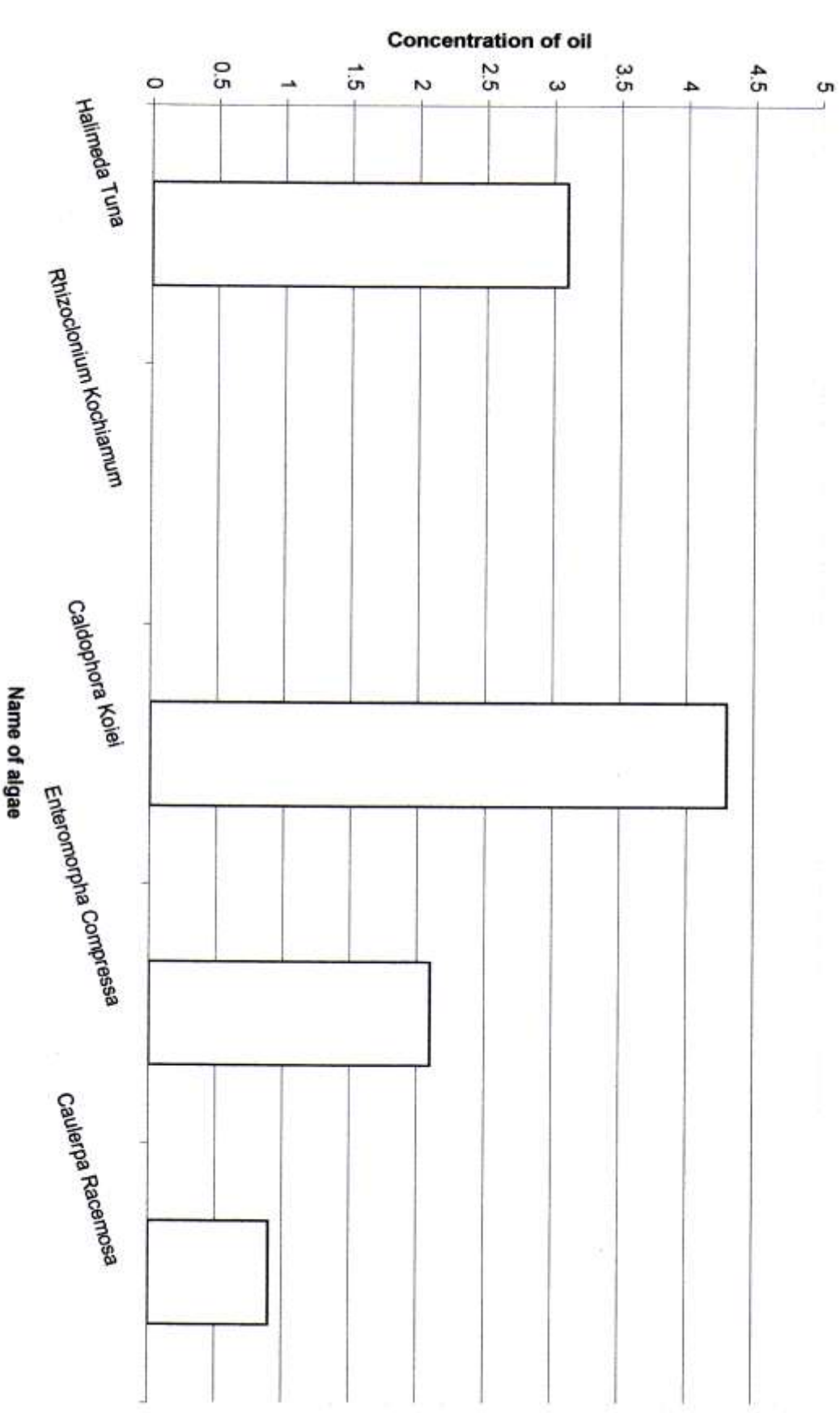

Fig. (1) Concentration of oil in Chlorophyta algae

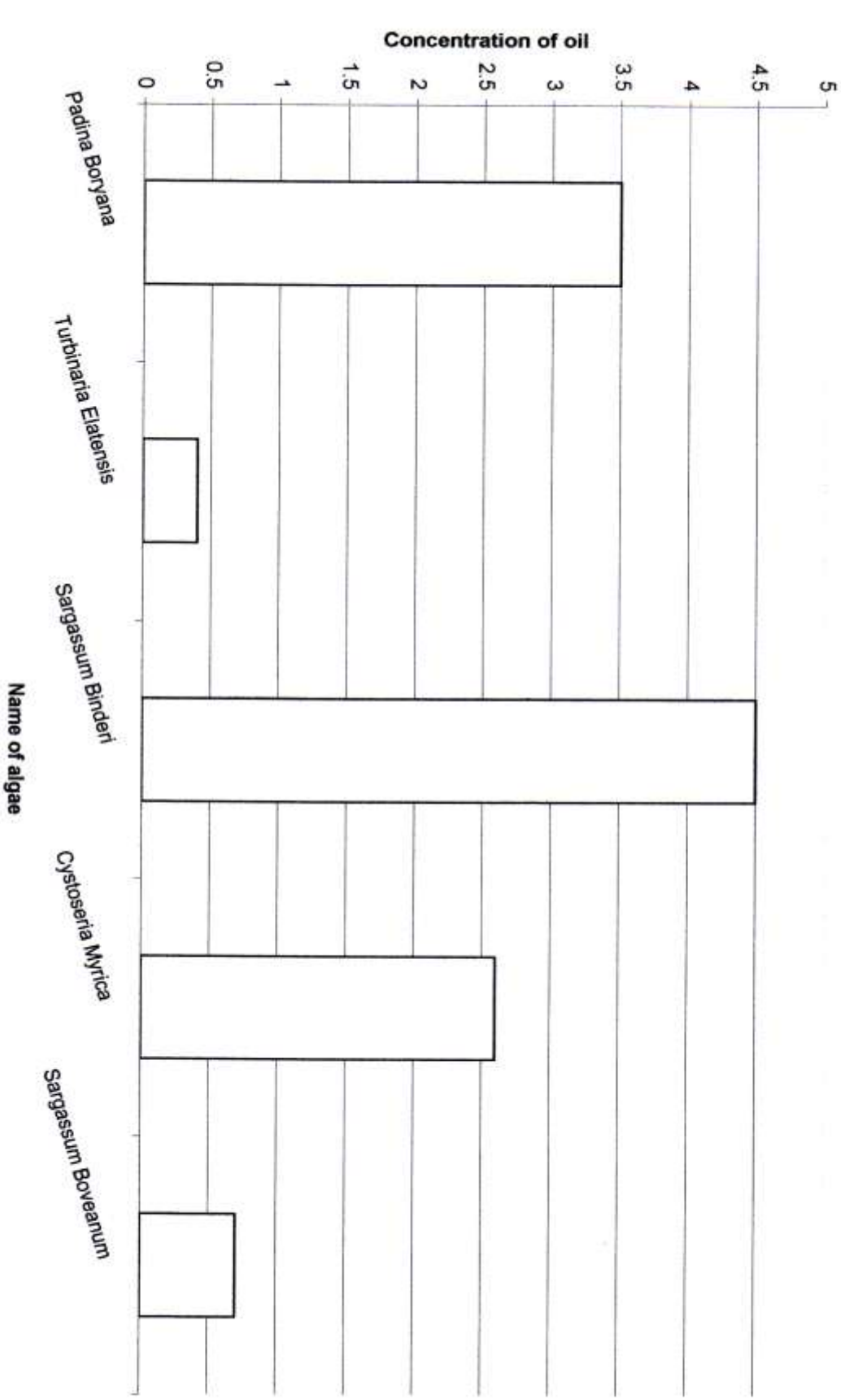

Fig.(2) Concentration of oil in Phaophyta algae

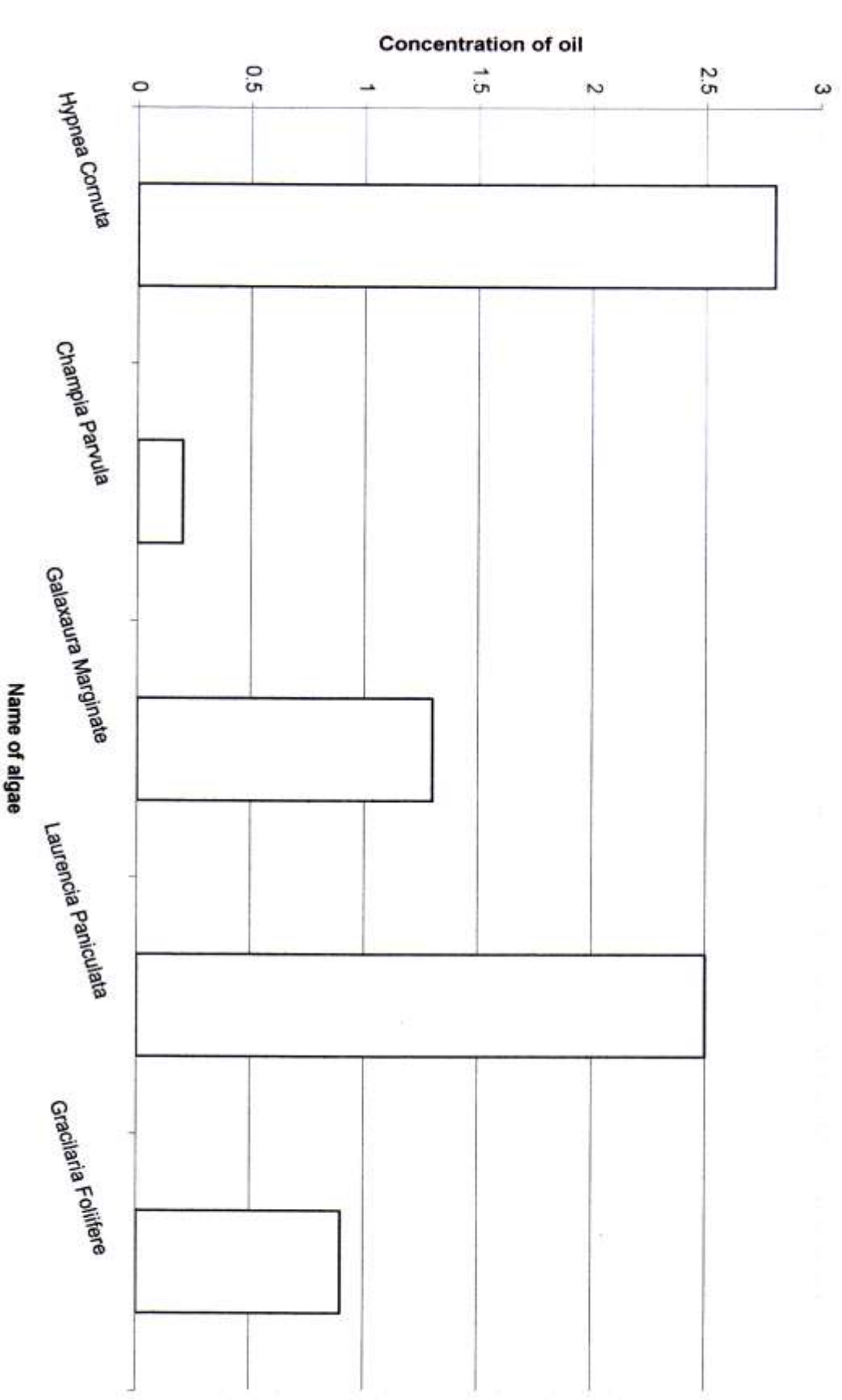

Fig. (3) Concentration of oil in Rhodophyta algae

References:

1. AL-SHAWAFI, N.A. ; DOUABUL ,A.A.Z. *Composition and Sources of hydrocarbons in the Red Sea and Gulf of Aden*. Paper accepted in the first Conference in the Chemistry and Environment, Yemen Chemical Society, April 20-24, 1996.
2. AL-SHWAFI, N. *A baseline study on petroleum hydrocarbons in the Southern Red Sea*. M.Sc. Thesis, Dep. Oceanoge., Fac., Sana'a Univ.,1997, 121
3. AL-SHWAFI,N.A.A. *Concentration of petroleum hydrocarbons in sea- water and coastal sediment around Aden city – Yemen* . Al-Azhar Bull. Sci. Vol. 18, N.1, 2007, 37-51.
4. AL-SHWAFI, N.A.A. *Concentration of petroleumhydrocarbons in sediment coastal of Aden city- Yemen*. J. Poll Res. 27 ,1, 2008, 37-40.
5. BA-ISS, A.A. ; AL-SHWAFI,N.A. *Petroleum hydrocarbons content in sediment from Red Sea coast of Yemen*. Egyptian Journal of Applied Science, Zagazig University , Egypt, Vol. 20 8b August 2005, 407-715.
6. DOUABUL, A.A-Z; AL-SHWAFI, N.A. *Dissolved/ Dispersed Hydrocarbons in the Arabian Regions*. U.K. Marine Pollution Bulletin Vol. 36 No. 4,1998, 844-850.
7. EHAHARDT, M. *Lipophilic organic Material: an apparatus for extracting solids used for their concentration from sea water*. ICES Techn, Environ. Sci., 4, 1987,1-14.
8. FACEY, R. *The Environment of the Aden Harbor*, Report 1996, 150.
9. LAITH, A.; JAWED, SHAWAFI,N.A.; HEBBA, H.M. *Osteological Studies on the caudal vertebrae of two teleost fishes from the Red Sea Coast of Yemen*. Torani, Vol., N 4 December 2002, 197-203.
10. MSRRC (Marine Science and Research Resources Center). *Beach Pollution Study of the Yemeni Coast of the Gulf of Aden*, final report, Visual Survey. Environmental Protection Council (EPC),Dutch Support Project to Technical Secretariat EPC, Yemen 1996.
11. AL-SHWAFI, N.A.; RUSHDI, A.I. ; BA-ISSA . *Trace metals in surface sea waters and sediments from various habitats of the Red Sea Coast of Yemen* Environ. Geol., U.S.A., Vol.48, 2005, 590-598.
12. Strategic Action Program for the Red Sea and Gulf of Aden (SAP). *Navigation Risk Assessment and Management plan*. PERSGA (Regional Organization for the Conservation of the Environment of the Red Sea and Gulf of Aden).2001, 103.
13. WADE,T.L.; ATLAS,E.; BROOKS,J.M.; KENNICUTTLL,M.C; FOX,R.G.; SERICANO, J.L; GARICIA-ROMERO,B.; DEFRITAS,D.A. NOAA Gulf of Mexico Status and Trends program: *Trace organic contaminant distribution in sediments and oyster*s. Estuaries ,Vol. 11, 1988, 171-179.
14. Yemen National Programme of Action for the Protection of the Marine Environment from Land – Based Activities (NAP), Republic of Yemen, Ministry of Water and Environment (MWE) and Environment Protection Authority (EPA), December 2003.