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Petroleum Hydrocarbons and Trace Metals in Mollusca (*Tivela ponderosa*) from the Gulf of Aden

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ABSTRACT. The present investigation represent an assessment of contaminants level including petroleum hydrocarbons and heavy metals in mollusca *Tivela ponderosa* from the Gulf of Aden-Arabian Sea aiming to establish their background concentrations.

The study revealed comparable levels of petroleum hydrocarbons and heavy metals in this region to that reported from other part of the world. The concentrations of petroleum hydrocarbons in the mussels range from 9.5 µg/g at (station 4) to 40.38 µg/g dry weight at Al-Zyiot port (station 1) expressed as Marib crude oil equivalent.

Fat content in the mussels ranged from 0.2 to 0.7 % at station 9 and 8 respectively. It was suggested that mollusca is subjected to oil pollution from the following resources: Tanker discharging of oily ballast water, effluent from the petroleum refineries located on the coastal areas, and loading facilities and transportation activities.

On the other hand, the heavy metals were found in comparable concentration to unpolluted marine environments. Level of Cd, Cu, Pb, and Zn in the study mussels were generally within the range of values reported for other parts of the world.

The result shows low degree of petroleum hydrocarbons and some trace metals pollution in the Gulf of Aden mussels. Hydrocarbons pollution may be due to transportation and other sources of oil pollution. The concentrations of trace metals may be attributed to natural rather than anthropogenic origin. Thus, it was concluded that the investigated heavy metals don't present environmental hazards for the present time. However, it is recommended to carry out continuous monitoring programs for the Gulf of Aden and that the concentration of petroleum hydrocarbons and heavy metals must remain within the prescribed worldwide ratio.

Introduction

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 trace metals. The increase of sewage and industrial effluent discharged into the Gulf of Aden have seriously endangered the ecosystem. Limited investigations dealing with presence of various pollutants have been carried out in this area (Heba *et al.*, 2000; Heba and Al-Mudaffer, 2000) as well as some limited ecological studies.

There are different types of impacts on the coastal and marine environment of Yemen. These impacts are mainly caused by human activities, which introduce pollutants to the marine environment and cause the destruction of some special habitats. The most widely recognized issues are those of oil related pollution and trace metals where a considerable attention has been focused (Heba *et al.,* 2000).

Most of oil produced in this region is exported via sea and pipeline, while local refineries and consumption facilities are located in costal area. The wide spread of oil pollution in the Gulf of Aden is not surprising (Heba *et al.*, 2000; DouAbul and Heba,1996).

The marine environment may be polluted with effluent containing trace element from both anthropogenic and natural processes. Such input could result from treated and/or untreated municipal industrial wastes, agricultural runoff and input from atmosphere.

Urban water runoff contains many constituents that may alter the quality of receiving water, thus harming the endemic biologic community. Although specific pollutants may vary among localities due to differing sources materials, petroleum hydrocarbons and trace metals are contaminants found in most urban runoff (Brown *et al.*, 1985; Heba *et al.*, 2000; Al-Saad *et al.*, 1998).

The sources of these hydrocarbons and trace metals include disposal of automobile and industrial lubricants, spillage from oil storage facilities and leakage from motor vehicles (Al-Shwafi, 2000). The relatively recent and deliberate oil discharge into the Aden water coupled with the improper and occasional lack of operational sewage treatment facilities in Aden resulted in discharge of sewage water into the Gulf of Aden water, caused us to monitor the health of surrounding water bodies.

The usually common pollutants in the coastal line of Aden originate from discharges from desalination power generation, sewage, and wastewater treatment plants in addition to hydrocarbons and trace metal compounds.

Some organisms can accumulate high concentration of hydrocarbons and trace metals. They may also represent moving time-averaged values for the relative biological availability of pollutants at each site (Aril & Wagh, 1988). Mollusca are being an important group of organisms that have been studied for their potentialities as an indicator organism (Al-Saad and DouAbul, 1987; Heba *et al.*, 2000). In the Aden water the mollusk *Tivela ponderosa* is the most widely distributed. The present study shows the result of the survey undertaken to obtain preliminary data on the existing levels of petroleum hydrocarbons and trace metals contamination in Aden water, using this mollusk as the indicator species, these data are the first of its kind in the region and could serve as a base for further study in the future.

Material and Methods

Mussels *Tivela ponderosa* were collected from the substratum below the moon tide mark to minimize the inclusion of individuals which has been exposed to oil concentrated at the air-water interface. Sampling was carried out in April 2001. We obtained mussel *Tivela ponderosa* from nine stations, which were selected as representative of a variety of pollution load conditions (Fig. 1).

FIG. 1. Sample locations.

Procedures were designed to minimize contamination from boats gear and handling. The mussel tissue (samples of 25 individuals) was dissected, excess water drained off and transferred to a pre-weighted glass specimen dish and a wet weight obtained. The animals were then freeze-dried, homogenized and then 5 gm of dried weight were soxhelt extracted in purified thimbles with methylene chloride for 24 hours.

The extraction method was based upon that of Wade *et al.* (1988). The extract was transferred to a storage flask and the sample was further extracted with fresh solvent. The combined extract was reduced in volume to 10 ml in a rotary vacuum evaporator. The hydrocarbons were partially separated from lipids in the extract by saponification the extract for 2 hours with a solution of 4NKOH in methanol. After extraction the unsaponified matter were separated with hexane and extract was dried over anhydrous Na_2SO_4 concentrated by stream of purified N_2 for analysis by Infra Red Spectrophotometric Method approved by Standard Method Committee (APHA, 1985). For the present work a Pye-Unicam Sp 3-300 Infrared Spectrometer was used. Blank determination were carried out by repeating the procedure with a pre- extracted samples, using a calibration with Marib light crude and reference oil prepared as a mixture by volume of 37.5% iso-octane, 37.5% hexadecane, and 25% benzene at 2930^{-1} absorbance.

Heavy metals in *Tivela ponderosa* were determined according to (ROMPE Method, 1983). The sample grind (a mixture of conc. nitric and perchloric acid were slowly added to 3 gm of dried samples in Teflon cups and left overnight before heating. Samples were heated for two hours, then, left to cool and filtered to remove non digested parts. The solutions was adjusted to volume 25 ml, the Cd,Cu, Pb, and were determined by flame A.A.S. using a Perkin-Elmer Model 2380.

Results and Discussion

Petroleum hydrocarbon concentration in *Tivela ponderosa* collected from different stations along the Aden coast range from 9.5 μg/g dry weight at station (4) to 40.38 μg/g at station (7) as presented in Table (1). It is apparent that mussel obtained from the study area along Aden coast were contaminated to some extent with oil. The oil concentration in different stations varied. Fat content in *Tivela ponderosa* ranged from 0.2% at station 9 to 0.7% at station 8 as shown in Table (1). The mean concentration of trace metals (Cd Cu, Pb, and Zn) are shown in Table (2). The lower concentrations were observed at station (1) for Cd, Cu and Zn 0.6,2.1 and 10.2 μg/g dry weight respectively, while concentrations of Pb (9.8 μg/g dry weight) were observed at station (4). However, higher concentrations of elements Cd, Cu, Pb and Zn were observed at station (7), with values of 1.9, 25.3 23.7 and 120.3 μg/g dry weight respectively.

Table 1. Mean concentration (µg/g dry weight) of petroleum hydrocarbons and fat content (%) in *Tivela ponderosa* collected from Aden coast.

Station	Petroleum hydrocarbons		Fat content	
	Range	Mean ± SD	Range	Mean ± SD
1	4.8 - 20.8	11.10 ± 7.17	0.35 - 0.56	0.530 ± 0.08
2	18.9 - 22.8	20.70 ± 1.37	0.47 - 0.75	0.632 ± 0.09
3	15.0 - 19.2	17.32 ± 1.52	0.47 - 0.70	0.604 ± 0.08
4	7.6 - 10.6	9.50 ± 1.02	0.30 - 0.37	0.336 ± 0.03
5	11.3 - 14.1	13.06 ± 1.02	0.38 - 0.42	0.400 ± 0.01
6	17.0 - 20.7	17.78 ± 1.24	0.28 - 0.32	0.300 ± 0.01
7	38.3 - 42.9	40.38 ± 1.66	0.58 - 0.62	0.600 ± 0.02
8	33.2 - 34.5	32.56 ± 1.75	0.68 - 0.72	0.700 ± 0.01
9	8.6 - 12.5	10.70 ± 1.24	0.18 - 0.22	0.200 ± 0.01

Table 2. Concentration and means of heavy metals (µg/g dry weight) in *Tivela ponderosa* collected from Aden coast.

Station	Zn		Cu		Pb		Cd	
	Range	Mean SD	Range	Mean SD	Range	Mean SD	Range	Mean SD
1	9.2 - 11.2	10.26 ± 1	1.1 - 2.8	2.13 ± 0.9	11.9 - 12.1	12.1 ± 0.2	0.47 - 0.76	0.6 ± 0.14
2	47.7 - 53.5	50 ± 2.89	19.1 - 19.5	19.3 ± 0.2	17.4 - 19.5	18.33 ± 1.06	1.2 - 0.2	1.56 ± 0.4
3	54.3 - 56.2	55.33 ± 0.96	17.5 - 18.2	17.83 ± 0.35	14.9 - 16.5	15.7 ± 0.8	1.4 - 2.3	1.73 ± 0.49
4	15.3 - 16.2	15.8 ± 0.45	3.9 - 4.9	4.5 ± 0.52	8.9 ± 10.7	9.83 ± 0.91	0.57 ± 0.86	0.7 ± 0.14
5	70.5 - 71.5	70.9 ± 0.52	13.3 - 13.9	13.53 ± 0.32	12.2 ± 12.6	12.36 ± 0.2	0.77 - 0.96	0.9 ± 0.004
6	81.9 - 85.2	83.53 ± 1.65	14.5 - 15.9	15 ± 0.73	10.5 - 11.6	11 ± 0.55	0.9 - 1.2	1.1 ± 1.73
7	119.6 - 121.2	120.36 ± 0.8	24.5 - 26.2	25.36 ± 0.85	23.2 - 24.5	23.76 ± 0.66	1.89 - 1.98	1.92 ± 0.004
8	114.8 - 116.6	115.7 ± 1.46	22.5 - 23.2	22.76 ± 0.37	20.9 - 22.7	21.8 ± 0.9	1.1 - 2.2	1.56 ± 0.58
9	84.9 - 85.6	85.33 ± 0.4	13.3 - 14.2	13.7 ± 0.45	8.9 - 9.7	9.36 ± 0.41	0.9 - 1.9	1.33 ± 0.51

The bioaccumulation of metals in any organism depends upon various factors such as bio-availability amount of uptake, their threshold and the physiological efficiency of the organism to excrete excess metals (Al-Saad *et al*., 1997). Cd is not regulated in many marine mollusca while Zn is regulated. The ability to regulate Cu has been established for various species of mollusca, whereas the concentrations of Pb in the organisms depend on the concentration in the environment. This regulation will lead to different variation in trace metal concentration in this organism. Cd accumulated in higher level at station (7) due to the effect of the waste discharge of Aden city, while higher levels of Pb in mollusca is due to the effect of petroleum product from oil refinery of Aden, and also heavily trafficked area leading to release Pb from exhaust of automobile burning fuel (Heba and Al-Mdaffer, 2000).

The higher concentrations of both hydrocarbons and trace metals at station (7) must be due to its proximity to Aden oil refinery at Aden City. The port area is subjected to pollution by hydrocarbons and trace elements from various sources (*e.g.* oil refinery discharge, municipal and industrial effluents and urban run-off). While the lower concentration were observed at station (1), because it only receives rural run-off. The remainder of the stations are influenced by an oil refinery; electricity generating station discharge; urban run-off of sewage effluent and the transport from other stations in the area. The hydrocarbons in *Tivela ponderosa* reflect the normal habitats and/or feeding strategies of the organisms.

Mollusca are effective in packing both soluble and particulate hydrocarbons residues in its fast sinking fecal pellets (al-Saad, 1995). Mollusca can metabolize and extract hydrocarbons. It is observed that they can ingest large quantities of small droplets of oil and eliminate them in fecal matter (Al-Saad *et al.,* 1998). Mollusca also take up dissolved hydrocarbons from water. The mollusca possess enzyme systems which metabolize the hydrocarbons to various hydroxylated metabolization and execration which might be responsible for the significant differences of petroleum hydrocarbons and trace element content in *Tivela ponderosa.*

However, the significance of the data obtained in the present work is best appreciated by comparing with values of petroleum hydrocarbons and trace element content in mussels collected from other part of the world (Table 3&4). Our data indicate that the quantity of hydrocarbons and trace elements observed in the *Tivela ponderosa* collected from Aden lie within the range of values reported from comparable areas.

It may be concluded that from result of the analysis the *Tivela ponderosa* is able to accumulate hydrocarbons and trace elements in its lipid pool. Thus, this organism might be utilized as a self-integrating index in monitoring oil pollution. Accumulation of hydrocarbons and trace metals in these species via food chain are hazardous to human being. The data indicate that the *Tivela ponderosa* are not contaminated by heavily toxic trace metals because they are well below potentially dangerous levels.

TABLE 3. Comparison of hydrocarbon content in mollusca collected from different region of the world.

Area	Concentration µg/g	Source
Western Port Bay (Australia)	0.0 - 23	Burns & Smith (1977)
Scottish coast	19 - 71	Mackie *et al.* (1980)
Northeast Gulf of Alaska	21	Wise *et al.* (1981)
The Sound of Copenhagen	11 - 47	Jenesen (1981)
Antarctica	0.0 - 124	Law (1981)
Arabian Gulf	13.1 - 34.6	Al-Saad & Dou Abul (1987)
Aden Coast	10.7 - 40.38	Present study

TABLE 4. Comparison of trace element content in molluscs collected from different region of the world.

Specie	Locality	Cd (ppm)	Pb (ppm)	Cu (ppm)	Zn (ppm)	References
Mytilus sp.	Port of Laspeza, Italia	2.0 - 6.8	–	6.90 - 33.0	203 - 379	Capelli *et al.,* (1978
Donax tranculus	Alexandria, Egypt	23.2	38.3	338.4	61.2	Ghazaly (1988)
Mya arenmaria	Gdansk Bay	1.80	17	11.50	130	Poitr (1986)
Pinctada radiaae	Arabian Gulf	0.90 - 2.40	5.90 - 7.60	1.41 - 1.63	8.7 - 333.8	Hashim *et al.* (1994)
Mystilus strigata	Mexico	1.63	–	9.32	140.50	Peaz *et al.* (1994)
Mytilus edulis	South Africa	1.3 - 4.3	0.60 - 224	3.0 - 4.80	124 - 282	Richardson *et al.* (1994)
Tivela ponderosa	Aden, Yemen	0.6 - 1.9	9.8 - 23.7	2.1 - 25.3	10.2 - 120.3	Present study

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الهيد روكربونات النفطية و المعادن النزرة (الثقيلة) في النواعم (الرخويات) *Tivela ponderosa* من خليج عدن

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المستخلص. أظهرت الدراسات الحالية تقديراً لمستوى التلوث بالهيدروكربونات النفطية والمعادن الثقيلة في النواعم (*Tivela ponderosa*) من سواحل خليج عدن - البحر العربى وذلك لمعرفة المستوى الأساسي لهذه التراكيز في النواعم .

تطابقت الدراسات بوجود مستويات متقاربة و يمكن مقارنتها مع تراكيز الهيدروكربونات النفطية والمعادن الثقيلة في هذة المنطقة مع مناطق أخرى من العالم.

تراوحت تراكيز الهيدروكربونات النفطية فى النواعم من ٥ ,٩ ميكروغرام / غم (في محطة٤) إلى ٣٨ ,٤٠ ميكروغرام/ غرام كوزن جاف في ميناء الزيوت (محطة ١) مكافىء لنفط خام مأرب (محتوى الدهن في هذة النواعم تراوح من ٢ ,٠ - ٧ ,٠ ٪ في محطة ٨ و٩ على التوالي) من الممكن أن تكون هذة النواعم معرضة إلى التلوث النفطي من المصادر التالية :

تفريغ مخلفات ناقلات النفط ومن مصافي النفط المتواجدة على الساحل إضافة إلى منصات التحميل وفعاليات ونشاط النقل البحري. وكذلك وجد أن تراكيز المعادن الثقيلة يمكن مقارنتها إلى تراكيز المناطق البحرية غير الملوثة . فمستوى الكادميوم والنحاس والرصاص والزنك في هذه النواعم ضمن تراكيز مناطق أخرى من العالم. كما أن تراكيز كل من الهيدروكربونات والعناصر الثقيلة كانت قليلة في نواعم خليج عدن.

التلوث بالهيدركربونات قد يتأتى من عمليات النقل و مصادر التلوث النفطي وأن تراكيز العناصر الثقيلة قد تكون ذات مصادر طبيعية أكثر مما هي صناعية وهذا يعطى دلالة على أن تراكيز هذه العناصر ليست ذات خطورة بيئية فى الوقت الحاضر ولذا نوصى با ستمرار عمليات المراقبة البيئية لخليج عدن وأن تراكيز كل من الهيدروكربونات و العناصر الثقيلة يجب أن تكون ضمن الحد المسموح به والموصى به عالميا.