

The Poly Cyclic Hydrocarbons levels in Some Fishes Tissues Collected from Derna City (LIBYA) Coast

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Abstract—The poly cyclic hydrocarbons(PAHs) were determined in two types of fishes collected from Derna city coast during summer 2012. The fishes types including (Mugi Cephalous and *Siganus rivulatus*) and the tissues including (Livers, Mussels).The results showed that , most of the studied samples containing different types of the polycyclic hydrocarbons. The total concentrations of aromatic hydrocarbons in Mugi Cephalus ranged between (3.46 – 69.32 $\mu\text{g/g}$) and (1.51 – 8.23 $\mu\text{g/g}$) in liver and mussels , respectively. While the (PAHs) in *Siganus rivulatus*) samples ranges between (36.62 - 127.42 $\mu\text{g/g}$) and (2.40 – 5.51 $\mu\text{g/g}$) in liver and mussels samples , respectively. The study indicated that there are high levels of aromatic hydrocarbons comparing with the standard limits of FAO /WHO guide lines for human consumer. Some ratios were calculated to evaluated the source these compounds in the area under investigation. The results showed that there pyrolytic and petrogenic sources.

Keywords— Poly Cyclic Hydrocarbons, Some Fishes Tissues, Derna City.

I. INTRODUCTION

PAHs are one of the more significant classes of organic chemicals that in the recent years have given rise to a growing concern regarding harmful effects to man and other living organisms. PAHs generally possess high chemical stability and hydrophobic properties, which result in enhanced accumulation and a high capacity for distribution in the environment. A number of PAH compounds are considered as hazardous environmental chemicals (Adel-Razeq ,2012).

Hydrophobic contaminants such as PAHs tend rapidly to be adsorbed on particles (Neff, 1979). The solubility of aromatic compounds decreases as the octanol-water partition coefficient (Kow) increases. PAHs solubility decrease with increasing molecular weight. Thus, low molecular weight PAHs are preferentially dissolved while, the heavier molecular weight compounds are preferentially absorbed onto or associated with particles. Consequently, the uptake of a contaminant is governed by its bioavailability, and organisms are often enriched in the lower molecular weight PAHs

relative to the sediments . Because of low solubility and hydrophobic nature, PAHs tend to be greatly enriched in the inorganic and organic air particles that, under the action of atmospheric agents, may be transported in all the ecosystems. Thus, freshwater and marine sediments often contain concentrations of PAHs of higher magnitudes than those in the overlying water. The deposition of suspended particulates transported by rivers may therefore have an increasing effect in the accumulation of PAHs. Once deposited in sediments, PAHs are less subjected to photochemical or biological oxidation, especially if the sediment is anoxic (Anyakora et al., 2004). Thus, sedimentary PAHs tend to be persistent and may accumulate to high concentrations. The partitioning of the PAHs between water and sediment is controlled by the sediment characteristics. Therefore, the accumulation of PAHs is not only determined by the mass flux to the seabed, but also by the sediment characteristics. The coastal ecosystem is an important resource throughout the Mediterranean for commercial as well as recreational purposes. In addition, the contamination of the sediment may pose a high toxic threat to the aquatic fauna, which tend to bio accumulate the organic pollutants. The analysis of sediment PAHs can serve as a useful index of the rates of PAHs input to the aquatic environment. Sediment samples have a substantial integrating effect on temporal patterns of PAHs input and offer good geographical resolution, especially when current patterns, sediment origin, and settling rates are known.

Numerous research studies assessed the PAHs inputs in the Northwestern and Central Mediterranean (Tolosa et al., 1996). Conversely, in the Eastern Mediterranean few data have been published on the presence of PAHs in coastal sediments close to point sources (municipal and river discharges, etc.)

In addition, hydrocarbon budgets are available for the Western part of Mediterranean Sea (Lipiatou et al., 1997; Dachs et al., 1999), but there is a tremendous lack of information regarding the Southern Mediterranean (El Sikaily et al., 2002; El Nemr et al.,2004). Although PAHs have been determined.

Hydrocarbon composition can be significantly changed due to selective photo-oxidation and biodegradation. Simple aromatic and short chain alkanes are rapidly lost, but higher

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molecules such as hopanes and steranes are little affected and can be particularly useful markers in investigations. According to the large scale application of petroleum hydrocarbons in Libya and their persistency, the present work is aimed to study the aliphatic and polycyclic aromatic hydrocarbons in the Derna. This could be perfectly done by studying the actual status of such compounds in the area. In addition to, the physicochemical characteristics of water of the Harbour, in addition to compare the present levels of hydrocarbons, in the area of investigation with the tolerable acceptable levels. Also, this work may be considered as a data base for studying the hydrocarbons of petroleum origin in the area because of paucity of such data in the literature.

II. SAMPLING AND METHODS

A. Area of study

The area of study is lie at the eastern coast of Libya which is also part of the south shore line of the Mediterranean basin.

Five stations were selected at **city Derna** is a coastal city with a population of (162,857) ref as the city is boarded from the south by a chain of rocky hills the city has expanded along the shore line, Derna is also home to Derna commercial harbour. Five stations were selected and including (Al – sahel El – shargi, Derna Hrbour, in front of Al gabal company, and bokaria station). Two types of fishes were collected from nearshore stations.

To achieve a more accurate scope of hydrocarbon levels in the mentioned cities a stratified sampling method was adapted as a number of five sub locations where sampled within the parameters of each city.

B. Determination of Hydrocarbons

Hydrocarbons have been determined in fish according to UNEP/IOC/IAEA (1991). The samples were analyzed for aromatic hydrocarbons following different steps including; extraction, cleaning up and fractionation, instrumental analysis and analytical quality control.

C. Fishes samples

Ten fishes samples from two types (*Mugi Cephalous and Siganus rivulatus*) were collected from five stations, and then kept frozen in the laboratory until extraction. Different tissues (mussels and liver) were separated from the samples to determine the bioaccumulation the hydrocarbons in each part.

1-Extraction step of hydrocarbons for fish

Ten grams of wet weight of every tissue (Mussels and liver) were treated with 30 g of anhydrous sodium sulfate and the mixture was blended at high speed for 5 min. Then the mixture was extracted using a soxhlet with 200 ml of methanol for 8 hrs. 20 ml of 0.7 M KOH and 30 ml of distilled water were added to the flask and the reflux was continued for 2hrs to saponify the lipids. The content of the extraction flask was extracted three times in a separating

funnel with 80 ml hexane. The three extracts were combined, dried with anhydrous sodium sulfate and filtered through glass wool. The hexane fraction was concentrated with a rotary evaporator down to about 15 ml at 30°C and concentrated down to a volume of 1 ml with nitrogen gas stream and then subjected to cleaning up and fractionation. (Emara et al, 2008).

2-Cleaning up and fractionation

Cleaning up and fractionation were performed by passing the concentrated extract through a silica/aluminum oxide column. The chromatography column was prepared by slurry packing 20 ml of hexane containing 10 g of silica, followed by 10 ml containing 10 g of aluminum oxide and finally 1 g of anhydrous sodium sulfate. The hydrocarbon sample extract (1 ml) was sequentially eluted from the column with 25 ml of hexane for the saturated aliphatic fraction (F1), and then 60 ml of hexane and dichloromethane (80:20) was used for the elution of the unsaturated aromatic fraction (F2). F1 and F2 were concentrated using gentle stream of nitrogen for instrumental analysis.

2 μ L of each sample of unsaturated aromatic fraction was injected in the split less mode and purge time was 1 min. the response factor of individual hydrocarbon compounds to the internal standard was measured and calculated at least three times (at the beginning, in the middle, and at the end for each batch of GC injections). Identification and quantification of hydrocarbon compounds were based on matching their retention time with a mixture of hydrocarbon standards.

D. Calculated ratios

Some of ratios used to determine sources of aromatic compounds are represented as (R1,R2,R3,R4,R5,R6) including the following:

$$R1 = \text{Inp} / (\text{Inp} + \text{Bghip})$$

$$R2 = \text{Flu} / (\text{Flu} + \text{Pyr})$$

$$R3 = \text{Bap} / (\text{Bap} + \text{Chr})$$

$$R4 = \text{Phe} / (\text{Phe} + \text{Ant})$$

$$R5 = \text{BbF} / \text{BKF}$$

$$R6 = \text{Ant} / (\text{Ant} + \text{Phe})$$

The calculation of these concentrations can be an indicator of the source of the aromatic hydrocarbons found in the samples.

R1 < 0.4 is an indicator of petroleum pollution, however R1 > 0.5 is an indicator of hydrocarbon pollution originating from combusted wood and grass (Yunker et al., 2003).

R2 in the range of 0.4 indicates the presence of petroleum derived hydrocarbon particles, however if higher than 0.4 this is an indicator of combusted fuel and coal

R3 < 0.2 indicates that the aromatic components are derivatives of petroleum combustion, however if the level of R3 is between 0.4 and 0.6 this is a indicator of uncombusted petroleum pollution (Budzink et al., 1997)

R4 < 0.1 is an indicator of aromatic compounds derived from a petro chemical source,

R5 > 0.1 is indicator of combusted

$R_6 > 0.1$ indicates the presence on diesel ,core oil and coal .

Ratio of Low Molecular Weight/ High Molecular weight of hydrocarbons

LMW = Naphthalene + Acenaphthylene + Acenaphthene + Fluorene + Phenanthrene + Anthracene

HMW = Fluoranthene + Pyrene + BaA + Chrysene + BbF+ BkF + BaP + DBA + B (ghi) perylene + indeno pyrene.

III. RESULTS AND DISCUSSION

The contents of Poly Aromatic Hydrocarbons (PAHs) in the fishes tissues and livers showed some variations between the locations and the collected samples , for the *Mugi Cephalous* samples the concentrations were fluctuated between (1.516 – 8.23 $\mu\text{g/g}$) the high level recorded in station (3) and the value recorded at station (2) , while in the other stations were (1.87 , 2.30 and 1.97 $\mu\text{g/g}$) in the stations 1, 4 and 5, respectively , on the side the PAHs in liver samples recorded high levels in fishes which collected from station (5) with value of(69.32) and the low value recorded in the fishes of station(1) with value (3.46) , while in the stations were 10.90 , 26.94 and 7.46 in the stations 2 ,3 and 4 , respectively , from these data we can say that the liver samples containing the highest level of PAH comparing with tissues ones. The PAHs values in liver of *Siganus rivulatus* samples recorded high values (127.426) at station (5) with ,while the lowest value was recorded (36.624 ng/g) at station (1), while at the other stations 2 , 3 and 4 the levels were 54.26 , 56.15 and 51.27 , respectively. While for the tissues samples the Aromatic hydrocarbon concentrations where found be the highest in tissue which collected from station (4) with a level of 5.51 ng/g , while the lowest value recorded at desalination station (3) (2.40 ng/g) ,other Derna locations are recorded in the Average of Aromatic hydrocarbons in *Siganus rivulatus* fishes showed the same pattern as tissue samples for the *Mugi Cephalous* fishes , where the high values recorded in liver samples comparing with tissues. In general. ΣPAHs in this study were lower than that recorded for the Arabian Gulf;

3000 - 4550 ng/l and those recorded for Saudi Arabia coasts; 1.88-412 ng/l (Awad , 1990). They are comparable with that recorded for the Gulf of Suez 0.033-2.41 ng/l (EI Agroudy et al .,2006). By comparing the present data with those reported by FAO/WHO for the guidelines of PAHs in food with value (0.001) for human consumer , its clear that the present data very high and may be toxic reason for human.

In general the ΣPAHs in this study were lower than that recorded for the Arabian Gulf; 3000 - 4550 ng/l and those recorded for Saudi Arabia fishes coasts; 1880 - 4120 ng/l (Awad , 1990) . They are comparable with that recorded for the Gulf of Suez (Egypt 300 - 2410 ng/l (EI Agroudy et al .,2006). Some ratios were calculated as attempt to identification the sources of the aromatic compounds. If the ratio of (flu/pyr) was < 1 was attributed petrogenic sources and if the ratio of (flu/pyr) > 1 is related to pyrolytic origin (Sicre et al., 1997). Combustion of coal and wood gave (Fluo/pyr) ratios of 1.4 and 1, respectively. while crude oil and fuel oil had values of 0.6 - 0.9 (Gschwend and Hites 1981). In the present study, most sites have (Fluo/Pyr) ratio < 1 (Tables 5&6) reflecting petrogenic origin. The ratio of major combustion specific compounds $\Sigma\text{COMB} = \text{Flu, Pyr. BaA. Chr. BbF, BkF, BaP, InP and BghiP}$ to the sum of total PAHs ($\Sigma\text{COMB} / \Sigma\text{PAHs}$) are ranged from 0.663 to 0.997 and the ΣCOMB concentrations displayed values from 5.27 – 58.01 ng/l (Table). Benzo(a)pyrene (BaP), the most potent carcinogenic PAHs, and the sum of six carcinogenic PAHs; ($\Sigma\text{PAHs}_{\text{CARC}}$ (IARC. 1983) ($\Sigma\text{PAHs}_{\text{CARC}} = \text{Flu, Pyr BbF, BkF, BaP and BghiP}$) were highest at most stations , with a concentration ranged between 1.69 – 88.29 ng/l (Tables) ,this is mainly attributed due the effect of the harbour of the city and fishing activity .. The HMW/LMW ratios values also were used to identification of the sources of the PAHs compounds , if this values < 1 ,this is indicate the source of PAHs compounds coming from pyrolytic source , and if this ratio > 1 this indicate the source of this compounds from petrogenic sources . In this all the calculated values of the HMW/LMW ratio are > 1 , and this is indicate the main source of the PAHs in the investigated area coming from petrogenic source (Tables 9 &10).

TABLE I
THE CONCENTRATIONS OF AROMATIC HYDROCARBONS IN THE *SIGANUS RIVULATUS* TISSUES

Station5	Station 4	Station 3	Station 2	Station 1	compound
0.0046	0.0017	0.0026	0.0003	0.0003	Naphthalene
0.0039	0.003	0.0109	0.0016	0.003	Acenaphthylene
0.0373	0.0169	0.0513	0.0162	0.0341	Acenaphthene
0.0003	0.0001	0.0001	0	0.0003	Phenanthrene
0.0002	0.0001	0.0136	0.0005	0.0158	Anthracene
0.0079	0.0015	0.0022	0.0013	0.0047	Fluoranthene
0.0012	0.0004	0.0013	0.0018	0.0017	Fluorene
0.0956	0.0997	0.0832	0.0241	0.1036	Pyrene
0.2456	0.0274	0.0106	0.1241	0.0205	BaA
2.0629	2.1681	2.0158	2.1601	1.5862	Chrysene
1.2411	0.0502	0.1902	0.0181	0.7288	BbF
0	3.0147	0	0	0	BkF
0.0589	0.1012	0.0232	1.9819	0.0242	BaP
0.0002	0.0131	0.0011	0.0224	0.0003	Indeno Pyrene
0.0289	0.0116	0.0004	0.0033	0.0005	DBA
0.0002	0.0005	0.0028	0.0011	0.0068	Benzo (ghi) perylene
3.7888	5.5102	2.4093	4.3568	2.5308	TOTAL

TABLE II
 THE CONCENTRATIONS OF AROMATIC HYDROCARBONS IN THE *MUGI CEPHALOUS* TISSUES

Station5	Station 4	Station 3	Station 2	Station 1	compound
0.0049	0.0232	0.0175	0.0246	0.0153	Naphthalene
0.888	0.7057	0.0458	0.5729	0.0282	Acenaphthylene
0.0833	0.007	0.0036	0.0212	0.0011	Acenaphthene
0.0072	0.2756	0.0017	0.0079	0.3041	Phenanthrene
0.6892	0.0051	0.0191	0.0734	0.0081	Anthracene
0.5701	0.0115	0.0113	0	0.0108	Fluoranthene
0	0	0	0	0.0039	Fluorene
1.7223	0.2348	1.8363	0.7411	0.6042	Pyrene
1.5475	0.1221	0.6054	0.1043	0.1703	BaA
1.8211	46.3031	22.8264	30.4467	23.7664	Chrysene
64.2027	0.5286	0.3673	0	0.0472	Bbf
0	0	0	21.0409	9.7134	BKF
10.1593	0	25.707	1.1746	0.0225	Bap
45.6721	2.8861	4.2024	0.0232	1.8788	Indeno Pyrene
0.0355	0.1632	0.3789	0.0307	0.0484	DBA
0.0235	0.0086	0.1309	0.0024	0.0016	Benzo (ghi) perylene
127.4267	51.2746	56.1536	54.2639	36.6243	TOTAL

 TABLE III
 CARCINOGENIC COMPOUNDS IN *SIGANUS RIVULATUS* SAMPLES

Carcinogenic compounds	Stations
1.6985	1
23.0268	2
28.3544	3
4.0513	4
88.2998	5

 TABLE IV
 CARCINOGENIC COMPOUNDS IN *MUGI CEPHALOUS* SAMPLES

Carcinogenic compounds	stations
4.4872	1
11.2365	2
33.8869	3
8.2314	4
41.6736	5

 TABLE V
 SUM OF SOME RATIOS AND CARCINOGENIC COMPOUNDS IN *SIGANUS RIVULATUS*

Phe/Anth	Fluo/Pyr	Σ COMB/PAHs	Σ COMB	stations
12.73	0.0218	0.9881	38.6903	1
0.1069	0.0016	0.9864	55.896	2
0.0550	0.0070	0.9906	58.0161	3
53.0192	0.0388	0.9786	55.5716	4
0.0108	0.3179	0.9864	129.431	5

 TABLE VI
 SUM OF SOME RATIOS AND CARCINOGENIC COMPOUNDS IN *MUGI CEPHALOUS*

Phe/Anth	Fluo/Pyr	Σ COMB/PAHs	Σ COMB	Ratio
1.9230	0.0144	0.9891	5.2758	1
0.9473	0.0331	0.9873	11.6314	2
0.0000	0.0233	0.9979	35.1163	3
1.7894	0.2993	0.9809	9.5837	4
2.0000	0.0305	0.6636	47.2014	5

 TABLE VII
 THE CALCULATED SOURCES RATIOS FOR *SIGANUS RIVULATUS*

Ratios	R ₁	R ₂	R ₃	R ₄	R ₅	R ₆
1	0.9955	0.0078	0.0017	0.9272	0.0798	0.0727
2	0.9287	0.0023	0.0354	0.0965	0.0008	0.9034
3	0.9691	0.0006	0.5087	0.0521	0.0000	0.9478
4	0.9968	0.0011	0.0020	0.9814	0.1919	0.0185
5	0.9994	0.0006	0.7245	0.0107	0.0000	0.9892

 TABLE VIII
 THE CALCULATED SOURCES RATIOS FOR *MUGI CEPHALOUS*

Stations	Ratios	R ₁	R ₂	R ₃	R ₄	R ₅	R ₆
1		0.8159	0.0292	0.2179	0.6578	0.0000	0.3421
2		0.4717	0.0245	0.9650	0.4864	0.0000	0.5135
3		0.9755	0.0065	0.9539	0.0000	0.0000	1.0000
4		0.4715	0.2078	0.7296	0.6415	0.0000	0.3584
5		0.0198	0.0088	0.1988	0.6666	0.0000	0.3333

 TABLE IX
 HMW/LMW RATIOS OF *SIGANUS RIVULATUS* SAMPLES

HMW/LMW Ratio	stations
93.02	1
77.6	2
346.3	3
53.5	4
75.2	5

TABLE X
HMW/LMW RATIOS OF SAMPLES *MUGI CEPHALOUS*

Ratio HMW/LMW	stations
101.5	1
167.6	2
860.6	3
82.9	4
67.73	5

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