Polycyclic Aromatic Hydrocarbons (PAHs) in Muscles of Two Commercial Fish Species from Al-Kahlaa River in Missan Governorate, Iraq

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Abstract

Al-Kahlaa River is one of main tributaries of the Tigris River in Missan city and rises from northwest side of Amara city and continues to flow in the direction to the east of city center. Two commercial fish species (Liza abu and Carassius auratus) were collected seasonally (autumn, winter, spring and summer) during period from 2012 to 2013 from Al-Kahlaa River in Missan governorate. The concentrations of Polycyclic Aromatic Hydrocarbons (PAHs) in fish muscles were determined in the laboratories of Nihran Omer (South Oil Company in Basrah province), using Gas Chromatography. Total concentrations of PAHs in muscles of L. abu ranged between 2.301 and 16.661 ng.g^{-1} dry weight during winter and summer respectively and in C. auratus between 1.095 and 8.675 ng.g^{-1} dry weight during winter and summer, respectively. Results of this study revealed that high molecular weight of PAHs were more than low molecular weight in both fish species, and according to ratios of Low molecular weight Polycyclic Aromatic Hydrocarbons (LPAHs) to High molecular weight Polycyclic Aromatic Hydrocarbons (HPAHs), Benzo(a) Anthracene /(Benzo(a) Anthracene+ Chrysene) BaA/(BaA+Chr),Indeno (1,2,3-cd) pyrene /(Indeno (1,2,3-cd) pyrene + Benzo (ghi) perylene) InP/(InP+BghiP) and Fluoranthene/Pyrene (Fl/Py), they certainly reflected that the PAHs sources in both species are pyrogenic as a main sources and petrogenic as a small part. Also results of this study revealed the presence of seasonal variations in total concentrations of PAHs in both fish species. The study area was generally contaminated with hydrocarbons and continuous consumption of food from this area may pose public health hazards.

***Keywords**: polycyclic aromatic hydrocarbons, PAHs, fish, pollution*

Abstrak

Polisiklik Aromatik Hidrokarbon (PAH) pada Otot Dua Spesies Ikan Komersial dari Sungai Al-Kahlaa, Missan, Irak

Al-Kahlaa adalah salah satu anak sungai utama Sungai Tigris di kota Missan dari sisi barat laut kota Amara dan terus mengalir ke arah ke timur dari pusat kota. Dua spesies ikan komersial (Liza abu dan Carassius auratus) diperoleh pada musim berbeda (gugur, dingin, semi dan panas) selama periode 2012-2013 dari Al-Kahlaa. Konsentrasi polisiklik aromatik hidrokarbon (PAH) pada otot ikan dianalisis di laboratorium Nihran Omer (South Oil Company di provinsi Basrah), menggunakan Gas Chromatography. Total konsentrasi PAH pada otot L. abu berkisar antara 2,301 dan 16,661 ng.g^{-1} berat kering pada musim dingin dan musim panas. Sedangkan pada C. auratus antara 1,095 dan 8,675 ng.g^{-1} berat kering pada musim dingin dan musim panas. Hasil penelitian ini menunjukkan bahwa berat molekul tinggi PAH lebih dari berat molekul rendah pada kedua spesies ikan, dan menurut rasio berat molekul rendah polisiklik aromatik hidrokarbon (LPAHs) untuk berat molekul tinggi polisiklik aromatik hidrokarbon (HPAHs), Benzo (a) Anthracene / (Benzo (a) Anthracene + Chrysene) BAA / (BAA + Chr), Indeno (1,2,3-cd) pyrene / (Indeno (1,2,3-cd) pyrene + Benzo (ghi) perylene) InP / (InP + BghiP) dan fluoranthen / Pyrene (Fl/Py), hal ini mencerminkan bahwa sumber PAH di kedua spesies adalah pirogenik sebagai sumber utama dan petrogenic sebagai bagian kecil. Hasil penelitian ini juga mengungkapkan adanya variasi musiman total konsentrasi PAH di kedua spesies ikan. Daerah penelitian umumnya terkontaminasi dengan hidrokarbon sehingga konsumsi makanan dari daerah ini secara berkelanjutan dapat menimbulkan bahaya kesehatan masyarakat.

***Kata kunci**: polisiklik aromatik hidrokarbon, PAHs, ikan, polusi*

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Introduction

Hydrocarbon compounds enter to fishes tissues either during direct contact, contaminate their gill sand they may eat contaminated food, also the water column may contain toxic and volatile components of oil, therefore might be accumulated in adipose tissues especially aromatic compounds with higher concentrations in their tissues such as glands, brain, gills, liver, gonads and muscles (Ackman *et al.,* 1996). Reaching levels higher than those in the ambient medium, therefore this can affect human in areas that have commercial fisheries (Neff, 1985). Chronic exposure to some chemicals found in oil may cause genetic abnormalities or cancer in sensitive species or suffering from changes in heart beats, respiratory rate, enlarged liver, reduce growth, fin erosion, a variety of biochemical and cellular changes, and reproductive and behavioral responses. (Al-Saad *et al.,* 1997; Deb *et al*., 2000). Fish eggs and larvae are generally very sensitive to oil pollution, whereas adult fish may have the possibility to avoid the oil contaminated areas, eggs or fish larvae do not have this option and oil may be toxic to fish larvae at low concentrations (Teal and Howarth, 1984; Dragsund *et al*., 2004). Reynaud and Deschaux (2006) stated that fishes are quite sensitive especially PAHs, leading to several specific and non-specific response by the immune system. The specific responses may involve the production of antibodies, while unspecific responses may involve the effect on increased activities such as lysozyme and/or phagocytosis, these responses may depend on concentrations of PAHs compound and the route of exposure. Also Mcintosh (2009) stated that these compounds impaired fertilization success, and the ages of embryos were negatively correlated with their sensitivity to this pollutant. The present study aimed to estimation of Polycyclic Aromatic Hydrocarbons (PAHs) in muscles of two commercial fish species from Al-Kahlaa River in Missan province.

Materials and Methods

Fish samples were collected seasonally (autumn, winter, spring and summer) during 2012 and 2013 from Al-Kahlaa River in Missan governorate. Number of *Liza abu* species were 24, 32, 29 and 23 during autumn, winter, spring and summer, respectively, whereas number of *Carassius auratus* species were 18, 24, 27 and 31 during autumn, winter, spring and summer, respectively. The age ranged from two to four year for both species. The samples were rinsed thoroughly with distilled water in the laboratory the muscles were cut to small parts and dried in freeze-drier, grounded and sieved using a 63 μm metal sieve then placed in clean a glass vial to become ready for analysis. The procedure of Grimalt and Oliver (1993) was used for the extraction of hydrocarbon compounds from fish muscles. The concentrations of PAHs in muscles were determined by using capillary Gas-Chromatography.

Evaluation indices of PAHs pollution

Many parameters have to be analyzed in order to evaluate the probable origin of Polycyclic Aromatic Hydrocarbons (pyrogenic or petrogenic). These are as follow:

A-ratio of low molecular weight (LMW-PAHs) to high molecular weight (HMW-PAHs). Values greater than one indicate petrogenic origins from crude oil and their derivatives and values less than one are attributed to pyrogenic sources (Vrana *et al*., 2001).

B-ratio of benzo(a) anthracene / (benzo(a) anthracene + chrysene). Ratio of BaA /(BaA+CHR) less than 0.2 implies petrogenic, from 0.2 to 0.35 indicates either petrogenic or pyrogenic origins, and larger than 0.35 implies pyrogenic sources (Guo *et al*.,2007).

C-ratio of indeno (1,2,3-cd) pyrene /(indeno (1,2,3-cd)pyrene + benzo(ghi)perylene). InP/(InP + BghiP). Values less than 0.2 implies petrogenic, from 0.2 to 0.5 indicates either petrogenic or pyrogenic origins and higher than 0.5 are implies pyrogenic origins (Guo *et al*., 2007).

D-ratio of fluoranthene to pyrene (Fl/Py). Values greater than 1 have been used to indicate pyrogenic origins and values less than 1 are attributed to petrogenic source (Qiu *et al.,* 2009).

Results and Discussion

Results of the present study revealed that the total concentrations of PAHs ($ng.g^{-1}$) in muscles of *L. abu* were 2.301, 3.007, 16.661 and 4.036 during winter, spring, summer and autumn respectively, Table 1., while in *C. auratus* were 1.095, 1.289, 8.675 and 5.294 during winter, spring, summer and autumn respectively, Table 2., the highest values were recorded during summer, while the lowest values during winter in both species, this seasonal variations may be due to the differences in type of nutrition, fats content, abundant of food, habitat, food habit, size, weight, age, sex and ecological conditions such as temperature, dissolved oxygen (Nasir, 2007; Al-Khatib, 2008; Al-Shwafi, 2008). Temperature has a considerable effect on the ability of microorganisms to degrade PAHs. In addition to that oxygen solubility decreases with increasing temperature, which will reduce the metabolic activity of aerobic microorganisms (Al-Khatib, 2008).

The lower molecular weight-PAHs was less than higher molecular weight-PAHs in both species in all seasons, this is due to that the higher molecular weight-PAHs more resistant to degradation processes compared with the lower molecular weight-PAHs (Anyakora and Coker, 2007), in addition to that the fishes have high ability to metabolize the lower molecular weight -PAHs compared with the higher molecular weight-PAHs (Ramalhosa *et al.*, 2012) .Since PAHs can be eliminated out of the body by the fast and effective metabolism through the active Mixed Function Oxidase (MFO) system in fishes (Hylland, 2006).

It can been noticed that levels of PAH compounds in *L. abu* were more than in *C. auratus* along the period of study because these fishes have varies ability to accumulate PAH compounds in their tissues through water and food (Hellou *et al.*, 1993). In order to determine the sources of PAHs in muscles of fishes according to the data (Table 1 and 2). LMW-PAHs/HMW-PAHs ratios were less than one in all seasons ranged from 0.050 to 0.205 and 0.035 to 0.807 in *L. abu* and *C. auratus,* respectively. BaA/(BaA+Chr) ratios were more than 0.35 in both species in all seasons and ranged from (0.44 to 0.913) and (0.379 to 0.807) in *L. abu* and *C. auratus,* respectively. The results indicate that the sources of PAHs compounds in both species were pyrogenic (Tolosa *et al.*, 2004; Guo *et al.*, 2007).

Table 1. Seasonal variations of PAHs (ng.g^{-1} d.w) in *Liza abu*

Name compound	Seasons			
	Winter	Spring	Summer	Autumn
Naphthylene	0.006	0.005	0.043	0.004
Indol	0.004	0.010	0.345	0.013
2-methyl naphthylene	0.015	0.026	0.116	0.024
1-methyl naphthylene	0.003	0.009	0.209	0.008
Biphenyl	0.004	0.006	0.693	0.048
Acenaphthylene	0.009	0.055	0.515	0.025
Acenaphthene	0.020	0.011	0.230	0.072
Dibenzofuran +fluorene	0.043	0.143	0.137	0.019
Anthracene+phenthrathrene	0.003	0.004	0.246	0.022
Fluoranthene	0.017	0.130	1.765	0.061
Carbazole	0.098	0.791	5.672	0.242
Pyrene	1.060	1.223	2.260	2.692
Benzo(a)anthracene	0.554	0.409	2.057	0.138
Chrysene	0.096	0.038	0.221	0.170
Benzo(b+k)fluornanthene	0.082	0.011	0.304	0.403
Benzo(a) pyrene	0.011	0.006	0.347	0.019
Indeno (1,2,3-cd)pyrene	0.063	0.015	0.321	0.010
Dibenzo(a,h)anthracene	0.196	0.064	0.767	0.052
Benzo(ghi)perylene	0.009	0.042	0.406	0.005
Total	**2.301**	**3.007**	**16.661**	**4.036**
LPAHs	0.108	0.273	2.536	0.239
HPAHs	2.175	2.603	12.358	3.734
L/H	0.050	0.105	0.205	0.064
BaA/(BaA+Chr)	0.851	0.913	0.902	0.44
InP/(InP+BghiP)	0.244	0.197	0.295	0.169
Fl/py	0.016	0.106	0.781	0.023

Table 2. Seasonal variations of PAHs (ng.g-1 d.w) in *Carassius* auratus.

Name compound	Seasons			
	Winter	Spring	Summer	Autumn
Naphthylene	0.010	0.008	0.008	0.003
Indol	0.023	0.012	0.047	0.003
2-methyl naphthylene	0.039	0.022	0.122	0.008
1-methyl naphthylene	0.007	0.008	0.038	0.008
Biphenyl	0.031	0.016	0.080	0.012
Acenaphthylene	0.033	0.116	0.272	0.022
Acenaphthene	0.114	0.169	0.291	0.070
Dibenzofuran +fluorene	0.040	0.122	0.234	0.015
Anthracene+phenthrathrene	0.170	0.038	0.434	0.024
Fluoranthene	0.040	0.033	0.133	0.331
Carbazole	0.095	0.082	0.581	0.537
Pyrene	0.118	0.047	5.054	0.262
Benzo(a)anthracene	0.082	0.137	0.531	2.311
Chrysene	0.135	0.049	0.242	0.552
Benzo(b+k)fluornanthene	0.0132	0.279	0.066	0.462
Benzo(a) pyrene	0.0122	0.024	0.046	0.064
Indeno (1,2,3-cd)pyrene	0.0321	0.020	0.011	0.193
Dibenzo(a,h)anthracene	0.0573	0.083	0.084	0.363
Benzo(ghi)perylene	0.0369	0.014	0.392	0.043
Total	**1.095**	**1.289**	**8.675**	**5.294**
LPAHs	0.471	0.516	1.530	0.171
HPAHs	0.583	0.739	7.011	4.792
L/H	0.807	0.698	0.218	0.035
BaA/(BaA+Chr)	0.379	0.737	0.686	0.807
InP/(InP+BghiP)	0.359	0.198	0.122	0.347
Fl/py	0.339	0.702	0.026	1.263

Table 3. Comparison of concentrations of PAHs compounds in fishes samples from Al-Kahlaa river with their concentrations in other fish species from other areas in Iraq and the world .

References	Concentrations (ng.g-1) d.w	Area
Al-Saad*et al.,*2006	6.78-23,83	NW Arabian Gulf
Al-Khatib ,2008	0.1-92.7	Hor Al-Howaiza
Al-Khion ,2012	12.19-86.48	Iraqi coast regions
Anayakora and Coker, 2007	0.41-39.64	Niger Delta /African
Da Silva *et al*., 2006	4-53	Guanbara bay, Brazil
Present study	1.095 -16.661	Al-Kahlaa River / Missan province

While InP/(InP+BghiP) ratios ranged from 0.169 to 0.295 and 0.122 to 0.359 in *L. abu* and *C. auratus* respectively. The results indicate that the origin of PAHs in *L. abu* and *C. auratus* were pyrogenic and few of them petrogenic. Fl/py ratios ranged from 0.023 to 0.781 and from 0.026 to 1.261 in *L. abu* and in *C. auratus,* respectively, this ratio was less than one in both species during all seasons except autumn in *C. auratus* species, this referred to that the origin of PAHs were petrogenic except in autumn season which was pyrogenic (Chen *et al.,* 2006; Qiu *et al.*, 2009). From the data in table

3. it can be noticed that the levels of PAHs compounds in the muscles of these fishes were less than their levels in other fishes collected from other regions of Iraq and the world, but these species contain the dangerous compounds in their muscle tissues like Pyrene, Carbazole, Anthracene+ phenthrathrene, Benzo(b+k) fluornanthene and Benzo(a) anthracene because many studies reported that these compounds have a high carcinogenic activity for human and other living organisms (Al-Khion, 2012).

When ingested, PAHs are rapidly absorbed into the gastrointestinal tract due to their high lipid solubility. The rapid absorption of PAHs by human result in a high potency for bio-magnification through food chain. Generally, the greater the number of benzene rings, the greater the toxicity of the PAHs (Cerniglia, 1992). Neff (1982) suggested that consumption of contaminated fish by PAHs compounds may cause a carcinogenic effects of human. This indicated that the study area was generally contaminated with hydrocarbons and continuous consumption of food from this area may pose public health hazards. There is therefore the need to develop a management plan to ensure that petroleum hydrocarbon contamination of this area is prevented in order to achieve good aquatic life and to avoid possible health problems through the consumption of contaminated fresh water resources such as fishes by the local communities.

Conclusion

High molecular weight of PAHs were more than low molecular weight in both fish species, and according to the ratios ofLMW-PAHs /HMW-PAHs ,BaA/(BaA+Chr), InP/(InP+BghiP) and Fl/py the sources of PAHs in fish muscles were pyrogenic as a main and few petrogenic. This indicated that the study area was generally contaminated with hydrocarbons and continuous consumption of food from this area may pose public health hazards, therefore should be preventing the various kinds of industrial and domestic contaminants to be discharged into the river.

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