# Estimation of Polycyclic Aromatic Hydrocarbons (PAHs) in Some Fishes of Shatt Al-Arab River-Iraq

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**Abstract**
Levels of sixteen polycyclic aromatic hydrocarbons (PAHs) in six edible tissues of selected frequently-consumed fish collected from Shatt Al-Arab river, namely, *Luciobarbus xanthopterus* , *Ctenophyngodon idella, Cyprinus carpio, Tilapia zillii, Palaniza abu* and *Leuciscus vorax* were investigated in 2015. High Pressure Liquid Chromatography (HPLC) analysis was employed for determination of PAHs. Total PAHs in the samples ranged from 0.02 ng/g dry weights in *Cy. carpio* to 3.34 ng/g dry weights in *Le. vorax* . Some ratios were calculated to evaluate the sources of these compounds in the area. The results showed that there was pyrolytic and petrogonic sources.Low molecular weight (LMW) PAHs was the predominant compounds, suggesting the gill-water transfer might be the major exposure route for PAHs in the studied fish species.
***Keywords:*** Shatt Al-Arab River, Polycyclic aromatic hydrocarbons (PAH), Edible fishes, sources.

## Introduction

Water is an essential natural resource for sustaining the environment and life, that cycle through various reservoirs within and among ecosystems. Thus any effect upon resource due to addition of some materials and can be harmful to living organisms referred to pollution (Weiner, 2000). Water resources play a vital role in various sectors of economy such as agriculture, livestock production, industrial activities, hydropower generation, fisheries and other creative activities. It has been put under tremendous pressure, and has been deteriorated due to some important factors like increasing urbanization, industrialization, and agriculture activities (Tyagi *et al.,* 2013).

The Shatt Al-Arab River is formed after the confluence of the Euphrates and the Tigris Rivers near the city of Qurna in southern Iraq. The southern part of the river constitutes the border between Iran and Iraq until it discharges into the Arabian Gulf, with a total length of 192 km, the Shatt Al- Arab widens over its course, expanding from a width of 250-300 m near the Euphrates-Tigris confluence to almost 700 m near the city of Basrah and more than 800 m as it approaches the river mouth (AL-Saad *et al.*, 2015). The Shatt al Arab Delta is 140 km wide and splits into more than 10 branches. The landscape is characterized by green marshy areas, lakes, lagoons and estuaries, bordered by irrigated lands and date palm plantations and surrounded by desert (UN-ESCWA and BGR, 2013).

Fish exposed as marine biologist at risk of oil pollution, which may be fatal as that of oil products such as gasoline or diesel oil or kerosene, causing mass death of fish and other aquatic organisms (Wu, *et al.*2012).

Polycyclic Aromatic Hydrocarbons (PAHs) is another large group of hydrocarbons materials with two or more fused aromatic rings. PAHs contamination is present in incomplete combustion of organic and fossil fuel as phenanthrene, fluorine, benzo[a]pyrene and pyrene in car exhaust, while phenanthrene, fluorine, and pyrine in diesel vehicles exhaust (Azhari *et al.*, 2011). Naphthalene and acenaphthalene have been reported to be present in fuel oil used extensively in Shatt Al-Arab region , and these compounds are not easily attacked by microorganisms , and numerous of these compounds as well as their derivatives are potential carcinogens (Al-Saad , 1995). The solubility of these compounds in the water is low and they tend to be bounded to suspended organic matter in the water column and finally accumulate in the marine sediment (Mahmoodi, *et al*., 2012).

Due to the large number of studies on aromatic compounds in marine fish (AL-Khion, *et al.*2016) so that it is necessary to study these compounds in fresh fish because of their economic importance . Therefore, the aim of the present study was to evaluate and determine 16 compounds of PAHs residues in six fresh commercial fish species at Shatt al-Arab River.

## Materials and methods

Six species of fish samples which were commonly available at Shatt Al-Arab River, namely Cattan (*Luciobarbus xanthopterus* ), Gareeba (*Ctenophyngodon idella*) , Samti (*Cyprinus carpio*), Bultti (*Tilapia zillii* ) ,Khishni ( *Palaniza abu* ) and Shillig (*Leuciscus vorax* ) were collected during 2015 by the local fishermen using drag net (Mesh size 1.27 cm, thickness 9 ply) . The samples were kept refrigerated in polyethene boxes with ice during transport to the laboratory. The fish samples then stored at -20°C until further analysis. Samples were removed from the deep freezer, thawed, and cleaned very well in tap water to remove any dirt. Dissection was performed on thawed fish using aseptic instrument and glass dishes, muscle tissues were dissected. Each fish sample was cut into pieces and crushed in a pestle mortar. 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 High Pressure Liquid Chromatography (HPLC) Shimadzu CBM20A with UV-visible detector. The fish samples were analyzed for a suite of 16 PAHs ; naphthalene (NAP), acenaphthylene (Acy), acenaphthene (Ace), Fluorene (Flu) , Phenanthrene (Phe) , anthracene (Ant), Fluoranthene(Flut), pyrene (Pyr) , Benzo[a]anthracene (BaA), chrysene (Chr), benzo(b)fluoranthene (BbF) , Benzo[k]fluoranthene (BkF) , benzo(a)pyrene (BaP), Dibenzo[a,h]anthracene (DahA) , benzo(ghi)perylene (BPY) and Indeno[1,2,3-cd] pyrene (InP) . Some of ratios used to determine sources of PAHs compounds which including the following: (Flut / Pyr), (Phe / Ant), (Ant / (Ant + Phe)), (BaP / (BaP + Chr)) and (LMW /HMW). The calculation of these concentrations can be an indicator of the source of the aromatic hydrocarbons found in the fish samples, ratio of (Flut / Pyr) Values greater than 1 have been used to indicate pyrogenic origins and values less than 1 are attributed to petrogenic source (Zhu *et al.*, 2004). Ratio of (Phen/Ant) less than 1 indicates petrogenic (Vrana *et al*., 2001). ratio of(LMW /HMW) values greater than 1 indicate petrogenic origins and values less than 1 are attributed to pyrogenic sources [13].

(Ant/ (Ant+Phe)) ratio presumes that ratios less than 0.1 indicate PAHs source to be of petroleum origin while ratios larger than 0.1 indicate PAHs source to be of combustion origin and the 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) .

(Flut/Py) = fluoranthene to pyrene.

(Phen/Ant) = Phenanthrene to Anthracene.

(Ant / (Ant + Phe)) = Anthracene to (Anthracene + Phenanthrene).

(Bap / (Bap + Chr)) = benzo (a) anthracene to (benzo (a) anthracene + chrysene).

LMW (low molecular weight) = Naphthalene + Acenaphthylene + Acenaphthene + Fluorene + Phenanthrene + Anthracene.

HMW (high molecular weight) = Fluorananthene + Pyrene + Benzo[a]anthracene + Chrysene + benzo(b)fluoranthene + Benzo[k]fluoranthene + benzo(a)pyrene + Dibenzo[a,h]anthracene + benzo(ghi)perylene + Indeno[1,2,3-cd] pyrene.

## RESULTS AND DISCUSSION

From the results obtained levels (ng/g dry weight) of the sixteen PAHs distribution in *Lu. xanthopterus* , *Ct. idella* , *Cy. carpio*, *T. zillii* , *P. abu* and *Le. vorax* are presented in Tables 1. The total concentrations of PAHs in fishes vary from 0.02 ng/g dry weights to 3.34 ng/g dry weights (Figure 1). Shatt Al-Arab River is affected by hydrocarbons pollution by sewage, industrial wastes and the activities of refining in addition to natural seeps, and other human activities (Farid, *et al.*, 2016). This may explain the difference that observed between the PAHs concentrations in the fish species.

The comparison revealed, elevated PAHs concentrations in Shatt AL-Arab River compared to those reported by Wang *et al*. (2011) and Zrafi *et al*. (2013). It also indicated that Shatt Al-Arab River showed lower concentrations of PAHs compared to those found by De luca *et al*. 2004; Trabelsi *et al*. 2005; Bin *et al*., 2007; Zrafi-Nouira *et al*. 2008; Qiu *et al*. 2009; Mahmoodi *et al*. 2012 and Chen ,*et al.*2015.

**Table 1:** List of fish species included lipids content (%) in present study.

| Fish species | No. Of fish | Total weight (g) | Total length (cm) | Fat% |
|---|---|---|---|---|
| ***Lu. xanthopterus*** | 10 | 916 | 40 | 7.5 |
| ***Ct. idella*** | 18 | 1117 | 57 | 2.72 |
| ***Cy. carpio*** | 30 | 1019 | 35 | 2.6 |
| ***T. zillii*** | 60 | 75 | 15 | 2.5 |
| ***P. abu*** | 46 | 43 | 21 | 3.5 |
| ***Le. vorax*** | 30 | 750 | 35 | 2.5 |

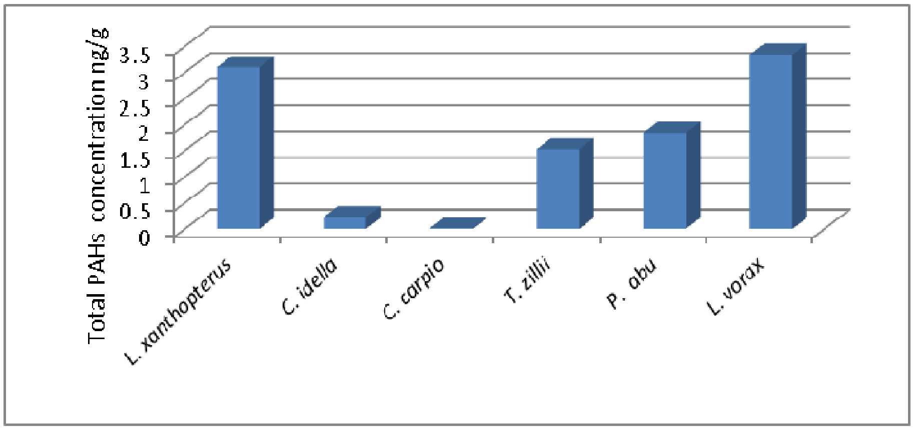


**Figure1:** Total concentrations of PAHs in some fishes of Shatt Al-Arab River.

The maximum concentration of PAHs in fish species was found in *L. vorax* and the minimum concentration of PAHs was found in *C. carpio*. (Table 2). The various components of PAHs in present studies Nap, Ace, Flu and Ant observed in *L. xanthopterus* (Figure 2). Residual levels of Acy,Ace , Flu, Phe, Ant, Flut, BaA, Chy and BbF were high in the tissues of *Ct.idella* (Figure 3). It is obvious from (Figure 4), that Nap, Ace, Phe, Pyr, BaA, Chyr and BbF are abundant in *Cy. carpio* . The predominant components of PAHs in the *T. zillii* were ACY, Flu, Phe, Ant, Pyr ,BaA and BPY(Figure 5). In the muscle of *P. abu* , the most abundant PAHs are Nap , Ace ,Acy, Phe, Flue , BbF and BkF (Fig. 6). In the muscle of *Le. vorax* the most abundant PAHs are Ace ,Acy, Flu, Flue, Pyr, BaA, Chy, BbF, BkF, BaP and DahA (Fig.7).

**Table 2:** Concentrations of Polycyclic Aromatic Hydrocarbons in the fish samples.

| Name compound | *Lu. xanthopterus* | *Ct.idella* | *Cy. carpio* | *T. zillii* | *P. abu* | *Le. vorax* |
|---|---|---|---|---|---|---|
| **Naphthalene** | 0.024 | | 0.008 | | 0.006 | |
| **Acenaphthylene** | | 0.097 | | 0.271 | 0.903 | 1.560 |
| **Acenaphthene** | 0.723 | 0.005 | 0.003 | | 0.210 | 0.030 |
| **Fluorene** | 0.529 | 0.003 | | 0.784 | | 0.071 |
| **Phenanthrene** | | 0.017 | 0.002 | 0.020 | 0.056 | |
| **Anthracene** | 1.824 | 0.082 | | 0.396 | | |
| **Fluoranthene** | | 0.003 | | | 0.009 | 0.012 |
| **Pyrene** | | | 0.001 | 0.003 | 0.134 | 0.013 |
| **Benzo[a]anthracene** | | 0.014 | 0.003 | 0.025 | | 0.014 |
| **Chrysene** | | 0.0004 | 0.001 | | | 0.005 |
| **Benzo[b]fluoranthene** | | 0.002 | 0.002 | | | 0.002 |
| **Benzo[k]fluoranthene** | | | | | 0.523 | 0.034 |
| **Benzo[a]pyrene** | | | | | | 0.014 |
| **Dibenzo[a,h]anthracene** | | | | | | 1.588 |
| **Benzo[g,h,I,]perylene** | | | | 0.026 | | |
| **Indeno[1,2,3-cd] pyrene** | | | | | | |
| **∑ 16 PAHs** | 3.100 | 0.226 | 0.025 | 1.528 | 1.844 | 3.348 |

PAH isomeric ratios such as Flue/Pyr, Phe/Ant, Ant/(Ant+Phe), BaA/(BaA+Chry) and(LMW/HMW) low molecular weight to high molecular weight have been used to identify sources that contribute PAHs to the environment (Yu *et al*., 2013). In the present study (Tables 3), the ratio of (Flu / Pyr ) < 1 reflecting petrogenic origin, while the ratio of (Phe/Ant) less than 1 indicates petrogenic. (Ant/ (Ant+Phe)) ratio presumes that ratios larger than 0.1 indicate PAHs source to be of combustion origin and the ratio of (BaA /(BaA+Chr)) larger than

0.35 implies pyrogenic sources. ratio of(LMW /HMW) values less than 1 are attributed to pyrogenic sources (Vrana *et al*., 2001).

**Table 3.** Values of PAHs ratios for the fishes of Shatt Al Arab River.

| **PAHs ratios** | ***Ct.idella*** | ***Cy. carpio*** | ***T. zillii*** | ***P. abu*** | ***Le. vorax*** |
|---|---|---|---|---|---|
| **fluoranthen/pyrene** | | | | 0.070 | 0.956 |
| **Phen/Ant** | 0.217 | | 0.051 | | |
| **Ant/(Ant+Phen)** | 0.821 | | 0.950 | | |
| **BaA/(BaA+Chry)** | 0.972 | 0.669 | | | 0.717 |
| **LMW /HMW** | 12.058 | 1.473 | 26.889 | 1.802 | 1.000 |

In fact, the presence of fluoranthene and pyrene indicates the importance of pyrolytic inputs since these compounds are considered as products formed from the condensation of aromatic compounds of low molecular weight at high temperature (Zrafi *et al*., 2013). The value of the Phen /Anth ratio in this study is much lower than 10 which is generally considered indicative of a predominance of petrogenic sources (Tolosa ,*et al.* 2004).
The results of the present study indicated that fish were contaminated mainly with low-molecular weight (LMW) compounds, while the high-molecular weight (HMW) (Malik et al.,2008).
In this all the calculated values of the LMW/HMW ratio are >1 , and this is indicate the main source of the PAHs in the investigated area coming from petrogenic source LMW-PAHs are preferentially degraded during PAH transport and burial into sediments (Berto *et. al.,* 2009). The ratios indicate that the main sourceof the PAHs, petrogenic input may also be a source of PAHs in these sites because many of the oil activities in the Shatt Al-Arab river that could contribute to PAHs (Farid *et al.*2016).
The less carcinogenic polyaromatic hydrocarbon of lower molecular weight (LMW PAHs) was detected with clearly observed naphthalene and its substituent in all the studied fish species (Table 3) The more carcinogenic high molecular weight (HMW) PAHs (BaA, BbF, BkF, BaP, and InP) were low detected in the fish samples analyzed . This shows that the source of PAHs in the river was mainly from petrogenic sources. The ratio of low molecular weight PAHs (LMW- PAHs) to high molecular weight PAHs (HMW-PAHs) has been used to characterize the origin of PAHs in the environment (Olaji,*et al.*2014) .The accidental discharge hazardous materials such as petroleum and chemical solvents to the aquatic environment has become the focus of increasing regulatory and public concenrn because of the adverse impacts of such materials on human health and the environment ( Al-Shwafi,2008) .

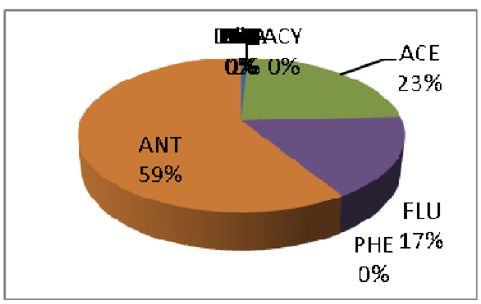


**Figure2:**The percentage of the PAHs compound in ***L. xanthopterus***

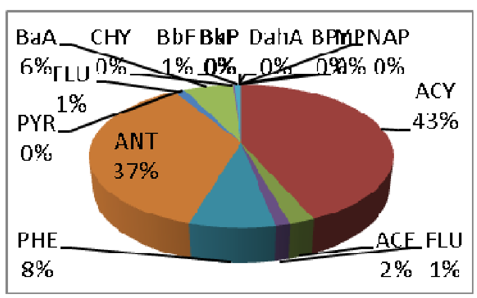


**Figure3:**The percentage of the PAHs compound in ***Ct. idella***

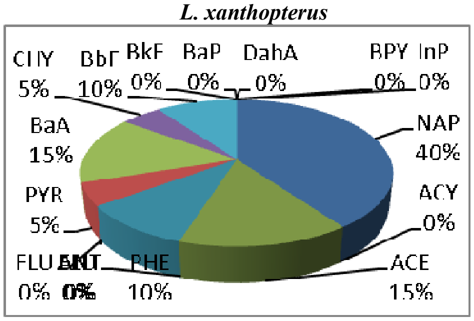


**Figure4:**The percentage of the PAHs compound in ***C. carpio***

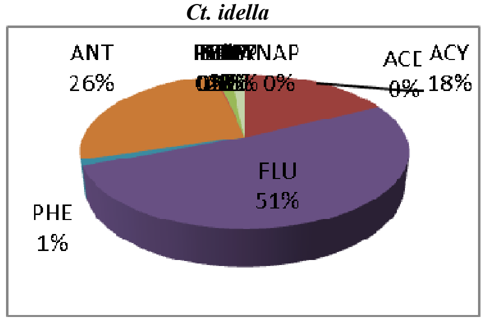


**Figure5:**The percentage of the PAHs compound in ***T. zillii***

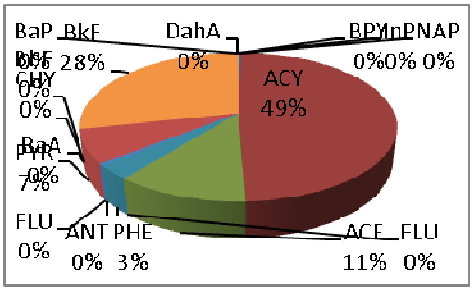


**Figure6:**The percentage of the PAHs compound in ***P. abu***

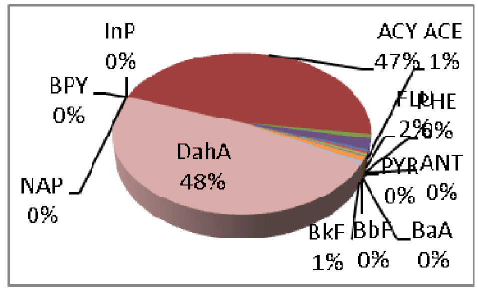


**Figure7:**The percentage of the PAHs compound in ***Le. vorax***

**Conclusion**

Total concentrations of PAHs in the fishes were in the range of between 0.02 to 3.34 ng/g dry weight, which is considered by (Ulun *et al.*2006) as slightly polluted. Several ratio of PAHs species concentration were applied to identify sources of the anthropogenic pollutants, which indicate that the pyrolytic and petrogenic sources therefore should be preventing the various kinds of industrial and domestic contaminants to be discharged into the river.

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