DISTRIBUTION OF POLYCYCLIC AROMATIC HYDROCARBONS AND THEIR SOURCES IN THE WATERS OF THE TIGRIS RIVER IN IRAQ

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ABSTRACT

The present study was performed to have knowledge of Polycyclic Aromatic Hydrocarbons pollution status in surface water along tigris river in sallahuddin province. The samples were collected during 2020 from five different stations. The distribution of fifteen polycyclic aromatic hydrocarbons (PAHs) was detected in the waters of the Tigris River. liquid-liquid extraction was used for water samples, and finally analyzed using gas chromatography. The highest concentrations were associated with Benzo [a] Fluoranthene (5-rings), whose mean value (ppm) at four consecutive sites was 685.83, 135.84, 455.74, 143.84. It was followed by pyrene (5-rings), whose mean values (ppm) in the five sites respectively were 70.916, 201.19, 79.32, 126.6, and 169.4. It is followed by Dibenzo [ah] anthracene (5 rings), whose average value (ppm) in the five sites respectively was 66.067, 37.375, 68.876, 14.8418, 7.733. Diagnostic ratios such as Phenanthrene / anthracene, BaA/(BaA+Chry), LMW/HMW and Fluorene / pyrene were achieved. To assess the emission sources of polycyclic aromatic hydrocarbons. These ratios indicated a source, as well as a thermal analyzer or pyrogenic origin of the water samples (with the predominant pyrolysis inputs) in the study area.

I. INTRODUCTION

Water pollution limits the abundance of this important resource, with the associated potential to cause health problems for humans and wildlife, reduce biodiversity, environmental degradation, hunger and poverty, among others. Among the list of priority emerging micro-pollutants identified for water quality degradation is the group of PAHs [1].

Polycyclic aromatic hydrocarbons (PAHs) are part of a larger group of many hosts of organic compounds, including polychlorinated biphenyls (PCBs), dioxins and furans (PCDD / Fs), and these are described as semi-volatile organic compounds (SVOCs) and pollutants. Persistent organic matter (POPs), and that these pollutants have high stability in the environment, meaning that they can remain in the environment for long periods and have the potential to cause harmful environmental effects [2].

PAHs and polychlorinated biphenyls, PCDD / Fs fall under these two titles due to the tendency of these similar compounds to be described as significant in the environment (each of them is a family that covers an average of vapor pressures, an affinity for lipids and stability in the environment). With this similarity, individual compounds will behave over a wide range of chemical and physical properties [3].

In recent times, studies of polycyclic aromatic hydrocarbons (PAHs) have been greatly studied because they accumulate on a large scale in soils, water and sediments and also because they are associated with risks of toxicity and cause carcinogenicity and are also mutagenic. Typically, PAHs present in aqueous environments are strongly absorbed by suspended organic and inorganic particles due to the decrease in their solubility in water [4,5]. Thus, water and more than sediments are among the most important reservoirs of PAHs[6,7].

PAHs can cause the formation of reactive epoxides that can bind to DNA covalently after exposure and during metabolism. These PAH-DNA additives are well-established markers of cancer risk.
PAH exposure has been associated with epigenetic changes, including genomic cytosine methylation. Both low global blood methylation and hypermethylation of certain genes have been associated with cancer [8].

A well-known technique for characterizing the primary sources of PAHs is to use relative PAH ratios that take into account isomers formed by different processes [9]. These ratios are based on the thermodynamic stability of some of the PAH isomers. Specifically, and typically, PAHs are found in clusters and are classified into three main sources: pyrogenic, petrogenic, and biogenic [10].

II. MATERIAL METHODS

1. Study area

The Tigris River is an important river throughout historically, and it is one of the main sources of ancient Mesopotamian civilizations. This river originates from the Taurus Mountains, which are located east of Anatolia in Turkey, and the Tigris River takes a southeastern course towards Iraq, as this river forms a border between Turkey and Syria for a distance of 32 km before entering Iraq [11]. The length of the river is about 1900 km, and most of it (77%) is located in Iraq, followed by Turkey (22%) and Syria (1%), approximately (450) km long, of which it is through Turkey [12].

Thus, Iraq receives from the area and length of the Tigris basin a share greater than its area and length in Turkey and Syria. The extension of the Tigris basin lies between latitude 30°75 north to 38°8 east, and the Tigris basin is shared by four countries: Turkey, Syria, Iraq and Iran. The total area of the Tigris basin is (471606) km², and Iraq's share of it is (53.6%). Which is equivalent to (32.9%) of the total area, as the total area of the Tigris River and its branches within the Turkish borders until the river entered the Iraqi lands in the village of Fishkhabur is about 57614 km², equivalent to (12.22%) of the total area [13].

The study area is located in this part of the Tigris River in the city of Dhuluiya within Salah al-Din Governorate, which lies between two longitudes (44° 15 - 43° 30) east and two latitudes (35° 45 - 35° 5) north. The river crosses about 250 km within the governorate, and the Tigris River is the main resource for surface water in Salah al-Din Governorate, as the river penetrates this city from north to south, and agricultural districts abound on both sides of the river.

In view of the fact that the Dhuluiya sub-district is one of the major sub-districts within Salah al-Din Governorate, due to its population density and its great need for water, a number of irrigation projects have been established. It is located on the eastern and western banks of the river and is used for drinking purposes, agricultural land irrigation, and various household uses.

2. Site Description

The study area is located on the Tigris River within Salah al-Din Governorate, which lies between two longitudes (44° 15 - 43° 30) east and two latitude (35° 45 - 35° 5) north. The river crosses about 250 km within the governorate, and the Tigris River is the main resource for surface water in Salah al-Din Governorate, as the river penetrates this city from north to south, and agricultural districts abound on both sides of the river.

Since Dhuluiya sub-district is one of the major sub-districts within Salah al-Din Governorate due to its population density and its great need for water, a number of irrigation projects have been established. It is located on the eastern and western banks of the river and is used for drinking, irrigation of agricultural lands and various household uses. The research examined some of the physical and chemical properties of five stations on the Tigris River in the city of Dhuluiya in Salah al-Din Governorate as (shown in Figure 1).

The first station: This station is located northwest of the city of Dhuluiya and in the village of Hardaniyah, which is a rural residential and agricultural area at the same time at longitude (34 34 0422) degrees north and latitude (14 51 44 08) degrees east. All types of agriculture are spread in this area and are characterized by dense housing It is adjacent to the Tigris River in a large area of the village, and agricultural land occupies most of its area.

The second station: This station is located northwest of the city of Dhuluiya and in the village of al-Bahariya specifically near the new Al-Bahariya water complex in a rural residential agricultural area at the same time at longitude (93 34 01 31) degrees north and latitude (11 97 44 13 degrees) east and is 4 km away from the station.
The first is characterized by the density of dwellings adjacent to the Tigris River in a large area of the village. Agricultural lands occupy the least amount of its area.

The third station: This mostly rural area station is located in the center of the city of Dhuluiya and in the village of Daoudia with (250 m) at longitude (05 43 0241) degrees north and latitude (31 12 44 14) degrees east and km 3 from the third station. With the density of dwellings adjacent to the Tigris River in a large area of the village, agricultural land is the almost non-existent part of this region.

Fourth station: This station is located southeast of the city of Dhuluiya in a rural mostly agriculture area. The longitude is (01 34 72 32) degrees north and latitude (17 44 40 40) degrees east. In a large area of the village and agricultural land occupies the largest part of its area.

Fifth station: This station is located southeast of Dhuluiya and has the advantage of being agricultural lands devoid of housing adjacent to the Tigris River at longitude (93 33 5954) degrees north and latitude (38 19 44 16) degrees east, and it is 3.5 km away from the fourth station.

Figure (1) (The studied stations map in Al-Dhuluiya city)  

https://www.google.com/maps/place

III. MATERIALS AND METHODS

Water samples were collected seasonally during the period from January 2020 to December 2020 from four sampling stations. Location of the stations was determined by the https://www.google.com/maps/place. Each sampling was carried out in five replicates. Water samples were taken at the surface and 50 cm below the surface level. All samples were instantly transferred to the laboratory for further experiments. Prior to analysis samples were allowed to air dry in dark condition for 48 hours. PAHs were extracted using liquid–liquid extraction (LLE) with 100 ml of n-hexane and dichloromethane mixture (1:1 v/v) as described in APHA [14]. Before extraction, (1000 ml) of the water sample was filtered using a (70 mm) Whatman filter paper to remove suspended matter. The extract was concentrated to a final volume of 2 ml under an appropriate level of nitrogen using a rotary evaporator and then analyzed using gas chromatography. The air-dried sediment (500 lm mesh) was sieved and homogenized in a mixer. The PAHs were extracted from the sediments using Soxhlet extraction.

10g of the homogenized sample was extracted with 250 ml of dichloromethane for 16 hours and concentrated to 2 ml using a vacuum rotary evaporator. (silica/alumina column) chromatography was used to clean and separate water and sediment. Saturated aromatic hydrocarbons with 20 mL of ordinary hexane and 30 mL of a mixture of
hexane and dichloromethane (10:90) (v/v) respectively. For the detection of 15 PAHs, 1 ml of the aromatic hydrocarbon fraction in (liquid-gas) chromatography equipped with a flame ionization detector (GC/FID), GC analysis was carried out on a fused silica capillary column of 30m length, 0.32 mm ID thickness and 0.5 lm. With a flow rate of (1.5 ml/minute) the following PAHs were found:

naphthalene, naphthalene, acenaphthylene, acenaphthene, fluorene, phenanthrene, pyrene, chrysene, benzo [a] anthracene, benzo [a] pyrene, dibenz [a,h] anthracene, benzo [g,h,i] indene, 1,2,3-cd) Pyrene, benzo [k] Fluoranthene, fluorene,.

To correct the data, the recoveries were accomplished by adding 1, 5 and 10 lg of the standard mixture of polycyclic aromatic hydrocarbons. The mean percentage recovery for the total PAH was 97.90%[4,15,16,17].

## IV. RESULTS AND DISCUSSION

The results of the concentrations of PAHs detected in surface waters of the Tigris River are summarized in Table 1. We understand that the total PAHs (also ΣPAHs) is the sum total of 15 PAHs studied.

In terms of the individual composition of PAHs that were studied in water, most of the analyzed compounds were detected in all sites except the fifth quasi-zero. The distribution of PAHs in water models from the studied sites was relatively comparable. The five-ring polycyclic aromatic hydrocarbons were the most abundant, followed by the 4-ring aromatic hydrocarbons, then the 3-ring isomers in all study sites, and the least abundant were the 2-ring polycyclic aromatic hydrocarbons (PAHs) and the 6-rings PAHS, as shown in (Fig.2).

As can be seen from the water samples, the highest concentrations were associated with Benzo [a] Fluoranthene (5 - rings), whose mean value (ppm) at four successive sites was 685.83, 135.84,455,74,143.84. It is followed by Pyrene (5 - rings), whose mean values (ppm) in the five sites respectively were 70.916, 201.19, 79.32, 126.6, 169.4. It is followed by Di benz [ah] Anthracene (5- rings), whose average value (ppm) at the five sites respectively was 66.067, 37.375, 68.876, 14.8418, 7.733.

### Table 1: Concentrations of PAHs (ppm) in surface water of the Tigris River.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Station 1</th>
<th>Station 2</th>
<th>Station 3</th>
<th>Station 4</th>
<th>Station 5</th>
</tr>
</thead>
<tbody>
<tr>
<td>Naphthalene</td>
<td>Mean 0.05517</td>
<td>Range 0.0-0.5</td>
<td>Mean 0.0334</td>
<td>Range 0.00139</td>
<td>Mean 0.046523</td>
</tr>
<tr>
<td>Naphthalene</td>
<td>1.125</td>
<td>0-6.313</td>
<td>0.221</td>
<td>0-0.93</td>
<td>0.4355</td>
</tr>
<tr>
<td>Fluoranthene</td>
<td>1.438</td>
<td>0-14.2</td>
<td>0.2548</td>
<td>0-1.62</td>
<td>0.4092</td>
</tr>
<tr>
<td>Acenaphthylene</td>
<td>15.905</td>
<td>0-73.4</td>
<td>2.58</td>
<td>0-15.114</td>
<td>2.2485</td>
</tr>
<tr>
<td>Fluoranthene</td>
<td>7.3765</td>
<td>0-43.58</td>
<td>1.277</td>
<td>0-8.41</td>
<td>1.2272</td>
</tr>
<tr>
<td>Fluoranthene</td>
<td>2.12</td>
<td>0-14.1</td>
<td>0.3415</td>
<td>0-3.35</td>
<td>0.1268</td>
</tr>
<tr>
<td>Phenanthrene</td>
<td>7.3765</td>
<td>0-43.58</td>
<td>1.277</td>
<td>0-8.41</td>
<td>1.2272</td>
</tr>
<tr>
<td>Total HPAH</td>
<td>926.0966</td>
<td>0-6599.549</td>
<td>303.4857</td>
<td>0-2038.512</td>
<td>606.7676</td>
</tr>
</tbody>
</table>

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The sources of PAHs can be determined from the individual proportions of PAHs based on the characteristics in the formation of PAHs and the distribution patterns as a function of the emission sources [17,18]. PAH fingerprint ratios, such as Ant/(Ant+Phen), BaA/(BaA+Chry), Flt/(Flt+Py) and InP/(InP+BghiP) Ratios were applied in some studies to distinguish between the petrogenic and pyrogenic inputs [19, 9,20]. These ratios are based on differences in formation heat in the same molecular mass isomers. Pyrogenic processes are fast reactions that form more energy isomers (the kinetic product). Diagenesis prefers a more stable isomer (thermodynamic product) by increasing the reaction time [21].

A BaA / (BaA + Chry) ratio of (0.2) indicates petrogenic input and a ratio of (0.35) indicates pyrogenic processes, while a ratio of (0.2) to (0.35) is a feature of combustion processes [9]. Values less than 0.4 are consistent with petroleum pollution and values between 0.4 and 0.5 are more related to liquid fossil fuel combustion, such as vehicle and crude oil combustion [9]. Values greater than 0.5 are for combustion properties of weed, wood or charcoal [9].

Petrogenic pollution is characterized by low molecular weight dominance of polycyclic aromatic hydrocarbons (LMW with two and three aromatic rings), while high molecular weights (HMW with four, five and six rings) indicate of pyrolytic origin [22].

An LMW / HMW ratio of less than 1 indicates a pyrogenic contribution [23]. In this study LMW/HMW ratio (Table 2) was less than 1 suggesting that the sources of the PAHs in that site were mainly from pyrolytic origin.

Table 2. Mean LMW/HMW ratio of individual PAHs compounds in water samples of Tigris River sites during period study.

<table>
<thead>
<tr>
<th>Stn No.</th>
<th>LMW</th>
<th>HMW</th>
<th>LMW /HMW</th>
<th>Source</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>33.08967</td>
<td>926.0966</td>
<td>0.03573</td>
<td>pyrogenic</td>
</tr>
<tr>
<td>2</td>
<td>6.79864</td>
<td>303.4857</td>
<td>0.022402</td>
<td>pyrogenic</td>
</tr>
<tr>
<td>3</td>
<td>7.49823</td>
<td>606.7676</td>
<td>0.012359</td>
<td>pyrogenic</td>
</tr>
<tr>
<td>4</td>
<td>14.76945</td>
<td>362.3761</td>
<td>0.040757</td>
<td>pyrogenic</td>
</tr>
<tr>
<td>5</td>
<td>15.50186</td>
<td>78.9278</td>
<td>0.196406</td>
<td>pyrogenic</td>
</tr>
</tbody>
</table>

In spite of the well-established ratios found in the above literature for source indications, the BaA/(BaA+Chry), Fl/(Fl+PYR) ratios are shown on (Tables 3 and4) of this study did not give consistent information because Ant and BaA were usually low with a scarce peak in the chromatographic profile, thus leading to analytical errors and difficulties in quantification. In general, no more than two PAH ratios are used to determine the possible sources because additional ratios can lead to different and ambiguous interpretations [24]. The group corresponding to sites of study tends to be mainly of a combustion source, a combustion of biomass or petroleum derivates.

5-ring PAHs represent (68.749819%) of the total PAHs in the Tigris River sites in this study, while a low percentage (0.074321%) was recorded for PAHs indicating that PAHs were the most abundant.(5-ring PAHs > 4-ring PAHs > 3-ring PAHs > 2-ring PAHs > 6-ring PAHs).

Figure (2) Percentage of mean concentration of 2-ring, 3-ring, 4-ring, 5-ring and 6-ring PAHs in water samples of tigris River stations.
Figure 3 Mean percentage of PAHs in the water samples of Tigris River.
### Table 3. Mean FL/(FL + PYR) ratio of individual PAHs compounds in water samples of Tigris River sites during period study.

<table>
<thead>
<tr>
<th>Stn No.</th>
<th>Flourene</th>
<th>Pyrene</th>
<th>FL/(FL + PYR)</th>
<th>Source</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>2.12</td>
<td>169.4</td>
<td>0.01236</td>
<td>Petrol emissions</td>
</tr>
<tr>
<td>2</td>
<td>0.3415</td>
<td>126.61</td>
<td>0.00269</td>
<td>Petrol emissions</td>
</tr>
<tr>
<td>3</td>
<td>1.815</td>
<td>79.32</td>
<td>0.02237</td>
<td>Petrol emissions</td>
</tr>
</tbody>
</table>

**Diagram:**
- Benzo [a] Pyrene: 0.144137809
- Fluro bipheyl: 0.149918751
- Naththalene: 0.117286923
- Naphthalene: 0.005751751
- Fluorene: 0.22102069
- Phenanthrene: 0.528573065
- Acenophylene: 0.76903732
- Acenophthene: 1.658176449
- Benzo [k] Fluomthene: 0.022519089
- Benzo [a] anthracene: 0.11103162
- Benz[a]anthracene: 6.887817884
- Benz[a]fluoranthene: 71.5012357
- Chrysene: 0.179318673
- Di benz [ah] Anthracene: 0.005751751
- Pyrene: 0.11103162
- Fluoranthene: 17.66080418
- Benz[b]pyren: 0.043370098
- Benz[a]fluoranthene: 0.022519089
Table 4. Mean BaA/(BaA+Chry) ratio of individual PAHs compounds in water samples of Tigris River sites during period study.

<table>
<thead>
<tr>
<th>Stn No.</th>
<th>Benz[a] anthracene</th>
<th>BaA/(BaA+Chry)</th>
<th>BaA/(BaA+Chry)</th>
<th>Source</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>pyrogenic</td>
</tr>
<tr>
<td>1</td>
<td>1.065</td>
<td>1.72</td>
<td>2.785</td>
<td>0.3824</td>
</tr>
<tr>
<td>2</td>
<td>2.545</td>
<td>0</td>
<td>2.545</td>
<td>1</td>
</tr>
<tr>
<td>3</td>
<td>1.5</td>
<td>0.478</td>
<td>1.978</td>
<td>0.758</td>
</tr>
<tr>
<td>4</td>
<td>1.023</td>
<td>0.7289</td>
<td>1.7519</td>
<td>0.5839</td>
</tr>
<tr>
<td>5</td>
<td>0.1345</td>
<td>0</td>
<td>0.1345</td>
<td>1</td>
</tr>
</tbody>
</table>

V. CONCLUSION

Polycyclic aromatic hydrocarbons listed in the US Environmental Protection Agency were discovered in water samples collected from the Tigris River. The Tigris River flows through different land use areas; Agricultural activities in the upper reaches of the river dominate agricultural activities, and are considered formal and informal settlements, as well as industrial facilities (oil refinery in Baiji, chemical, fertilizer and detergent factories, Samarra pharmaceutical factory, industrial quarters and power plants, as well as a sewage and sewage treatment plant. Hospitals) anthropogenic sources of downstream PAHs. Industrial activities were a major source of contamination with PAHs.

The spatial and temporal levels of PAHs in the water samples from the Tigris River showed seasonal variations. The mean annual detected levels of Benzo[a] Fluoranthene (5-rings), Pyrene (5-Rings), Di benz [ah] Anthracene (5-rings) in water samples from all sampling sites were higher compared to other PAHs. The surface water samples of the Tigris River were heavily contaminated with carcinogenic PAHs.

Polycyclic aromatic hydrocarbons present in the aquatic environment undergo photolysis, which may alter proportional diagnostic values.

The diagnostic ratios of PAHs should be used with caution, as their values may change during the environmental fate of these compounds.

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