Determination of Polycyclic Aromatic Hydrocarbon (PAHs) in the Tigris River through Passing Baghdad Province

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Abstract
Tigris River receives many pollutants while passing through Baghdad province due to increasing of population, discharge of untreated industrials, agricultural wastes on the river. The present study was conducted from January 2013 to December 2013 on the Tigris River starting from Al-Muthana Bridge to Al-Zaufurania city before it’s jointed with Diyalla Tributaries. Six stations were chosen on the Tigris River along Baghdad city. The study was included measuring the bimonthly concentrations and distributions of polycyclic aromatic hydrocarbons (PAHs) in the samples of surface water. The sixteen polycyclic aromatic hydrocarbons (PAHs) listed by USEPA as priority pollutants (Naphthalene, Acenaphthalene, Acenaphthene, Fluorene, Phenanthrene, Anthracene, Flouranthene, Pyrene, Benzo(a)anthracene, Chrysene, Benzo(b)flouranthene, Benzo(k)fluoranthene, Benzo(a)pyrene, Pyrene, Dibenzo(a,h)anthracene, benzo(g,h,i)pyrene and Inden(1,2,3-cd)pyrene) were detected. The highest value of total PAHs was 0.279 ppm recorded during August 2013 whereas the lowest value was 0.007 ppm during October 2013 at Al-Durah power plant discharge sit. The lowest value of (0.0002) ppm was recorded for Fluorene and Fluoranthene, while the highest value of (0.2) ppm for Naphthalene at Al-Durah power plant sit.

Keywords: PAHs, petroleum, oil spill, Tigris River.
Six stations were chosen from north to south of Baghdad government to collect water samples to determine the concentration of polycyclic aromatic hydrocarbons which discharge from industrial institutions toward Tigris River, the locations of these stations were in figure 1: Station one (S1): located at Al-Tajiy area near Al-Muthana Bridge, this area is an agricultural area consist of a grove of orange and other citrus tree, this station was considerable as reference station. Station two (S2): Located at Al-Jadriyah area near Al-Jadriyah Bridge and Baghdad University. The vertical distance between S1and S2 was 27 Km. Station three (S3): Located at Al-Durah area about 500 m from Al-Durah power plant discharge. The vertical distance between S2and S3 was 3 Km. Station four (S4): Located at Al-Durah area about 2800 m from Al-Durah refiner discharge. The vertical distance between S3and S4 was 6.570 Km. Station five (S5): Located at Al-Rasheed area about 500 m from Al-Rasheed power plant discharge. The vertical distance between S4and S5 was 6 Km. Station six (S6): Located at Al-Rasheed area near Al-Zafarania city southern Baghdad city before the jointed point between the Tigris River and Diyala Tributary. The vertical distance between S5and S6 was 10 Km. Sampling was collected bimonthly from January to December 2013.

The determination of polycyclic aromatic hydrocarbon (PAHs) by high- performance liquid chromatography (HPLC) with UV and fluorescence detection has been well established [10, 11]. Least significant difference –LSD test was used to compare between means.
Results & Discussion

Total Polycyclic Aromatic Hydrocarbons

The concentrations of total PAHs in water surface showed significant variations during the study period figure 2. The results were varied from 0.279 ppm to 0.007 ppm during August and October, respectively at station 3. Statistically, no significant differences (P > 0.05) between stations for total PAHs compounds, whereas there were significant differences (P ≤ 0.05) between months with highly significant differences at August table 1.
### Table 1 - Range (First Line), Average and Standard Deviation (Second Line), for Polycyclic Aromatic Hydrocarbons compounds concentrations (ppm) at study stations during (January - December) 2013.

<table>
<thead>
<tr>
<th>PAHs</th>
<th>Station</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
<th>6</th>
</tr>
</thead>
<tbody>
<tr>
<td>Naphthalene</td>
<td>ND.033</td>
<td>0.004±0.003</td>
<td>0.004±0.002</td>
<td>0.004±0.002</td>
<td>0.004±0.002</td>
<td>0.004±0.002</td>
<td>0.004±0.002</td>
</tr>
<tr>
<td>Acenaphthylene</td>
<td>ND.012</td>
<td>0.002±0.002</td>
<td>0.002±0.002</td>
<td>0.002±0.002</td>
<td>0.002±0.002</td>
<td>0.002±0.002</td>
<td>0.002±0.002</td>
</tr>
<tr>
<td>Fluoranthene</td>
<td>ND.001</td>
<td>0.001±0.001</td>
<td>0.001±0.001</td>
<td>0.001±0.001</td>
<td>0.001±0.001</td>
<td>0.001±0.001</td>
<td>0.001±0.001</td>
</tr>
<tr>
<td>Pyrene</td>
<td>ND.004</td>
<td>0.003±0.003</td>
<td>0.003±0.003</td>
<td>0.003±0.003</td>
<td>0.003±0.003</td>
<td>0.003±0.003</td>
<td>0.003±0.003</td>
</tr>
<tr>
<td>Anthracene</td>
<td>ND.006</td>
<td>0.005±0.005</td>
<td>0.005±0.005</td>
<td>0.005±0.005</td>
<td>0.005±0.005</td>
<td>0.005±0.005</td>
<td>0.005±0.005</td>
</tr>
<tr>
<td>Benzo(a)anthracene</td>
<td>ND.014</td>
<td>0.002±0.002</td>
<td>0.002±0.002</td>
<td>0.002±0.002</td>
<td>0.002±0.002</td>
<td>0.002±0.002</td>
<td>0.002±0.002</td>
</tr>
<tr>
<td>Chrycene</td>
<td>ND.007</td>
<td>0.001±0.001</td>
<td>0.001±0.001</td>
<td>0.001±0.001</td>
<td>0.001±0.001</td>
<td>0.001±0.001</td>
<td>0.001±0.001</td>
</tr>
<tr>
<td>Benzo(b)fluoranthene</td>
<td>ND.012</td>
<td>0.005±0.005</td>
<td>0.005±0.005</td>
<td>0.005±0.005</td>
<td>0.005±0.005</td>
<td>0.005±0.005</td>
<td>0.005±0.005</td>
</tr>
<tr>
<td>Benzo(k)fluoranthene</td>
<td>ND.005</td>
<td>0.003±0.003</td>
<td>0.003±0.003</td>
<td>0.003±0.003</td>
<td>0.003±0.003</td>
<td>0.003±0.003</td>
<td>0.003±0.003</td>
</tr>
<tr>
<td>Benzo(a)pyrene</td>
<td>ND.005</td>
<td>0.001±0.001</td>
<td>0.001±0.001</td>
<td>0.001±0.001</td>
<td>0.001±0.001</td>
<td>0.001±0.001</td>
<td>0.001±0.001</td>
</tr>
<tr>
<td>Dibenzo(a,h)anthracene</td>
<td>ND.005</td>
<td>0.004±0.004</td>
<td>0.004±0.004</td>
<td>0.004±0.004</td>
<td>0.004±0.004</td>
<td>0.004±0.004</td>
<td>0.004±0.004</td>
</tr>
<tr>
<td>Benzo(g,h,i)perylene</td>
<td>ND.005</td>
<td>0.001±0.001</td>
<td>0.001±0.001</td>
<td>0.001±0.001</td>
<td>0.001±0.001</td>
<td>0.001±0.001</td>
<td>0.001±0.001</td>
</tr>
<tr>
<td>Indeno(1,2,3-cd)pyrene</td>
<td>ND.005</td>
<td>0.005±0.005</td>
<td>0.005±0.005</td>
<td>0.005±0.005</td>
<td>0.005±0.005</td>
<td>0.005±0.005</td>
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</tbody>
</table>

*Station that carrying similar character were no any significant difference between the

**Naphthalene**

It was found that the highest value of Naphthalene was 0.2 ppm in August at station 3. On the other hand, there was recorded undetected value in different month such as: in August and October at the station 3 and in October and April at station 3, in August and October at station 4, in October and December at station 5, in October at station 5 figure 3. Naphthalene represents 24.94% of total PAHs. Statistically, no significant differences (P > 0.05) between stations for Naphthalene whereas significant differences (P ≤ 0.05) between months with highly significant differences at August table 1.
Figure 3- Bimonthly and site variations in the concentration of Naphthalene in water samples of Tigris River sites during (February –December 2013).

Acenaphthalene

Acenaphthalene concentrations during the study period showed the values were ranged from the highest value was 0.01 ppm recorded at station 4 in February 2013 and no concentrations of Acenaphthalene were detected at station 2 for all months of the study period figure 4. Acenaphthalene represent 2.3% of total PAHs. Statistically, no significant differences (P > 0.05) between stations for Acenaphthalene, whereas significant differences (P ≤ 0.05) between months with highly significant differences at August table 1.

Figure 4- Bimonthly and site variations in the concentration of Acenaphthalene in water samples of Tigris River sites during (February -December 2013).

Acenaphthene

The present study indicates that the concentration of Acenaphthene was varied from none detected at all stations to 0.47 ppm on August at station 6 figure5. Acenaphthene represent about 4.07% of total PAHs. Statistically, no significant differences (P > 0.05) between stations for Acenaphthene, whereas significant differences (P ≤ 0.05) between months with highly significant differences at April table 1.

Figure 5- Bimonthly and site variations in the concentration of Acenaphthene in water samples of Tigris River sites during (February -December 2013).
Flourene

The values of Flourene were varied from no concentration detected at stations 1, 3, and 5 in August to 0.013 ppm at station 4, as well as no concentration of Flourene were detected at all stations of study during December except at station 1 and 3 which were 0.003 and 0.006 ppm respectively figure 6. Flourene represent about 1.96% of total PAHs. Statistically, no significant differences (P > 0.05) between stations for Flourene, whereas significant differences (P ≤ 0.05) between months with highly significant differences at August table 1.

![Figure 6](image_url)

**Figure 6**- Bimonthly and site variations in the concentration of Flourene in water samples of Tigris River sites during (February -December 2013).

Phenanthrene

The results were varied from none detected concentration at all stations in different months to 0.0035 ppm in April at station 1, figure 7. Phenanthrene represents about 6.5% of total PAHs. Statistical analysis showed that there were no significant differences (P > 0.05) between stations and between months for Phenanthrene table 1.

![Figure 7](image_url)

**Figure 7**- Bimonthly and site variations in the concentration of Phenanthrene in water samples of Tigris River sites during (February -December 2013).

Anthracene

The results of this study showed that no concentrations of Anthracene were detected in June and October. In February the Anthracene value were ranged from no concentrations at station 3 to 0.021 ppm at station 1 and in April figure 8. Anthracene concentrations were varied from no concentration was recorded at station 3 to 0.011 ppm at station 4 and 6. As well as there were no concentrations of Anthracene were detected during August and December at all stations except at station 3 which were 0.05 and 0.008 ppm, respectively. Anthracene represents about 5.6% of total PAHs. Statistical analysis showed that there were no significant differences (P> 0.05) between stations and between months for Anthracene table 1.
Flouranthene
The amounts of Flouranthene at station 1 were ranged from none detected during different month at all station to 0.015 ppm that recorded in December at station 3 figure 9. Flouranthene represents 2.7% of total PAHs. Statistical analysis showed that significant differences (P ≤ 0.05) between stations and months, the highest significant differences at station 3 during August for Flouranthene table 1.

Pyrene
The amounts of Pyrene were ranged from none detected at all stations on different months to 0.028 ppm in October at station 5, figure 10. Pyrene represents about 5.2% of total PAHs. Statistical analysis showed that significant differences (P ≤ 0.05) between stations and months, the highest significant differences at station 5 during August for Pyrene table 1.
Benzo(a)anthracene

The amount of Benzo(a)anthracene were varied between none detected in different months at all stations, and 0.078 ppm in August at station 6, (Figure11). Benzo(a)anthracene represent 11.05% of total PAHs. Statistical analysis showed that there were no significant differences (P > 0.05) between stations and between months for Benzo (a) anthracene table 1.

Chrycene

The results of this study showed that no concentrations were detected during different months at all stations to the highest value 0.0079 ppm recorded at station 1figure 12. Statistical analysis showed that there were no significant differences (P > 0.05) between stations and between months for Chrycene. Generally, Chrycene represent 1.5% of total PAHs table 1.

Benzo(b)fluoranthene

The amount of Benzo(b)fluoranthene were ranged from none detected was recorded in different months , to the highest value which was 0.027 ppm recorded in August at station 6, figure 13. The Benzo(b)fluoranthene represent 2.9% of total PAHs. Statistical analysis showed no significant differences (P ≤ 0.05) between stations, but highly significant differences at August for Benzo(b)fluoranthene table 1.

Benzo(k)fluoranthene

The results of this study indicate that Benzo(k)fluoranthene Varied between none detected at all stations for different months of the study period to 0.014 ppm in December at station 5, figure 14. Benzo(k)fluoranthene represent 2.5% of total PAHs. Statistical analysis showed that significant
differences (P ≤ 0.05) between stations and between months, the highly significant differences at station 1 during August 2013 for Benzo(k)flouranthene table 1.

**Figure 13**: Bimonthly and site variations in the concentration of Benzo (b)flouranthene in water samples of Tigris River sites during (February -December 2013).

**Benzo(a)pyrene**

The amount of Benzo(a)pyrene were varied from none detection in different months to 0.136 ppm in April at station 2. Figure 15. Benzo(a)pyrene represent 16.4% of total PAHs. Statistical analysis showed that no significant differences (P > 0.05) between stations and between months for Benzo(k)flouranthene table 1.

**Figure 14**: Bimonthly and site variations in the concentration of Benzo(k)flouranthene in water samples of Tigris River sites during (February -December 2013).

**Figure 15**: Bimonthly and site variations in the concentration of Benzo(a)pyrene in water samples of Tigris River sites during (February -December 2013).
Dibenzo(a,h)anthracene

The results of this study were recorded no concentration of Dibenzo (a, h) anthracene at station 4 at all months of the study period. Also the amounts of Dibenzo(a,h)anthracene at all stations were varied from none detected in different months to 0.01 ppm in April at station 3, figure16. Dibenzo(a,h)anthracene represent 2.7% of total PAHs. Statistical analysis showed that no significant differences (P > 0.05) between stations and between months for Dibenzo(a,h)anthracene table 1.

![Figure16-Bimonthly and site variations in the concentration of Dibenzo(a,h)anthracene in water samples of Tigris River sites during (February -December 2013).](image)

Benzo(g,h,i)perylene

The values of Benzo(g,h,i)perylene were varied from none detected at all stations in different months of the study period, to 0.025 ppm on August at station 4, figure 17. Benzo(g,h,i)perylene represent 4.28% of total PAHs. Statistical analysis showed that no significant differences (P > 0.05) between stations, but the highly significant differences recorded in August for Benzo(g,h,i)perylene table 1.

![Figure17-Bimonthly and site variations in the concentration of Benzo(g,h,i) perylene in water samples of Tigris River sites during (February -December 2013).](image)

Indeno(1,2,3-cd)pyrene

The results of this study indicated that the amount of Indeno(1,2,3-cd)pyrene were varied from none detected in different months at all stations to the highest value was 0.03 ppm in August at station 1, figure 18. Indeno(1,2,3-cd)pyrene represent 3.4% of total PAHs. Statistical analysis showed that no significant differences (P > 0.05) between stations and between months for Indeno(1,2,3-cd)pyrene table 1.
The results of the present study referred to the fluctuation in the concentration of PAHs among seasons. The highest concentration of PAHs recorded during summer while the lower concentrations observed during the autumn. This due to that temperature has an effect on the aqueous solubility of PAHs as higher temperatures cause more PAHs to be soluble in the water [12]. Opposite observations were obtained by Mohammad [13]; Al-Saad et al. [14]; Al-Timari [15]; Al-Timari [16], the high temperature in summer that causes volatilization of LMW-PAHs and rabid assimilation by aquatic organisms.

The highest concentrations of HMW-PAHs were recorded during February and April of 2013 whereas most of them not detected during October. This may be due to exposure to anthropogenic activities. PAHs enter water through discharges from industrial and waste water treatment plants. Most PAHs do not dissolve easily in water; they stick to solid particles and settle to the bottom of lakes or Rivers [17]. Zhu et al. [18] found a higher concentration of PAHs in summer than in winter which may be contributed to the sorption of PAHs on to the suspended particles and atmospheric deposition which increase during hot season. The concentration of PAHs may be reduced or diluted during periods of high flow of water [19]. These findings were agreeing with present study in which high flow of water during winter and autumn, whereas low levels of flow were recorded during the summer.

In general the concentrations of PAH in water depend on several factors, including properties of PAHs as hydrophobic nature with low solubility [20, 21], the interaction of several processes such as volatilization, bioconcentration, sedimentation, solubilization and biodegradation [22].

The most frequently detected PAHs in water samples at present study have been Naphthalene (24.9%), Benzo (a) pyrene (16.3%), Benzo (a) anthracene (11.05%) at the lower levels of Chrysene (1.5%) of total PAHs. Whereas the other individual parents PAHs in water sample fluctuated between (6.4% and 1.9%) of total PAHs.

Naphthalene, Phenanthrene and Anthracene, tend to exist as vapors in the atmosphere. Higher molecular weight compounds, such as pyrene exist as solid and are usually associated with soot particles. In general the high molecular weight PAHs tend to be more carcinogenic than that the smaller molecules. Due to their nonpolar behavior, PAHs are hydrophobic and have very low water solubility [8].

The total Polycyclic Aromatic Hydrocarbons levels at all stations of present study are higher than maximum admissible concentrations of Environmental Quality Criteria of United States, Σ PAHs= 0.03 µg/l for protection of human consumes of aquatic life [23] and was (7.9 µg/l to 273 µg/l) more than those recorded in other aquatic ecosystem in the world, suggesting that Tigris River sites was heavily contaminated depending on WHO[24] which considered the water as heavily polluted when the concentration of total PAHs in it exceeding 10 µg/l. Similar results were obtained in the Shatt Al-Arab River and northwest Arabian Gulf by [14,15,25] and in Langkawi Island of Malaysia by [26].

Figure 18-Bimonthly and site variations in the concentration of Indeno(1,2,3-cd) pyrene in water samples of Tigris River sites during (February -December 2013).
Reference

