Sources and Compositional Pattern of Polycyclic Aromatic Hydrocarbons in Water of Tigris River throughout Passing Baghdad Governorate

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Abstract. The present study was conducted on the Tigris River in Baghdad Governorate which starting from Al-Muthana bridge to Al-Zaufurania City before its jointed with Diyalla River. Six Sites were chosen on Tigris River along Baghdad Governorate. Surface water samples were collected bimonthly from January to December 2013 to measuring the concentrations and distributions of polycyclic aromatic hydrocarbons (PAHs) once every two months and predicting their source of the samples of surface water. The lowest of total PAHs value was 0.007 ppm which recorded during October 2013 at Site 3 whereas the highest value was 0.279 ppm which recorded during August 2013. The lowest value of 0.0002 ppm was recorded for Fluorene and Fluoranthene while the highest value of 0.2 ppm for Naphthalene was recorded at Site 3. The composition patterns of PAHs in water were determined. The lowest and highest value of 0.0037 and 0.204 ppm was recorded for 2-ring PAHs at site 3 and 6 during summer and winter of 2013, respectively. Whereas the lowest and highest value of 0.001 and 0.095 were recorded for 3-ring PAHs at site 5 and 6 during winter and summer 2013, respectively. On the other hand, the lowest and highest values of 4-ring PAHs were 0.001 and 0.078 which recorded at site 4 and 6, respectively. The lowest concentration of 6-ring PAHs was 0.03 ppm which recorded at site 1 in summer 2013 whereas the lowest concentration was 0.0031 ppm which recorded at site 1 and 3 in winter and spring 2013, respectively. According to the values of ratios (Phen/Ant, Flur/Py, LMW-PAHs/HMW-PAHs), the distribution of PAHs in water may have the origin from different source pyrogenic and petrogenic at site 4 and 5 and from pyrogenic and urban air in other sites of the present study.

Keywords: total PAHs, ring PAHs, Pyrogenic and Petrogenic, Tigris River.

1. Introduction

Global chemical pollution, especially contamination by PAHs has been greatly investigated in recent years. These have been of interest amongst scientists due to their toxicity, environmental persistence, and high bioaccumulation in organisms and long-term adverse impacts on ecosystems as well as human health [1]. The aquatic environment may be considered as the reservoir for PAHs generated in the environment. Apart from discharges from domestic, industrial and commercial effluents, aquatic environment also receives urban runoff loaded terrestrial contaminants, leaching from contaminated soil and airborne particles washed by rainfall [2]. Adverse effects of PAHs have been observed in marine organisms and they include growth reduction, endocrine alteration [3], malformation of embryos and larvae [4] and DNA damage [5]. It is important to note that PAHs get the one of the first and largest set of compounds known to be strongly mutagenic to laboratory animals and man, many studies have suggested a link between PAHs exposure and incidences of immune toxicities and cancer [6].

Polycyclic aromatic hydrocarbons (PAHs) are among the most abundant contaminants to which people and wildlife are commonly exposed and may have adverse effects on human health when they enter the food chain [7] which can can originate from biosynthetic, geochemical and anthropogenic sources and
are ubiquitous in the environment, which can be frequently found in food [8], air[9], soil[10] and sediments[11].

The introduction of PAHs into the environment via anthropogenic sources can fall under two categories. The first is through the intentional dumping or accidental spillage of petroleum products, creosote or coal tar, and the second is from the incomplete combustion of organic material arising from automobile emissions, industrial discharge or municipal incineration [12] and according to the United State Environmental Protection Agency (US-EPA) and also the European Environment Agency PAHs have been placed on the list of priority pollutants [13]. So the main aim of this study was to determine the sources and compositional pattern of Polycyclic Aromatic Hydrocarbons in Tigris River.

2. Materials and Methods

2.1. Description of the Study Area

Tigris River is one of the most important twin rivers in Iraq, sharing with Euphrates River as the main source of man use, they pass through the major cities in the country [14]. Tigris River enters the Baghdad City at a distance of 5 Km north of Al – Muthana Bridge, either a point of exit, about 3 Km from its joining with Diyala River, and a length between those two points about 58Km, the river divides Baghdad Governorate into a right side (Karkh) and left (Rusafa) sections with a flow direction from north to south [15]. The present study designed to assess the source and compositional pattern of (PAHs) in the Tigris river through passing Baghdad Governorate by choosing six sites (Figure 1)

- Site 1: Located at Al- Tajiy near Al- Muthana Bridge, this site was considered as reference site.
- Site 2: Located at Al-Jadriyah area near Al- Jadriyah Bridge and Baghdad University. The vertical distance between S1 and S2 was 27 Km.
- Site 3: Located at Al- Durah area about 150 m from Al- Durah power plant discharge. The vertical distance between S2 and S3 was 3Km.
- Site 4: Located at Al-Durah area about 2800 m from Al- Durah refiner discharge. The vertical distance between S3 and S4 was 6.570 Km.
- Site 5: Located at Al- Rasheed area about 500 m from Al-Rasheed power plant discharge. The vertical distance between S4 and S5 was 1.5 Km.
- Site 6: Located at Al –Rasheed area near Al –Zafarania City southern Baghdad Governorate before the jointed point between the Tigris River with Diyala River. The vertical distance between S5 and S6 was 10 Km.

Water samples were collected bimonthly from January to December 2013, at each sampling site, and the results represented as seasons. The samples were kept in a well stopped black glasses bottle (1L), then tested according to the determination of polycyclic aromatic hydrocarbon (PAHs) by high- performance liquid chromatography (HPLC) with UV and fluorescence detection which has been well established by [16]. The application of this method for determination of PAHs in extracted waste water and soil samples by using solid phase extracting (SPE – PAHs) method for pre concentration of the samples from 200-400 fold (200 fold by passing 1 litter of aqueous sample through (Sepack C-18) mini column and eluted the retained PAHs by 5 ml acetonitrile or methanol which means 1000/ 5 = 200) to get the peaks belong to each individual sample detected by UV at 254 nm, and then return to real concentration in each sample by comparison with authentic standard mixture solution are obtained from SUPELCO Company catalogue No 4-8905[17].

Calculation : \[ \text{Conc. of sample (µg/ml)} = \frac{\text{area of sample}}{\text{area of STD}} \times \text{conc. of standard} \times \frac{1}{\text{per- con. factor}} \]
| Loc. No. | Site                | GPS Coordinates (N, E) |
|---------|---------------------|------------------------|
| 1       | Muthana Bridge      | 33° 25' 42" N 44° 20' 48" E |
| 2       | Jadriya Bridge      | 33° 17' 12" N 44° 22' 19" E |
| 3       | Al-Dora Refinery    | 33° 16' 04" N 44° 26' 53" E |
| 4       | Al-Dora Power Plant | 33° 15' 43" N 44° 22' 40" E |
| 5       | Al-Rasheed Power Plant | 33° 12' 18" N 44° 21' 35" E |
| 6       | Zaafaraniya         | 33° 13' 59" N 44° 28' 45" E |

![Map of Iraq and Baghdad showing the sites. (Ministry of Water Resources, 2012), Map Scale 1/100000.](image)

**Figure 1.** Map of Iraq and Baghdad showing the sites. (Ministry of Water Resources, 2012), Map Scale 1/100000.
3. Results and Discussion

The bimonthly changes and mean concentrations of PAHs in water samples by ring numbers showed in figures (2,3,4,5 and 6), while the mean percentage of PAHs by ring numbers showed in (Fig.7). The highest concentration of 2-ring PAHs, naphthene and acenaphthylene was 0.204 ppm which recorded at site 3 during Summer whereas the lowest concentration was 0.0037 ppm which recorded at sites 4 and 6 during in Winter and Summer, respectively. Whereas the maximum value of 3-ring-PAHs (acenaphthene, fluorene, phenanthrene and anthracene) was 0.095 ppm which recorded at site 6 during summer and the minimum value was 0.001 ppm which recorded at site 5 during winter.

Nevertheless, the concentrations of 4 ring-PAHs (flouranethene, pyrene, benzo(a)anthracene) were ranged from 0.001 ppm at site 4 and 0.0787 ppm at site 6 in Summer. The concentrations from 0.0023 – 0.27 ppm were observed for 5 ring-PAHs (BbF, BKF, BbP and DbA) at site 1 during winter and spring, respectively. The highest concentration of 6 ring-PAHs was 0.0317 ppm which recorded at site 1 during summer whereas the lowest concentration was 0.0012 ppm at site 1 and 3 in winter and spring, respectively. The 2-ring PAHs represent (27.39%) of total PAHs in the Tigris River sites at the present study, while low percentage (7.68%) was recorded for 6-ring PAHs indicated that 2-ring PAHs were the most abundant than the others (2-ring PAHs > 5-ring PAHs > 4-ring PAHs > 3-ring PAHs > 6-ring PAHs).

The results of the present study disagree with Nasher et al. [18]; Mohammed et al. [19] and Koh et al. [20], the composition pattern of PAHs in sediments is mostly dominated by 4-ring PAHs, while water samples are dominated by 3-ring PAHs.

Figure 2. Bimonthly changes in the concentrations of 3 rings -PAHs compounds in water samples of Tigris River sites.

Figure 3. Bimonthly changes in the concentrations of 4 rings -PAHs compounds in water samples of Tigris River sites.
Figure 4. Bimonthly changes in the concentrations of 5 rings -PAHs compounds in water samples of Tigris River sites.

Figure 5. Bimonthly changes in the concentrations of 6 rings -PAHs compounds in water samples of Tigris River sites.

Figure 6. Composition pattern of PAHs by ring number and total PAHs in water samples of Tigris River sites.
The sources of PAHs can be either petrogenic, from petroleum-related activities, or pyrogenic (pyrolytic) from the incomplete combustion of diesel fuel and engine oil, wood, coal, biomass of forest, grass fires, water incinerators and fossil fuels that are used in industrial operations and power plants [21].

The sources of PAHs, whether from fuel combustion (pyrolytic) or from crude oil (petrogenic) contamination, may be identified by ratios of individual PAHs compounds based on peculiarities in PAHs composition and distribution pattern as a function of the emission source. Ratio of Phenanthrene to Anthracene (Ph/An) and Fluoranthene to Pyrene (Fl/Py) have been widely used to distinguish petrogenic and pyrogenic (pyrolytic) source of PAHs [22]. PAHs of petrogenic origin are generally characterised by Ph/An values >10, whereas combustion processes often result in low Ph/An ratios (<10). For the Fl/Py ratios, values greater than 1 have been used to indicate pyrolytic origins and values less than 1 are attributed to petrogenic source [23].

The present study indicates Phenanthrene/Anthracene ratios <10 which suggest that PAHs in Tigris River may be originate from pyrolytic source at all sites (Table 1) and according to the ratio of Fluoranthene/Pyrene (Table 2) at site 1 was 1.29 which was greater than 1 and LMW/HMW ratio (Table 3) was less than 1 suggesting that the sources of the PAHs in that site were mainly from pyrolytic origin. At site 2 the Fluoranthene/Pyrene ratio was 1.21 and the LMW/HMW ratio was 0.301 which indicated pyrolytic PAHs contamination in that site. Whereas the Fluoranthene/Pyrene ratio at site 3 was 2.02 and LMW/HMW ratio was 0.34 which indicated of pyrolytic PAHs source at this site. The ratio of Fluoranthene/Pyrene at site 4 was 0.7 which less than 1 and LMW/HMW ratio was 0.53 which less than 1 suggesting that the sources of PAHs at site 4 were mainly from pyrolytic origin and petroleum pollution originating from industries, domestic waste along the river and oil leakage. Whereas the Fluoranthene/Pyrene ratio at site 5 was 0.14 and LMW/HMW ratio was 0.52 which indicated that the main sources of the PAHs contamination were pyrogenic and petrogenic in origin while at site 6, the Fluoranthene/Pyrene ratio was 1.29 and LMW/HMW ratio was 0.69 suggesting that the main source of PAHs contamination was pyrogenic source at that site.

Ratios of Fluoranthene to Pyrene [24]or the low molecular weight (LMW) PAHs to high molecular weight (HMW) PAHs [25]are the two indexes that are most frequently used to assess the origin PAHs. This is because concentrations of Pyrene are much higher in the fossil fuel and their byproducts than the concentrations of Fluoranthene [26] and the petrogenic contamination with LMW-PAHs [27] while the pyrolytic contamination is characterised with HMW-PAHs[28]. Therefore ratio of Fluoranthene/Pyrene being less than 1 or those of LMW/HMW being greater than 1 indicates petrogenic derived PAHs contamination, while the opposite indicates pyrolytic PAHs contamination.

In general the mean ratio of (1.45) was recorded for Fl/Py ratio at sites 1, 2, 3 and 6 indicated pyrogenic input whereas the mean ratio of (0.45) at sites 4 and 5 indicated petrogenic contamination of Tigris River.
Whereas the mean ratio of (LMW-PAHs/HMW-PAHs) was (0.461) indicated pyrogenic source of PAHs at all sites of present study. Similar results were obtained by [29] and according to above showed that sites 4 and 5 contaminated by petrogenic and pyrogenic origin of PAHs.

Petrogenic PAHs may be more available for biological uptake than pyrogenic PAHs, since it tends to bind more strongly to sedimentary particles. Hence, to evaluate the risk of PAHs to aquatic biota, source-distinction is essential[30]. The concentration ratios of specific PAHs compounds are often used for characterizing possible pollution source, their ratios are influenced by several processes such as photoxidation, chemicaloxidation and biodegradation. In addition seasonal changes can be found in degradation intensities [30]. It’s clear from the result that the distribution and origin of PAHs at all site in the Tigris River may be due to different sources (petrogenic, pyrogenic and urban air).

| Site No. | Phenathrene | Anthracene | Ph/An  | Source  |
|----------|-------------|------------|--------|---------|
| 1        | 0.0181      | 0.03       | 0.60333| pyrogenic|
| 2        | 0.027       | 0.00407    | 6.63391| pyrogenic|
| 3        | 0.0125      | 0.0137     | 0.91241| pyrogenic|
| 4        | 0.0103      | 0.06       | 0.17167| pyrogenic|
| 5        | 0.0275      | 0.009      | 3.05556| pyrogenic|
| 6        | 0.0588      | 0.0163     | 3.60736| pyrogenic|

| Site No. | Flouranthene | Pyrene | Flou/Pyr | Source  |
|----------|--------------|--------|----------|---------|
| 1        | 0.01335      | 0.01029| 1.29738  | pyrolytic|
| 2        | 0.0046       | 0.0038 | 1.21053  | pyrolytic|
| 3        | 0.0301       | 0.0149 | 2.02013  | pyrolytic|
| 4        | 0.00883      | 0.0111 | 0.7955   | petrogenic|
| 5        | 0.00873      | 0.0588 | 0.14847  | petrogenic|
| 6        | 0.03147      | 0.02438| 1.29081  | pyrolytic|

| Site No. | LMW  | HMW  | LMW/HMW | Source  |
|----------|------|------|---------|---------|
| 1        | 0.06299| 0.17051| 0.36942 | pyrolytic|
| 2        | 0.06497| 0.21537| 0.30167 | pyrolytic|
| 3        | 0.04993| 0.1434 | 0.34819 | pyrolytic|
| 4        | 0.09013| 0.1691 | 0.533   | pyrolytic|
| 5        | 0.12677| 0.24112| 0.52576 | pyrolytic|
| 6        | 0.16509| 0.23798| 0.69371 | pyrolytic|

4. Conclusion
- Deterioration of the water quality of Tigris River was increased towards the downstream of Baghdad Governorate because of the discharge pollutants to the river.
- This study revealed that the pollution level by PAHs compounds was comparatively higher where the industrial activities are more compared to other parts and exceed the standard limits established by WHO[32].
According to the ratios of (flourantheine / pyrene, phenanthrene / anthracene and LMW-PAHs /HMW-PAHs), the PAHs in water samples have the origin from different sources including pyrogenic and petrogenic.

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