Distribution and sources of polycyclic aromatic hydrocarbons in water and sediments of the Soltan Abad River, Iran

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KEYWORDS
Polycyclic aromatic hydrocarbons (PAHs); Gas chromatograph; Pyrolytic; Petrogenic; Soltan Abad River

Abstract Distribution of the sixteen polycyclic aromatic hydrocarbons (PAHs) was detected in water and sediments of the Soltan Abad River. Liquid–liquid extraction was used for water samples, while PAHs in sediments were extracted using Soxhlet Extraction and finally analyzed by means of gas chromatography. Results showed that in water samples, the highest concentration was related to acenaphthene (3-ring PAH), whereas fluoranthene (4-ring PAH) was the most important pollutant in sediments. The mean concentrations of PAHs was the highest in autumn and the lowest in summer, in both water and sediment samples. Diagnostic ratios such as phenanthrene/anthracene and fluoranthene/pyrene were achieved to evaluate the emission sources of PAHs. These ratios indicated a pyrolytic source of PAHs for sediments, as well as a pyrolytic or pyrogenic origin for water samples (with a dominant pyrolytic input) in the study area.

Introduction

Polycyclic aromatic hydrocarbons (PAHs) are a ubiquitous group of different organic compounds with fused aromatic rings that are detected in a variety of environmental conditions. Their physical and chemical characteristics are varying with both the number of aromatic rings and the pattern of ring linkage. PAHs have carbon and hydrogen atoms in their structures but some carbons can be substituted by some elements such as nitrogen, sulfur and oxygen, resulting in polycyclic heteroaromatic hydrocarbons, e.g. carbazole and furans (Bayoumi, 2009). PAHs are lipophilic compounds that their solubility and so their concentration in water is trivial (Nasr et al., 2010; Qiu et al., 2009). PAHs' solubility in water decreases with increase in their molecular weight (Nikolaou et al., 2009). As a consequence of PAHs' hydrophobic properties, they tend to settle out of water and accumulate in the bottom sedimentation. Therefore, concentration of PAHs should be high in the sediments of polluted aquatic environments. Both anthropogenic activities and natural emissions are the PAH sources of coastal sediments. Anthropogenic sources include petrogenic and pyrolytic PAH contaminations. Pyrolytic sources include incomplete combustion of organic matter such as fossil fuels and biomass whereas the petrogenic PAHs are formed by petroleum products (Qiu et al., 2009; Perra et al., 2009). The PAH composition within the sediments reflects the origin(s) from which they were derived (Simpson * Tel.: +98 9171140799.
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et al., 1998; Yan et al., 2009). Lower molecular weight PAHs most often come from natural resources (petrogenic) of PAHs and higher molecular weight PAHs often originate from combustion (pyrolytic) (Helfrich and Armstrong, 1986).

Since some of PAHs and their metabolites, can form DNA adduct which can induce mutations; therefore their entrance into the bodies of organisms can be dangerous. Their carcino- genic and mutagenic properties causse to classify 16 of them as priority pollutants by the USEPA. Some authors mentioned that PAHs can be synthesized by unicellular algae, bacteria or higher plants but they accumulate PAHs rather than synthe- size them (Magi et al., 2002).

The Soltan Abad River is located in the south of Shiraz. It passes through the industrial town of Shiraz, and flows into Maharlu Lake. The industrial town of Shiraz has numerous factories and industries (industrial materials and chemical products, rubber and plastics, metal artifacts, etc.) which all have organic matter like PAHs. Shiraz urban sewage and agricultural lands around Shiraz are other PAH sources in the Soltan Abad River (Kafilzadeh and Moghtaderi, 2015). The purpose of this study is to analyze the distribution of the sixteen PAHs in water and sediments of the Soltan Abad River through four seasons and to determine their source (s) on the basis of their concentrations.

Materials and methods

Water and sediment samples were collected seasonally during the period from April 2013 to March 2014 from four sampling stations. Location of the stations was determined by the global positioning system (GPS) (Table 1). Each sampling was carried out in five replicates. Water samples were taken at the surface and 50 cm below the surface level. Simultaneously sediment samples were taken at a depth of 5 cm of sediment surface from the idem sites. 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 (APHA, 1998). Before extraction, water sample (800 ml) was filtered with Whatman filter paper (i.d. 70 mm) to remove debris and suspended materials. The extract was concentrated to a final volume of 2 ml under a gentle stream of nitrogen using a rotary evaporator and then ana- lyzed with Gas Chromatograph (Siriwong et al., 2009).

Air-dried sediments were sieved (mesh size 500 µm) and homogenized in mortar. PAHs in sediments were extracted using Soxhlet Extraction. A 10 g homogenized sample was extracted with 250 ml of dichloromethane for 16 h and concentrated to 2 ml using vacuum rotary evaporator (USEPA, 1996).

Silica/alumina column chromatography was used for clean- up and separation of water and sediments. Saturated aliphatic and aromatic hydrocarbons were washed with 20 ml of n-hexane and 30 ml of a mixture of hexane and dichloromethane (90:10) respectively. To detect 16 PAH components, 1 ml of aromatic hydrocarbon fraction was injected into a gas liquid chromatography equipped with a flam ionization detector (GC/FID) (Nasr et al., 2010). GC analysis was implemented on a fused silica capillary column of 60 m length, 0.25 mm ID and 0.5 µm film thicknesses. The following PAHs were used for quantitation: naphthalene, acenaphthylene, acenaphthene, fluorene, phenanthrene, anthracene, fluoranthene, pyrene, chrysene, benzo[a]anthracene, benzo[b]fluoranthene, benzo[k]fluoranthene, benzo[a]pyrene, dibenzo[a,h]anthracene, benzo[g,h,i]perylene, Indeno [1,2,3-cd] pyrene.

For correction of the data, recoveries were fulfilled by the addition of 1, 5 and 10 µg of PAH standard mixtures. The average percentage recovery of total PAHs achieved 96.80% and 91.26% for water and sediment samples, respectively. An analysis of variance (ANOVA) was performed using SPSS software (version 16), and mean comparison was con- ducted with Duncan test.

Results and discussion

The concentrations of the 16 detected PAHs in surface water and sediments of Soltan Abad River are shown on Tables 2 and 3. Most PAHs were detected at water and sediments of all stations. As can be seen in water samples, the highest concent- ration was related to acenaphthene (3-ring PAH), whose mean value (ng L$^{-1}$) in four sites was 16.20, 22.66, 45.58 and 66.30, respectively. ANOVA and Duncan tests showed a signif- icant difference between mean concentration of acenaphthene and other detected PAHs ($P < 0.01$). At the same time, the lowest concentration of PAH components in water samples of Soltan Abad River was related to Indeno [1,2,3-cd] pyrene. The associated mean values (ng L$^{-1}$) were 0.40, 0.63, 0.95 and 1.12. According to our results, the concentration of low molecular weight (2-3 ring) polycyclic aromatic hydrocarbons (LP AHs) in water samples of Soltan Abad River is higher than high molecular weight (4–6 ring) PAHs (HPAHs) (Fig. 1A). The mean values of total concentration (mg L$^{-1}$) of LP AHs and HPAHs in four sampling sites were 120.23 and 28.58 respectively, which are significantly different ($P < 0.01$).

As far as the sediment samples are concerned, fluoranthene (4-ring PAH) was the most important pollutant with mean concentrations (ng g$^{-1}$) of 27.33, 52.15, 67.59, and 65.24 in four stations, respectively. The difference between fluoran- thene and other PAH concentration was highly significant ($P < 0.01$). Meanwhile, in terms of the lowest concentration, fluorene (3-ring PAH) ranked the first position, followed by phenanthrene (3-ring PAH). The respective Figures (ng g$^{-1}$) in four stations are 6.75, 7.55, 8.39, and 9.85 for fluorene and 6.82, 7.53, 7.18, and 9.76 for phenanthrene. Contrary to the observed compositions of PAHs in surface water, HPAHs are more dominant in the sediments of the Soltan Abad River rather than LP AHs (Fig. 1B). The mean total concentration values (ng g$^{-1}$) were 270.27 for the former and

<table>
<thead>
<tr>
<th>Table 1</th>
<th>Location of sampling stations.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Station</td>
<td>Region</td>
</tr>
<tr>
<td>1</td>
<td>River sediments under the Soltan Abad entrance bridge</td>
</tr>
<tr>
<td>2</td>
<td>River sediments under the Soltan Abad town center bridge</td>
</tr>
<tr>
<td>3</td>
<td>River sediments under the bridge of Fasa Road Traffic Police</td>
</tr>
<tr>
<td>4</td>
<td>Entrance of Maharlu Lake</td>
</tr>
</tbody>
</table>
60.50 for the latter which are significantly different ($P \leq 0.01$). According to Nasr et al. (2010), Mohammed et al. (2009) and Koh et al. (2004), high molecular weight PAHs (four-ring) are often in sediments, whereas water samples are dominated by low molecular weight PAHs (two or three-ring). The difference between PAH pattern in water and sediments may be due to molecular weight and bacterial degradation. A wide array of microorganisms including fungi, algae and bacteria are known to degrade PAHs. However, bacteria play by far the most important role in complete mineralization. Lower molecular weight PAHs such as naphthalene and anthracene are more soluble and degradable, but higher molecular weight compounds such as pyrene and benzo[a]anthracene are more recalcitrant (Obayori and Salam, 2010). Because of their hydrophobic nature, relatively high molecular weight PAHs with high ring numbers and therefore more resistant to decomposition, that can adsorb onto settling particles, will reach the sediment bed. Octanol/water ratio (Kow) is used for calculation of the sorption degree of PAHs in water (Djomo et al., 1996). Therefore, the solubility of polycyclic aromatic hydrocarbons in water and sediments

### Table 2
Concentrations of PAHs (ng L$^{-1}$) in surface water of the Soltan Abad River.

<table>
<thead>
<tr>
<th>Components</th>
<th>Station 1</th>
<th>Station 2</th>
<th>Station 3</th>
<th>Station 4</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Mean Range</td>
<td>Mean Range</td>
<td>Mean Range</td>
<td>Mean Range</td>
</tr>
<tr>
<td>Naphthalene</td>
<td>4.9–9.9</td>
<td>6.5–15.3</td>
<td>6.6–15.1</td>
<td>42.3–58.5</td>
</tr>
<tr>
<td>Acenaphthylene</td>
<td>4.8–9.2</td>
<td>7.2–14.3</td>
<td>14.9–27.6</td>
<td>39.6–47.4</td>
</tr>
<tr>
<td>Acenaphthene</td>
<td>17.5–23.1</td>
<td>16.5–26.6</td>
<td>36.1–58.6</td>
<td>52.5–74.1</td>
</tr>
<tr>
<td>Fluorene</td>
<td>2.8–4.6</td>
<td>3.2–6.5</td>
<td>7.3–13.2</td>
<td>13.6–28.1</td>
</tr>
<tr>
<td>Phenanthrene</td>
<td>5.4–8.4</td>
<td>6.3–12.6</td>
<td>10.5–17.3</td>
<td>24.1–43.6</td>
</tr>
<tr>
<td>Anthracene</td>
<td>3.8–6.7</td>
<td>5.2–9.5</td>
<td>26.9–43.7</td>
<td>24.6–43.1</td>
</tr>
<tr>
<td>Total LPAH</td>
<td>39.2–61.9</td>
<td>44.9–84.8</td>
<td>102.3–175.5</td>
<td>196.7–294.8</td>
</tr>
<tr>
<td>Fluoranthene</td>
<td>0.9–1.5</td>
<td>1.2–2.4</td>
<td>2.8–5.5</td>
<td>5.9–12.8</td>
</tr>
<tr>
<td>Pyrene</td>
<td>0.8–1.3</td>
<td>1.2–3.1</td>
<td>2.8–5.4</td>
<td>3.2–7.5</td>
</tr>
<tr>
<td>Chrysene</td>
<td>0.8–1.3</td>
<td>1.8–3.7</td>
<td>3.4–7.1</td>
<td>5.8–11.6</td>
</tr>
<tr>
<td>Benzo[a]anthracene</td>
<td>1.2–2.6</td>
<td>2.3–3.5</td>
<td>2.9–5.8</td>
<td>6.2–13.3</td>
</tr>
<tr>
<td>Benzo[b]fluoranthene</td>
<td>0.8–1.6</td>
<td>1.3–2.7</td>
<td>3.3–5.3</td>
<td>5.5–9.3</td>
</tr>
<tr>
<td>Benzo[k]fluoranthene</td>
<td>1.1–2.0</td>
<td>1.2–2.8</td>
<td>1.5–3.8</td>
<td>2.4–4.1</td>
</tr>
<tr>
<td>Benzo[a]pyrene</td>
<td>1.2–2.1</td>
<td>0.9–2.7</td>
<td>3.2–5.3</td>
<td>6.2–11.3</td>
</tr>
<tr>
<td>Dibenzo[a,h]anthracene</td>
<td>0.5–1.3</td>
<td>0.8–1.9</td>
<td>1.3–3.9</td>
<td>2.5–6.5</td>
</tr>
<tr>
<td>Benzo[g,h,i]perylene</td>
<td>0.5–1.0</td>
<td>1.7–3.5</td>
<td>1.7–6.1</td>
<td>6.1–12.3</td>
</tr>
<tr>
<td>Indeno[1,2,3-cd]pyrene</td>
<td>0.3–0.7</td>
<td>0.5–0.8</td>
<td>0.7–1.5</td>
<td>0.7–1.5</td>
</tr>
<tr>
<td>Total HPAH</td>
<td>8.1–15.4</td>
<td>12.9–27.1</td>
<td>23.6–49.7</td>
<td>44.5–90.2</td>
</tr>
<tr>
<td>Total</td>
<td>47.3–77.3</td>
<td>57.8–111.9</td>
<td>125.9–225.2</td>
<td>241.2–385</td>
</tr>
</tbody>
</table>

### Table 3
Concentrations of PAHs (ng g$^{-1}$) in surface sediments of the Soltan Abad River.

<table>
<thead>
<tr>
<th>Components</th>
<th>Station 1</th>
<th>Station 2</th>
<th>Station 3</th>
<th>Station 4</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Mean Range</td>
<td>Mean Range</td>
<td>Mean Range</td>
<td>Mean Range</td>
</tr>
<tr>
<td>Naphthalene</td>
<td>8.9–15.1</td>
<td>7.9–17.1</td>
<td>9.9–18.5</td>
<td>8.7–18.8</td>
</tr>
<tr>
<td>Acenaphthylene</td>
<td>6.3–12.8</td>
<td>7.2–14.4</td>
<td>9.2–16.7</td>
<td>11.7–22.0</td>
</tr>
<tr>
<td>Acenaphthene</td>
<td>7.2–12.2</td>
<td>8.3–13.4</td>
<td>8.6–15.7</td>
<td>9.5–17.6</td>
</tr>
<tr>
<td>Fluorene</td>
<td>5.1–8.2</td>
<td>5.9–9.2</td>
<td>6.5–9.8</td>
<td>6.8–13.8</td>
</tr>
<tr>
<td>Phenanthrene</td>
<td>4.7–9.8</td>
<td>5.6–9.2</td>
<td>5.9–10.4</td>
<td>6.4–10.1</td>
</tr>
<tr>
<td>Anthracene</td>
<td>7.9–12.2</td>
<td>7.6–12.3</td>
<td>7.3–13.9</td>
<td>7.5–15.3</td>
</tr>
<tr>
<td>Total LPAH</td>
<td>40.1–70.3</td>
<td>42.5–75.6</td>
<td>47.4–84.5</td>
<td>50.8–97.6</td>
</tr>
<tr>
<td>Fluoranthene</td>
<td>17.5–41.5</td>
<td>40.6–80.4</td>
<td>52.1–91.8</td>
<td>47.5–92.6</td>
</tr>
<tr>
<td>Pyrene</td>
<td>16.2–33.7</td>
<td>19.2–39.8</td>
<td>20.8–44.5</td>
<td>29.2–55.4</td>
</tr>
<tr>
<td>Chrysene</td>
<td>15.4–32.5</td>
<td>18.3–40.0</td>
<td>16.8–40.6</td>
<td>19.7–45.4</td>
</tr>
<tr>
<td>Benzo[a]anthracene</td>
<td>20.4–36.3</td>
<td>31.2–38.3</td>
<td>28.4–39.9</td>
<td>30.6–44.7</td>
</tr>
<tr>
<td>Benzo[b]fluoranthene</td>
<td>11.5–27.7</td>
<td>21.5–37.0</td>
<td>18.4–29.6</td>
<td>20.5–35.2</td>
</tr>
<tr>
<td>Benzo[k]fluoranthene</td>
<td>7.3–15.9</td>
<td>8.8–13.3</td>
<td>13.6–25.4</td>
<td>31.6–48.6</td>
</tr>
<tr>
<td>Benzo[a]pyrene</td>
<td>11.5–25.3</td>
<td>13.5–27.5</td>
<td>16.5–29.4</td>
<td>25.3–36.7</td>
</tr>
<tr>
<td>Dibenzo[a,h]anthracene</td>
<td>16.2–34.2</td>
<td>21.4–36.9</td>
<td>21.4–37.3</td>
<td>17.2–40.8</td>
</tr>
<tr>
<td>Benzo[g,h,i]perylene</td>
<td>20.9–32.3</td>
<td>20.7–34.4</td>
<td>21.5–37.6</td>
<td>23.5–38.8</td>
</tr>
<tr>
<td>Indeno[1,2,3-cd]pyrene</td>
<td>3.3–8.8</td>
<td>4.7–10.0</td>
<td>3.9–9.9</td>
<td>6.5–12.9</td>
</tr>
<tr>
<td>Total HPAH</td>
<td>20.2–388.2</td>
<td>197.9–357.6</td>
<td>213.4–386.0</td>
<td>251.6–406.4</td>
</tr>
<tr>
<td>Total</td>
<td>180.3–358.5</td>
<td>240.4–433.2</td>
<td>260.8–471.0</td>
<td>302.4–504.0</td>
</tr>
</tbody>
</table>
hydrocarbons decreases as the Kow and molecular weight increase. As a consequence, the heavier molecular weight compounds are with higher Kow.

The present results referred to significant differences in the concentrations of PAHs in water and sediment samples among seasons ($P < 0.01$) during the study. The highest concentrations were obtained in autumn with 12.64 ng L$^{-1}$ for water and 28.38 ng g$^{-1}$ for sediment, while the lowest concentrations recorded in summer with respective figures of 4.72 ng L$^{-1}$ and 13.74 ng g$^{-1}$ for water and sediment samples (Figs. 2 and 3). This may be attributed to the climatic conditions, effect of photo oxidation, volatilization and high degradation during the hot season (Mohammed et al., 2009). The amount of some PAH compounds in Euphrates River sediments from Iraq was measured by Mohammed et al. (2009) which showed the highest levels in autumn and spring, while the lowest levels were in summer. These levels reported in Iraq were extremely high compared to levels recorded in this work.

The major sources of anthropogenic PAHs are fossil fuel combustion (pyrolytic) and petroleum spillage (petrogenic). PAH fingerprint ratios, such as phenanthrene to anthracene (Ph/An) and fluoranthene to pyrene (Fl/Py) have been calculated to evaluate both petrogenic and pyrogenic (pyrolytic) PAHs (Magi et al., 2002; Chen et al., 2006; Yunker et al., 2002). Petrogenic PAHs are often characterized by Ph/An values $>10$, whereas combustion processes that result in the production of pyrolytic PAHs are specified by low Ph/An ratios ($<10$). Generally Fl/Py ratios greater than 1 come from pyrolytic origins while ratios of less than 1 seem to show petrogenic source (Qiu et al., 2009). In the present research, Ph/An ratios for water samples were 1.35, 1.33, 0.47 and 0.98 in four stations, respectively. The associated figures for Fl/Py ratio values were 1.08, 0.85, 0.91 and 1.56. In terms of sediment samples, Ph/An ratios in four sites were 0.73, 0.84, 0.78 and 0.78, respectively, while the respective figures for Fl/Py ratio values were 1.12, 2.03, 2.39 and 1.74. The contrary results indicated by the Ph/An and Fl/Py ratio indicated that there are pyrolytic and petrogenic PAH sources in the Soltan Abad River. As can be seen, PAHs have pyrolytic sources in sediment samples of all stations. The PAHs in water samples of first and fourth stations originate from pyrolytic sources, while in second and third stations these pollutants come from both pyrolytic and petrogenic sources (pyrolytic sources are more dominant).

These results were jibe with the results of the Langat River, Peninsular Malaysia (Riyahi Bakhtiari et al., 2009). In another study, Duke (2008) reported that the composition of PAHs in surface water was found to be largely different from that of the sediment of Ekpan Creek of the Warri River. While the origin of PAHs in the surface water was determined to be petrogenic because phenanthrene, anthracene, fluoranthene, pyrene, chrysene and Benzo[a]anthracene were not detected, PAHs in sediments were from pyrogenic sources. The results obtained in this study generally agree with their findings.

**Conclusion**

Present study provided quantitative information in order to evaluate PAH contamination in water and sediments of the Soltan Abad River at different seasons.

In water samples, LPAH compounds (2–3 rings) were found in concentrations several times higher than HPAHs (4–6 rings). Vice versa, sediments were heavily polluted by HPAHs.
The highest and the lowest mean concentrations of PAHs in both samples were found in autumn and summer, respectively. According to the ratios of Fluoranthene/Pyrene and Phenanthrene/Anthracene, the PAHs in all sediment samples originate from pyrolytic sources, while in water samples have different origins including pyrolytic and petrogenic sources.

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References


