Distribution, sources and ecological risks of polycyclic aromatic hydrocarbons in an urban landscape river

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ABSTRACT

The contents of 16 priority water-borne polycyclic aromatic hydrocarbons (PAHs) in water, potential external pollution sources and sediment from the famous landscape of the Qinghuai River were measured by gas chromatography–mass spectrometry (GC-MS). The distribution, composition, source and ecological risk of PAHs were analyzed. The following results were obtained: (1) Benzo[a]pyrene and benzo[ghi]perylene were not detected in all samples. The total contents of 16 priority PAHs (PAH16) varied from 52.5 to 745.3 ng l⁻¹ with the average of 174.0 ng l⁻¹ in water, from 96.0 to 1,064.6 ng l⁻¹ with the average of 329.2 ng l⁻¹ in potential sources, from 931.7 to 15,295.5 ng g⁻¹ with the average of 7,133.6 ng g⁻¹ in sediments. (2) The concentration of PAH16 in water is lower than in sediment and higher rings are more easily detected in sediment. The percentage of higher ring (four- to six-rings) PAHs accounted for more than 55.6% of PAHs in sediment. (3) The value of FLA/(FLA+Pyr) was higher than 0.5 at most sampling points which illustrated the source was related with petrogenic such as liquid fossil fuel combustion. (4) The potential ecosystem risk of low ring PAH for upstream conflux of external Qinhuai River was less than 10%, while it was 10–50% for other sampling points; The four rings PAH shows lower potential ecosystem risk than other ring PAH in this study area; Dibenzo [ah] anthracene (DahA) shows high potential ecosystem risk at all sampling points.

Key words | composition, distribution, ecological risk, PAHs, source, urban landscape river

INTRODUCTION

Polycyclic aromatic hydrocarbons (PAHs) are a class of diverse organic compounds that contain two or more fused benzene rings in linear, angular or cluster arrangements. They are ubiquitous pollutants formed from the combustion of fossil fuels and are widespread environmental contaminants that occur in the atmosphere, water, soil, sediment and organisms (Countway et al. 2003; Stout et al. 2004; Xu et al. 2006). Because many PAHs and their derivatives are strongly potent carcinogens and/or mutagens (Liu et al. 2001), it is significant to research the source, occurrence, transportation and fate of PAHs in natural environments (Chen et al. 2004).

PAHs in urban landscape rivers derive from many sources (e.g. discharge from wastewater treatment, storm water runoff and upstream conflux). The investigations into the concentrations and distribution of PAHs were mainly conducted in estuaries and marine alongshore in the past (Yunker et al. 2007) and few studies have been carried out to assess the distribution and accumulation of PAHs in inland landscape rivers (Manoli et al. 1999). This paper presents a comprehensive survey of PAHs in water and sediments of the Qinghuai River. It is intended to determine the concentration distribution and potential sources of PAHs in the aquatic environments of the Qinghuai River Watershed, to assess the level of contamination and the ecological effects, and to provide useful background data for future studies, wastes disposal or management.

METHODS

Sampling and pretreatment

Eighteen water samples, nine samples from potential external pollution sources (five samples of sewage pumping
station outflow; one sample of outflow from a storm water pumping station; one sample of discharge from a wastewater treatment plant (WWTP); two samples from the upstream river and five sediment samples were collected from the Qinhuai River on 20th January, 20th April and 20th May 2010, respectively. The samples were taken on the same day in order to avoid the effect of weather. The urban landscape Qinhuai River is controlled manually by water gate. The samples from pumping stations were taken from the forebay of the pumping station, of which the concentration can be representative because each pumping has stable work conditions. So we planned to take the water samples and potential external pollution sources on the same day to investigate the general PAHs concentration in this studied river. The study area and sampling location are shown in Figure 1. The details about the sampling points are listed in Table 1.

Because of the low depth of the water column in the studied river, water samples used in this study were taken from the top layer (0.5 m depth) in dry weather conditions using 2 L pre-cleaned dark glass bottles. The samples from pumping stations were taken from the forebay of the pumping station. The samples from the discharge of the WWTP were collected from the outlet of the WWTP connected to the river.

Surface sediment (0-20 cm) samples were collected using a grab sampler (Van Veen Bodemhapper 2 l) and put in aluminum containers. The sediments were kept in the refrigerator at −60 °C before analysis. Frozen aliquots of sediments were freeze dried by a freeze drier (FD-1A, China), ground with a mortar, sieved through a 60-mesh sieve and then stored in pre-cleaned dark glass bottles before extraction.

All samples were placed in an icebox after sampling and transported to the laboratory immediately. The water was then filtrated through a 0.45 μm filter and all samples were stored in the refrigerator at 4 °C before analysis. All containers in contact with the sample were previously washed with deionized water, acetone, dichloromethane and the river sample in sequence to eliminate disturbance from other organic materials.

Chemical reagents

Reference PAHs (16 compounds, PAH-Mix63) were obtained from ANPEL Inc. (ANPEL, Shanghai); deuterated surrogate (Su) containing naphthene-d8 (200 μg ml−1),acenaphthene-d10 (200 μg ml−1), phenanthrene-d10 (250 μg ml−1) and chrysene-d12 (500 μg ml−1) were obtained from AccuStandard Inc. (AccuStandard, USA), and internal standards (IS) of hexamethylbenzene were obtained from Aldrich Co. (Aldrich Co., USA). All solvents used for
Filtered water samples (2 L) were extracted using a solid phase extraction (SPE) system from SUPELCO, following established procedures (Zhou et al. 2000, Zhao et al. 2009). Three grams of freeze-dried sediment were extracted with 50 ml dichloromethane/hexane (1:1, v/v) for 48 h in a water bath maintained at 60 °C (Mai et al. 2001; Tolosa et al. 2004).

The extract of water and sediment samples was passed to a C18 SPE column (Supelco, 500 mg) connected with a HLB column (Waters, 500 mg) for enrichment. The water was spiked with 5 ml (1 mg l⁻¹) acenaphthene-d₁₀ (in hexane) as a surrogate standard prior to extraction. Fifteen grams of freeze-dried sediment was spiked with 1 ml surrogate standard containing naphthene-d₈, acenaphthene-d₁₀, phenanthrene-d₁₀ and chrysene-d₁₂, and Soxhlet extracted with 250 ml dichloromethane/hexane (1:1, v/v) for 24 h in a water bath maintained at 60 °C. First, the aliphatic hydrocarbons were eluted with 15 ml of hexane by K-D concentration. Then, the effluents containing PAHs were collected by eluting 70 ml of hexane/DCM (7:3, v/v), and were concentrated to 0.5 ml under a gentle purified N₂ stream.

PAHs were analyzed using a ThermoQuest gas chromatograph/mass spectrometer (GC/MS) (ThermoQuest, San Jose, CA, US). The GC/MS conditions for sample analysis were as follows: the injection port, interface line, and ion source temperature were maintained at 280 °C. Column temperature was programmed at 80 °C (keep for 2 min) increasing at 3 °C/min to 120 °C, then increasing at 5 °C/min to 200 °C, 200–290 °C at a rate of 7 °C/min and kept at 290 °C for 15 min.

Every sample had three parallel samples which were subject to strict quality control procedures. For PAHs, deuterated surrogate standards were used to compensate for losses involved in the sample extraction and work-up. Surrogate standards in water and sediment samples were determined with good precision. The recovery and detection limits of PAHs using this method are shown in Table 2.

### RESULTS AND DISCUSSION

#### PAH distribution in water and sediment

The PAH concentrations in the surface water and sediment are listed in Table 3. There is also a comparison with other research results. The average percentage of PAHs composed of different rings in water and sediment in the Qinhuai River.
is shown in Figure 2. PAH content and composition in the Qinhuai River are shown in Figure 3. The benzo[a]pyrene (BaP) and benzo[ghi]perylene (BghiP) were not detected in all samples, the total PAH concentration in water ranged from 52.5 (W1) to 754.3 (W17) ng l$^{-1}$, with an average concentration of 174.0 ng l$^{-1}$. Compared with other research results, the average concentration of PAHs is lower than in the Daliao River (Zhao et al. 2003).
Watershed (Guo et al. 2007) and Tianjing River (Shi et al. 2008), while it is higher than Taihu Lake (Qiao et al. 2012). The total PAH concentration in the potential sources ranged from 96.0 (SP2) to 1,064.7 (SP5) with an average concentration of 329.2 ng l\(^{-1}\), and the effluent from the rainfall-sewage pumping station has an obvious effect on the PAH concentration downstream.

In terms of individual PAHs in sediment, the composition characteristic was different from that in water. The total PAH concentration in sediment ranged from 931.7 (S4) to 15,295.5 (S2) ng g\(^{-1}\), with an average concentration of 7,133.6 ng l\(^{-1}\). The upstream concentration of the external Qinhuai River is better than the upstream of the Yunliang River and the average concentration of PAHs in sediment is much higher than those found by other research listed in Table 3.

The percentage of three-ring PAHs accounted for more than 43.2% of PAHs in water (Figure 2). The composition of PAHs between water and potential sources are similar. The PAH concentration in water is lower than in sediment. The sediment samples were dominated by PAH compounds with four rings (29.6%) and five/six rings (26.0%). The presence of a high proportion of high-molecular-weight PAHs in sediments is similar to the results of previous studies. (Chen et al. 2004; Shen et al. 2009).

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**Figure 2** | The average percentage of PAHs composed of different numbers of rings in water, potential sources and sediments. **Note**: two rings (NAP, ACY, ACE, FLU); three rings (PHE, ANT, FLA); four rings (PIR, BaA, CHR, BbF, BkF); five to six rings (BaP, Daha, IcdP, BghiP).

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**Figure 3** | PAH content and composition in the Qinhuai River (a): water; (b): potential external sources; (c): sediments.
As shown Figure 3(a) and Figure 3(b), the potential external sources with high concentration (SP5) can obviously affect the concentration of PAH downstream (W5 and W4); the sampling points near the river confluence location (W1 and W7) has a higher concentration of PAH, which may be caused by the disturbance of sediment; the sampling points at the central urban area (W15, W16 and W18) have a higher concentration than the sampling points at urban areas or suburban areas (W2, W3, W6, W8, W9, W10, W12), which may be caused by the traffic and population density.

Comparing Figure 3(a) with Figure 3(c), the individual composition of PAHs in water samples varied from three-ring PAH to four- to six-ring PAH (Figure 2). Such a difference in contaminant composition by individual PAHs is expected to be due to different PAH input and the characteristics of the PAH. Firstly, river water receives direct PAH inputs from various sources, including wastewater discharge, runoff, atmospheric fallout, etc. Secondly, low molecular mass PAH gradually decrease by degradation and adsorption, only those PAHs that have relative high molecular mass are more resistant to degradation and so can succeed to reach the sediment.

Analysis for sources of PAHs

PAHs enter river environment systems mainly via atmospheric fallout, urban runoff, municipal/industrial effluents, and oil leakage (Wetzel & Van Vleet 2004; Shi et al. 2005). The sources of PAHs are mainly anthropogenic PAHs (Beg et al. 2005), which are formed mainly via two mechanisms: fuel-combustion (pyrolytic) and discharge of crude oil related materials (petrogenic). They may be identified by ratios of individual PAH compounds based on peculiarities in PAH composition and distribution pattern as a function of the emission source (Zhang et al. 2003, 2004). Some ratios of selected PAH compounds could be used to assess the possible origins of PAHs. For example, the abundance ratio of two- to three-ring hydrocarbons to four- to six-ring hydrocarbons PHE/ANT, FLA/(FLA+Pyr), IcdP/(IcdP+BghiP) can be applied to help distinguish the petrogenic and pyrolytic sources (Yunker et al. 2005; Doong & Lin 2004). However, the diagnostic ratios of PHE/ANT and IcdP/(IcdP+BghiP) were not suitable for use in this study because the concentration of ANT and BghiP were not detected in all samples.

In order to survey the sources of PAHs in the Qinhai River, FLA/(FLA+Pyr) were plotted (Table 4, Figure 4) FLA/(FLA+Pyr) ratio of 0.4 is defined as the pyrogenic origins/petrogenic origins transition point, i.e. the ratio less than 0.4 corresponded to petrogenic origin pollutants while higher than 0.5 is characteristic of pyrogenic origin combustion. As shown in Figure 4, the majority of the ratios is higher than 0.5, which illustrates that the sources are related with liquid fossil fuel combustion such as vehicle and crude oil.

Table 4 | Diagnostic ratios for source identification in the studied area

<table>
<thead>
<tr>
<th>Reference ratio</th>
<th>Pyrogenic origins</th>
<th>Petrogenic origins</th>
<th>Water samples</th>
<th>Potential external source samples</th>
<th>Sediment samples</th>
</tr>
</thead>
<tbody>
<tr>
<td>FLA/(FLA+PYR)</td>
<td>&gt;0.5</td>
<td>&lt;0.4</td>
<td>0.44–0.71</td>
<td>0.38–0.67</td>
<td>0.41–0.65</td>
</tr>
</tbody>
</table>

Figure 4 | The ratio FLA/(FLA+PYR) for each sampling location.
Potential ecosystem risk assessment

Lower molecular mass compounds usually tend to show higher lethal toxicity than the larger PAHs. The maximum concentration of benzo[a]pyrene in surface waters is generally 2.8 ng l\(^{-1}\) (Environmental Quality Standards for Surface Water 2002). The benzo[a]pyrene was not detected in this study which tends to indicate there is low potential ecosystem risk in the surface water of the Qinhuai River.

Although there are many research works about potential ecosystem risk assessment of sediment, a uniform standard has not been established. In order to assess the sediment quality, the PAH levels in sediment were compared against effect-based guideline values (Long et al. 1995, 1998) such as the effect range-low (ER-L) and effects range-median (ER-M) (Table 4). Concentrations of PAHs in sediments are less than ER-L, suggesting that the probability of negative toxic effect is lower than 10%; concentrations higher than ER-M indicated that the probability exceeded 50%. The following equation was used to assess the potential ecosystem risk of sediment:

\[ R = 100 \times \left( \frac{C}{C_{ERL}} \right) \]

Here, \( C \) is the concentration the PAHs; \( R \) is pollution ratio. The calculation results are listed in Table 5.

Due to the content of low ring PAH (NAP, ACY, ACE, FLO, PHE and ANT) in sediment of the Yunliang River and the external Qinhuai River varying between the ER-L (effects range low) and ER-M (effects range median), their probabilities of ecological risks were estimated between 10 and 50%. The potential ecosystem risk of low ring PAH for upstream conflux of the external Qinhuai River was less than 10% because the content of low ring PAH is less than ERL. The four-ring PAH shows lower potential ecosystem risk than PAHs composed of other rings in this study area. DahA shows high potential ecosystem risk in all sampling points.

CONCLUSIONS

PAHs in water and sediment samples collected from the landscape of the Qinhuai River in Nanjing city were evaluated. The results reveal that the level of PAHs in water samples was not so high in the dry weather in the nonfood season. However, the concentration in sediment was relatively high. The percentage of three-ring PAHs accounted for more than 43.2% of PAH in water. The PAHs concentration in water is lower than in sediment and higher rings are more readily detected in sediment. Furthermore, ratio analysis revealed that PAHs in the landscape of the river were primarily of pyrogenic origin, most likely due to high input from the combustion of gasoline and diesel emissions. Finally, the potential ecosystem risk of low ring PAH for upstream conflux of the external Qinhuai River was less than 10% and 10–50% for other sampling points; the four ring PAH shows lower potential ecosystem risk than other ring PAHs in this study area; DahA shows a high potential ecosystem risk at all sampling points.

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