Occurrence and health risk assessment of polycyclic aromatic hydrocarbons (PAHs) in water resources of the typical plain river network area

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Abstract. Drinking water sources play a significant role in providing water for urban residents and public services. The pollution and health risk of polycyclic aromatic hydrocarbons in drinking water sources have attracted extensive attention. In this study, river water samples were collected from two drinking water resources of the typical plain river network area in eastern China, and tap water samples were collected from public places. The concentration of the 16 priority PAHs in river water and drinking water were determined by SPE-GC-MS. The results indicated that the concentrations of Σ16PAHs ranged 128-183 ng/L in the autumn and 61.3-87.3 ng/L in the winter, respectively. The cancer risks and non-cancer risks of adults associated with drinking water intake were low, but it still deserved more attention.

1. Introduction
Polycyclic aromatic hydrocarbons (PAHs) are a class of persistent organic pollutants (POPs), which are hydrocarbons composed of two or more benzene rings in a linear, angular or cluster form [1,2,8]. In recent years, they have received widespread attention due to their persistence, bioaccumulation and biotoxicity in the water environment [1-4]. PAHs are mainly derived from human activities, such as coal burning and vehicle emissions [3]. They can enter surface water through oil spills, municipal and industrial wastewater, atmospheric subsidence and land runoff, which causes pollution of surface water and poses serious risks to the human health [4,5,8].

Jiaxing is located in the typical plain river network of the Yangtze River delta in Zhejiang Province, China [7]. The river network of Jiaxing is part of the Jiangnan River network and is closely connected with the river network of the neighboring cities. About 70% of the surface water comes from the upstream, which has a great impact on the water quality of the drinking water resources in Jiaxing. The protection of drinking water resources is deemed as a priority in administrative regions worldwide [8]. In consequence, it is essential to study PAHs in water source and drinking water.

The aims of the research were to: 1) detect the concentrations of 16 PAHs in the river water and drinking water; 2) conduct PAHs health risk assessment for adults in water resources locations.

2. Materials and methods

2.1. Sampling and experimental materials
River water samples were sampled from two water resources in Jiaxing, Zhejiang Province. The region of two drinking water resources belongs to the typical plain river network area in eastern China. Tap
water samples were collected from public places such as schools. Clean brown bottles (4L) were used to collect water during November 2018-January 2019. Eventually, total of 8 river water samples and 8 drinking water samples were collected and stored at 4 °C until analysis.

Dichloromethane (HPLC), acetone (HPLC), n-hexane (HPLC) and methanol (HPLC) used for PAHs extraction were supplied by J&K Scientific (Shanghai, China). The standard solution of 16 USEPA priority PAHs was purchased from J&K Scientific (Shanghai, China). The standard solution contained naphthalene (NAP), benzo(a)anthracene (BaA), acenaphthylene (ACL), phenanthrene (PHE), fluorene (FLE), anthracene (ANT), benzo(g,h,i)perylene (BghiP), pyrene (PYR), fluoranthene (FLU), chrysene (CHR), benzo(b)fluoranthene (BbF), benzo(k)fluoranthene (BkF), acenaphthene (ACE), indeno(1,2,3-cd)pyrene (IDP), dibenzo(a,h)anthracene (DBahA) and benzo(a)pyrene (BaP). Chrysene-d12 (CHR-d12) and phenanthrene-d10 (PHE-d10) purchased from J&K Scientific (Shanghai, China) were pre-treated with the sample as surrogate standards. HC-C18 solid-phase extracted (SPE) cartridges were purchased from ANPEL Laboratory Technologies (Shanghai, China) Inc.

2.2. Sample preparation and testing
All collected water samples were filtered through a 0.7 μm GF/F glass fiber filter. After adding 200 ng surrogate standards, one liter of water sample was extracted using the Supelco solid-phase extraction (SPE) system. Before sample loading, SPE cartridges were washed with 10 mL dichloromethane, 10 mL methanol and 10 ultrapure water, respectively. The sample was then drained into the column (5mL/min) under vacuum and eluted with a dichloromethane/n-hexane mixture (10mL, 1:1/v:v). Next, the extract was evaporated to near dryness under a mild nitrogen flow. Finally, the extract was transferred to a brown vial and re-dissolved to 0.5 mL with n-hexane.

The concentrations of PAHs in the extracts were measured by an Agilent 7890A-5975C gas chromatograph-mass spectrometer (GC-MS). The chromatographic column was a DB-5MS (30 m×0.25 mm×0.25 μm) capillary column. The inlet temperature was 280 °C. The stepped temperature procedure used was as follows: initial temperature was 80 °C (for 2 min), rose to 180 °C at 8 °C/min, then rose to 300 °C at 7 °C/min (for 5 min). The carrier gas was high purity helium gas, and the injection volume was 1 μL with splitless injection.

2.3. Quality assurance and quality control
In the process of sample detection, methods such as method blanks, spiked blanks and parallel sample were used for quality control. The recoveries of two surrogate standards range 59.1%-121.9% (CHR-d12) and 51.4%-124.2% (PHE-d10), respectively. The method detection limits (MDLs) were defined as the concentrations when signal-noise ratio (S/N) is three. If the sample concentration was lower than the MDL, it was identified as n.d (not detected). Target compounds were not detected in the blank sample.

2.4. Methods of assessing health risk
Incremental lifetime cancer risk (ILCR) in contact with carcinogens refers to the probability that an individual will afflict with cancer on account of lifetime exposure. The ILCR was calculated by equation (1) [3,4,6].

\[
\text{ILCR} = DI \times SF = \frac{C_{PAH} \times IR \times EF \times ED}{BW \times AT_{IL}} \times SF_{PAH}
\]  

where \(C_{PAH}\) is the concentration of carcinogenic PAH compounds (BaA, CHR, BbF, BkF, BaP, IDP and DBahA) in potable water (ng/L). BW is the body weight (kg); ED is the exposure duration (year); EF is the exposure frequency (365 day/year); IR represents the intake rate of drinking water (L/day); AT represents the lifetime (day) and SF_{PAH} means the slope factor of aforementioned PAH ((mg/kg/day)^{-1}).

When assessing the probability of non-cancer risk, it is necessary to compare the approximated daily intake of chemicals over a period of time with the RfD of the chemical obtained during the same exposure time. The comparison accounts for Hazard Quotient (HQ) of non-cancer risk that was calculated by equation (2) [3,4,6].
\[ HQ = \frac{DI}{RfD_{PAH}} = \frac{C_{PAH} \times IR \times EF \times ED}{BW \times AT \times RfD_{PAH}} \]  

(2)

where \( C_{PAH} \) is the concentration of non-carcinogenic PAH compounds (NAP, ACE, FLE, ANT, FLU, PYR and BaP) in potable water (ng/L); \( RfD_{PAH} \) means the reference dose of above-mentioned PAH compound (mg/kg/day).

### 3. Results and discussion

#### 3.1. Concentrations of 16 PAHs in the river water and drinking water

Four points (R1, R2, R3, R4) were selected from the upstream river of the two water sources. The overall concentration of 16 priority PAHs ranges were 128 to 183 ng/L in the autumn and 61.3 to 87.3 ng/L in the winter, respectively. It can be found that the concentration of PAHs in autumn is higher than that in winter. The main reason may be the low rainfall in winter and the decrease of PAHs entering the river by means of atmospheric deposition and surface runoff. In addition, due to the lower temperature in winter, the solubility of PAHs in surface water will also decrease. The concentration of \( \Sigma_{16} \)PAHs in winter (January) in this study is similar to the level of PAHs which ranged from 46.5 to 244 ng/L (January) in surface water from Taihu Lake Basin [9].

![Figure 1. Concentration and seasonal variation of \( \Sigma_{16} \)PAHs in the river water](image-url)
Figure 2. Concentration and seasonal variation of Σ16PAHs in the potable water.

Other four points (D1, D2, D3, D4) were tap water samples which collected from public places. The concentration of Σ16PAHs ranged from 17 to 34.5 ng/L in drinking water, and the concentration of BaP ranged n.d-0.84 ng/L. The measurement data of Σ16PAHs and BaP in this investigation are lower than China National drinking water standards (GB5749-2006) of 2000 ng/L and 10 ng/L, respectively. Compared with the studies in other cities, the concentration of Σ16PAHs and BaP were lower than the median (38.80 ng/L; 0.85 ng/L) of reported data from 78 cities in China [3].

3.2. PAHs health risk assessment for adults in potable water

According to USEPA (2019) [10] and Exposure Factors Handbook of Chinese Population (Adults) [11], the parameters in the risk assessment method were listed in Table 1 and Table 2.

Table 1. The parameters for health risk assessment.

| Gender | IR(L/day) | EF(day/year) | Lifetime(year) | ED(year) | BW(kg) | AT(day) |
|--------|-----------|--------------|----------------|----------|--------|---------|
| man    | 1.875     | 365          | 75.6           | 57.6     | 67.4   | 21389   |
| woman  | 1.62      | 365          | 80.2           | 62.2     | 55.3   | 23068   |

Table 2. The RfD and SF of PAHs

| Compounds       | Abbr. | RfD (mg/kg/day) | SF (mg/kg/day)^{-1} |
|-----------------|-------|-----------------|---------------------|
| Naphthalene     | NAP   | 0.02            |                     |
| Acenaphthylene  | ACL   |                 |                     |
| Acenaphthene    | ACE   | 0.06            |                     |
| Fluorene        | FLE   | 0.04            |                     |
| Phenanthrene    | PHE   |                 |                     |
| Anthracene      | ANT   | 0.3             |                     |
| Fluoranthene    | FLU   | 0.04            |                     |
| Pyrene          | PYR   | 0.03            |                     |
| Benzo[a]anthracene | BaA | 0.1             |                     |
| Chrysene        | CHR   | 0.001           |                     |
| Benzo[b]fluoranthene | BbF | 0.1             |                     |
The overall cancer risks of seven carcinogenic PAHs for adults (man and woman) by drinking water ingestion were \(7.07 \times 10^{-9} - 9.91 \times 10^{-9}\) and \(7.57 \times 10^{-9} - 1.06 \times 10^{-8}\), respectively. They were at the level of \(10^{-9} - 10^{-8}\). USEPA recommended the accredited risk level \((10^{-4} - 10^{-6})\), and the Dutch environmental protection department deemed that it was neglectable when the risk was at the level of \(10^{-8}\) [3]. The cancer risks level of PAHs for adults in water resources locations were lower than the former and were consistent with the latter. These pointed out that the PAHs in potable water resource of the typical plain river network area are not obvious to the human health risks, but it still deserved long-term attention. The total non-cancer risks of 16 PAHs for adults (man and woman) via drinking water ingestion were \(8.02 \times 10^{-6} - 1.96 \times 10^{-5}\) and \(8.44 \times 10^{-6} - 2.06 \times 10^{-5}\), respectively. The results of HQ were much lower than 1, so the non-cancer risks of PAHs in drinking water have a low impact on residents’ health.

4. Conclusion

In the study, concentrations of 16 priority PAHs in the river water and drinking water were detected, and adults (man and woman) cancer risks and non-cancer risks of PAHs in the location of drinking water resources were evaluated. The results suggested that the pollution of PAHs in potable water resources were relatively low. The health risks associated with drinking water intake were low and acceptable in drinking water resources of the typical plain river network area, but it still need to be concerned.

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