Characteristic polycyclic aromatic hydrocarbons and their sources in surface water in North China

J Zhang1, Y Z Wang1,2, X Z Meng1, S L Zhang1 and W Xu1
1Center of Monitoring and Scientific Research of Ecology and Environment, Administration of Ecology and Environment of Haihe Basin and Beihai Area, Ministry of Ecology and Environment of People’s Republic of China, Tianjin, 300170, China
2Email: xiaoyiw858@163.com

Abstract. Sixteen priority polycyclic aromatic hydrocarbons (PAHs) in nine typical surface water sources in North China have been analyzed by solid phase extraction-gas chromatography tandem triple four-stage mass spectrometry (SPE-GC-MS-MS). The results showed that eleven in sixteen PAHs were detected except BkFL, BaP, InP, BghiP and DBA. The range of total PAHs in spring water body of nine water sources is 23.76-71.47 ng/L, and that is 83.72-277.8 ng/L in summer. The results showed that the seasonal pollution of PAHs was significantly different, and the pollution status of PAHs in summer was significantly higher than that in spring because the non-point source pollutants including PAHs would easily enter surface water sources with rainfall-runoff. The results also showed that the PAHs are mainly composed of medium and low cyclic aromatic hydrocarbons (2-3 rings). In addition, the ratios of Ant/(Phe+Ant), Flu/(Pyr+Flu) and BaA/(BaA+Chr) indicate the PAHs pollutants should be mainly from coal and wood burning in the upstream area of these water sources, entering water sources through surface runoff, which is not obviously affected by the pollution of oil leakage and discharge. Generally, the concentration of the PAHs in surface water sources in North China is still lower, but it is suggested that we should pay more attention to PAHs risk assessment for the drinking water sources.

Keywords: Polycyclic aromatic hydrocarbons; North China; Surface water; GC-MS;

1. Introduction
Polycyclic aromatic hydrocarbons (PAHs) are a kind of persistent organic pollutants, and widely exist in the natural environment such as water, soil etc[1-3]. PAHs are of great concern for environmental toxicology, long-term transport and bioaccumulation [4-5]. In recent years, more and more research on PAHs pollution in the environment has been conducted all over the world[6]. PAHs are defined by having more than two benzene rings, including more than 10,000 possible individual compounds[7-8]. For the environmental toxicology, sixteen PAHs have been controlled as priority control pollutants by USEPA[9]. It is important to pay attention to the regional environmental risk assessment in North China in which some national development strategies such as Beijing-Tianjin-Hebei Cooperative Development Strategy and Plan for Xiongan New Area are located.

2. Materials and methods
2.1. Location and sampling
Most surface water sources in North China are big reservoirs along Yanshan and Taihang Mountains, located in the West and North of the Haihe River Basin. In this study, 9 reservoirs have been selected including Taolinkou Reservoir, Yanghe Reservoir, Yuecheng Reservoir, Gangnan Reservoir, Xidayang Reservoir, Yuqiao Reservoir, Panjiakou Reservoir, Daheiting Reservoir and Shihe Reservoir (Figure 1). All sampling points are near to water intake of these reservoirs, in which it is directly reflects the supply water quality of these reservoirs. All the samples were collected in 2017, which were under refrigerated conditions at 4°C during storage.

![Figure 1. The location of 9 surface water sources in North China.](image)

1. Yuecheng Reservoir; 2. Gangnan Reservoir; 3. Xidayang Reservoir; 4. Yuqiao Reservoir; 5. Panjiakou Reservoir; 6. Daheiting Reservoir; 7. Taolinkou Reservoir; 8. Yanghe Reservoir; 9. Shihe Reservoir

2.2. Instruments and chemicals
In the study, a gas chromatography-tandem mass spectrometry (Agilent 7890A/7000B) was used. In addition, a solid phase extraction equipment were used for samples pretreatment.
Sixteen PAHs compounds were purchased from AccuStandard, Inc, including acenaphthylene(AcPy), naphthalene(Nap), acenaphthene(AcP), fluorene(FL), phenanthrene(Phe), anthracene(Ant), fluoranthene(Flu), pyrene(Pyr), benz[a]anthracene(BaA), chrysene(Chr), benz[b]fluoranthene(BbFL), benz[k]fluoranthene(BkFL), benzo[a]pyrene(BaP), indeno[1,2,3-cd]pyrene(InP), benzo[g,h,i]pylene(BghiP) and dibenz[a,h]anthracene(DBA). Ethyl acetate and dichloromethane were purchased from Duksan Pure Chemicals. Methanol was purchased from J.T. Baker.

2.3. Sample pretreatment
All samples were filtered, and then enriched with extraction column, which were cleaned with 5ml ethyl acetate and 5 mL dichloromethane with 3 mL/min flow rate, and preconditioned using 10 mL methanol and pure water with 10 mL/min flow rate. 100ml water were treated under vacuum at 15
mL/min. Then the cartridges were eluted with ethyl acetate, dichloromethane, dichloromethane, respectively. The elutes were evaporated to near dryness under a gentle nitrogen stream and then dissolved in dichloromethane to a final volume of 1.0 mL for GC/MS/MS analysis.

2.4. GC/MS/MS analysis
The PAHs was measured by an Agilent 7890A/7000B GC/MS/MS with HP-5MS column (30m×0.25mm×0.25μm). The carrier gas is Helium and the initial temperature is 80°C. The temperature was maintained for 1 min, and increased to 250°C at 20°C/min, then to 300°C at 10°C/min, and maintained for 5.5 min. The mass spectrometer was operated with electron ionization energy of 70 eV. The temperature of ion source and quadruple was 230°C and 150°C, respectively. The parameters of MS were optimized by Scan and Productor mode. The samples are detected by the mode of multiple reaction monitoring (MRM).

2.5. Quality assurance and control
The quality control and assurance were implemented based on the requirements of the Regulations for Water Environment Monitoring of China. The whole program blank and laboratory blank were used for possible contamination. The results showed that the background of PAHs would be negligible in either in the field or in the lab. In addition, the recovery of the spiked samples ranged from 69.8% to 111.6% for sixteen PAHs with 4.9-12.6% of standard deviation of relative error.

3. Results and discussion
3.1. Seasonal occurrence of PAHs
Tables 1 showed the results of sixteen PAHs pollution of nine surface water sources in North China in spring and summer, respectively. The total amount of PAHs in each surface water sources is 23.76-71.47 ng/L with an average of 41.33 ng/L in spring, while is 83.72-277.8 ng/L with an average of 142.1 ng/L in summer. The total amount of PAHs is the highest in Yuqiao reservoir in spring and in Taolinkou reservoir in summer. For the 16 PAHs, eleven compounds were detected except BkFL, BaP, InP, BghiP and DBA in surface water sources in North China. Phe and Nap are the major compounds in these water sources. The results showed that pollution of PAHs is higher in summer than that in spring for all water sources, which is about 1.7 to 9 times. Therefore, the seasonal difference of PAHs pollution is quite obvious in these water sources, especially in Taolinkou reservoir. The phenomenon of seasonal difference of PAHs is similar to other reports that the concentration of PAHs is higher in summer [10-11]. The PAHs pollution is more serious in summer, presumably because summer is rainy season in North China. In rainy season, the non-point source pollutants including PAHs would easily enter surface water sources with rainfall-runoff.

The results indicate that the concentration of any compound of PAHs in the study area is lower than the limits of different water quality standards of China, US and EU. In addition, based on recent reports about PAHs pollution, concentration of PAHs in the research should be much lower compared with rivers and lakes at home and abroad [12-18].

Table 1. The concentration of PAHs in North China in spring and summer (ng/L).

| Season | 1   | 2     | 3     | 4     | 5     | 6     | 7     | 8     | 9     |
|--------|-----|-------|-------|-------|-------|-------|-------|-------|-------|
| Spring | 49.23 | 40.9 | 23.76 | 71.47 | 35.74 | 50.3 | 28.14 | 40.3 | 32.15 |
| Summer | 126.53 | 83.72 | 131.59 | 177.66 | 87.25 | 84.46 | 277.8 | 172.47 | 137.39 |

3.2. Composition of PAHs
Figure 2 and 3 shows the result of PAHs in spring and summer in these water sources. The results indicate that 3-ring PAHs are the main component, followed by 2- ring and 4-ring, and the proportion of 5-ring is very small. In spring, the proportion of 3-ring PAHs range from 32.6% to 77.4%, the proportion of 2-ring and 4-ring range from 3.5% to 58.6% and 7.5% to 43.6%. The concentration of 2-ring, 3-ring and 4-ring PAHs is the highest in Yuqiao Reservoir, Gangnan Reservoir, Xidayang Reservoir, respectively. In summer, the proportion of 3-ring PAHs range from 29.1% to 65.5%, the proportion of 2-ring and 4-ring range from 10.3% to 60.2% and 10.0% to 43.5%. The concentration of 2- ring, 3-ring and 4-ring PAHs is the highest in Taolinkou Reservoir, Xidayang Reservoir, Yuecheng Reservoir, respectively.

![Figure 2](image1.png)

**Figure 2.** The Proportions of PAHs rings in nine water sources in spring.

![Figure 3](image2.png)

**Figure 3.** The Proportions of PAHs rings in nine water sources in summer.

### 3.3. Sources of PAHs

Human activities are the main sources for PAHs in the water environment, including petrogenic and pyrogenic sources. Pyrogenic PAHs are mainly from incomplete combustion used in different human activities. Petrogenic PAHs are mainly from crude oil in the process of exploitation and use [19-20]. The ratios of Flu/(Pyr+Flu), Ant/(Phe+Ant), and BaA/(BaA+Chr) are frequently used to distinguish the sources of PAHs [21-24]. PAHs are usually from petrogenic sources when the ratio of Ant/(Phe+Ant) is less than 0.1, whereas are from vehicle exhaust emissions and the combustion of crude oil, coal et al when the ratio is more than 0.1. PAHs are usually from petrogenic sources when
the ratio of Flu/(Flu+Pyr) is less than 0.4, while are from combustion of gasoline, kerosene, crude oil when the ratio is between 0.4 and 0.5, and are from combustion of biofuel such as coal, grass and wood when the ratio is more than 0.5. PAHs are usually from petrogenic sources when the ratio of BaA/(BaA+Chr) is less than 0.2, while are from pyrogenic sources when the ratio is more than 0.35, and might be from a mixture of petrogenic and combustion sources when the ratio is between 0.2 and 0.35.

Table 2 shows the ratios of Flu/(Flu + Pyr), Ant/(Ant + Phe) and BaA/(BaA+Chr) in spring and summer. The results show that the ratios of Ant/(Phe+Ant) in nine water sources in spring and summer are all more than 0.1, the ratios of Flu/(Pyr+Flu) are all more than 0.5, and the ratios of BaA/(Chr + BaA) are all more than 0.35. There is with no significant difference between spring and summer. Therefore, it is suggested that the PAHs pollutants in nine water sources should be mainly from coal and wood burning in the upstream area of these water sources, entering water sources through surface runoff.

**Table 2. Characteristic Ratio of the PAHs of water sources in North China in spring and summer.**

| ratio              | season | 1   | 2   | 3   | 4   | 5   | 6   | 7   | 8   | 9   |
|--------------------|--------|-----|-----|-----|-----|-----|-----|-----|-----|-----|
| Ant/(Ant + Phe)    | spring | 0.14| 0.15| 0.12| 0.13| 0.16| 0.16| 0.14| 0.14| 0.11|
|                    | summer | 0.13| 0.14| 0.18| 0.16| 0.19| 0.13| 0.17| 0.14| 0.13|
| Flu/(Pyr+Flu)      | spring | 0.51| 0.87| 0.58| 0.64| 0.60| 0.61| 0.71| 0.70| 0.71|
|                    | summer | 0.64| 0.64| 0.63| 0.54| 0.52| 0.57| 0.65| 0.64| 0.64|
| BaA/(BaA+Chr)      | spring | 0.69| 0.70| 0.40| 0.68| 0.49| 0.81| 0.67| 1.00| 0.85|
|                    | summer | 0.58| 0.78| 0.70| 0.58| 0.72| 0.70| 0.71| 0.66| 0.58|

4. Conclusions

In this study, sixteen priority polycyclic aromatic hydrocarbons were detected in nine typical surface water sources in North China. The results indicated that eleven in sixteen PAHs were found except BkFL, BaP, InP, BghiP and DBA. The range of total PAHs in spring water body of nine water sources is 23.76–71.47 ng/L, and that is 83.72–277.8 ng/L in summer. The PAHs pollution is more serious in summer, presumably because the non-point source pollutants including PAHs would easily enter surface water sources with rainfall-runoff. In addition, the results showed the PAHs are mainly composed of medium and low cyclic aromatic hydrocarbons (2–3 rings). The ratios of Ant/(Ant + Phe), Flu/(Flu + Pyr) and BaA/(Chr + BaA) indicate the PAHs pollutants should be mainly from coal and wood burning in the upstream area of these water sources, entering water sources through surface runoff. It is not obviously affected by the pollution of oil leakage and discharge. Generally, the PAHs in surface water sources in North China is much lower than most published water quality standards and also lower than most rivers and lakes at home and abroad [1-2, 4-5,8]. However, it is important that we should take care of PAHs risk assessment in water sources for the health of people, especially for the drinking water sources.

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