The distribution characteristics of polycyclic aromatic hydrocarbons in typical water system of North China

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Abstract. The temporal and spatial distribution of PAHs in surface-water from the typical rivers of North China was investigated. PAHs in typical rivers ranged from n.d. to 1.98 ng/L. LMW PAHs (2 and 3-ring) were abundant in surface water with high detection frequencies in Beisanhe River, while HMW PAHs (4 and 6-ring) were abundant in Luanhe River. Specific PAHs with its ratios were measured in order to deduce the possible sources of PAHs contaminant. The results indicate that the PAHs were from combustion processes in Beisanhe River, while PAHs were from petroleum products in Luanhe River.

1. Introduction
Polycyclic aromatic hydrocarbons (PAHs) are series of typical persistent organic pollutants originating from fossil fuels or imperfect combustion, pyrolysis of other organic matter. PAHs are made up of two or more than two benzene rings arranging in linear, angular, or clumps of hydrocarbons. With the development of industry, the cost of coal and oil has risen sharply, which is the one of main reasons for PAHs [1]. PAHs have high octanol water partition coefficient, sediment/water partition coefficient, carcinogenicity, teratogenesis and mutagenicity [2, 3]. Therefore, PAHs can produce great harm to human health and ecological environment. In recent years, 16 PAHs have been enrolled in the items of priority-control pollutants [4, 5], and the issue of PAHs have been a great concern for scientist and the public.

Heihe River, one of the largest rivers in China, Luanhe River and Beisanhe River, two of the largest rivers in North China, flow across Hebei province and Tianjin. Previous studies focused on distribution, composition and sources of PAHs in water and sediments of upper reach of Huaihe River [6, 7]. However, there was little information about PAHs in Haihe River.

In this work, the distribution characteristics and possible sources of PAHs were detected to confirm the pollution levels in Luanhe River and Beisanhe River of North China. Furthermore, this work could provide the reference for the investigation of occurrence and trend of pollutants in river system.

2. Materials and methods

2.1. Instrument and method
Agilent HPLC 1260, Exlipse PAHs (3.5 μm, 2.1 × 100 mm), Oasis HLB (500 mg/ 6 mL, Waters, USA) was used in the study. PAHs are purchased from AccuStandard, 2 mg/mL. HPLC grade acetonitrile,
methanol, dichloromethane and formic acid were purchased from J.T. Baker Ltd, USA.

Equipment Condition: The mobile consist of water (A) and acetonitrile (B). The gradient was set up.
The temperature of column is 35°C, flow rate is 0.3 mL/min. The UV detection wavelength is 254 nm.

2.2. Sample pretreatment
The water samples gathered from Beisanhe River and Luanhe River in North China, including: 1 - SiDaoDian, 2 - DACaoPing, 3 - GuBeiKou; LuanHe River water system, 4 - PuHeKou, 5 - WuLongJi, 6 - LiuHeKou, 7 - KuanChengQu, 8 - TingBaShang, 9 - TingWangXiang, 10 - XiaChi, 11 - PanBaShang, 12 - PanJiaKou, 13 - ShiHeShuiKu, were chosen as research objects. 1 L of water samples of each section were kept in brown reagent bottle at 0°C.

Methanol and NaCl with 5 mL, respectively, solution (1 g/mL) were added into 500 mL water sample. The Oasis HLB was preconditioned with 5.0 mL of methanol, 5 mL dichloromethane and 5 mL ultra-pure water, successively. Thereafter, the water samples pass the Oasis HLB columns at 10 mL/min. The Oasis HLB column was then rinsed with 5 mL ultrapure water and dried under vacuum. After drying, each cartridge was eluted with 2 mL × 3 dichloromethane. The extracts were collected in a glass vial, reduced to minimum volume, and then dissolved in 40 % acetonitrile to a final volume of 1.0 mL.

![Figure 1. The concentration of PAHs in water sample from several rivers in north China.](image)

3. Results and discussion
The spatial and temporal distribution of PAHs in surface-water from the Beisanhe River and Luanhe River were investigated in this work. As shown in figure 1, 15 kinds of priority control of PAHs recommended by EPA of America including naphthalene (NAP), acenaphthene (ANA), benzo [a] anthracene (BaA), flexion (FLT), benzo [b] fluoranthene (BbP), benzo [k] fluoranthene (BKF) were not detected. However, fluorine (FLU), phenanthrene (PHE), anthracene (ANT), fluoranthene (FLU), Pyrene (PYR), benzo [a] pyrene (BAP), dibenzo (a, h) anthracene (DBA), Indeno (1, 2, 3 - cd) pyrene (IPY), Benzo (g, hi) perylene (BPE) were detected at all sampling sites. In addition, the PAHs in Beisanhe and Luanhe ranged from n.d. to 0.0581 ng/L, n.d. to 1.98 ng/L, respectively. The United States has released carcinogenic PAHs concentration in groundwater was 0.2 ~ 6.9 ng/L, and the concentration in the surface-water was 0.1 ~ 800 ng/L, most in 2 ~ 50 ng/L [9]. Thus, the concentration of PAHs in Beisanhe and Luanhe River are not cause of cancer.
3.1. **Source of PAHs**
PAHs were primarily derived from Chemical sources (e.g. oil spills) and pyrogenic processes, including the combustion of organic matter such as coal and wood combustion. According to research, the relative abundance of the PAHs reflects its origin [8]. Main sources of PAHs are surface-water with atmospheric precipitation, city life sewage, industrial emissions (waste water and waste), surface runoff. PAHs in the groundwater mainly come from polluted surface-water leakage or supply, sewage irrigation, the soil pollution by solid waste disposal site and the infiltration [9, 10]. The United States has released carcinogenic PAHs concentration in groundwater which was 0.2 ~ 6.9 ng/L, and the concentration in the surface-water was 0.1 ~ 800 ng/L, most in 2 ~ 50 ng/L [11].

The low molecular weight (LMW) PAHs (2~3 rings, LPAHs) mainly originated from the pollution of petroleum and the PAHs (4 rings and above, PAHs) were derived from the fossil fuel combustion. The detected percentages of LPAHs (mainly including naphthalene acenaphthene, ANA, PHE, ANT and FLU and PAHs, PYR and BaA, BkF, BaP, DBA, IPY, BPE) were shown in figure 2. As can be seen, the distribution characteristics of PAHs changed with monitoring section. Considering the similar sampling period, the low ring PAHs were important component in Beisanhe River. While in Luanhe River the percentage of low ring PAHs was lower than that of middle ring PAHs.

![Image](https://via.placeholder.com/150)

**Figure 2.** The percentage of low and high ring PAHs in water sample from the section in north China.

The sources of PAHs could be diagnosed by the ratio of isomers [12, 13]. For example, when the ratio of Ant/(Ant + Phe) was above 0.1, [14] the PAHs was originated from combustion processes. When the ratio was below 0.1, the sources were fossil fuels burning [15]. When the Fla/(Fla + Pyr) [16] among 0.4 and 0.5, PAHs was originated from petroleum combustion. When ratio was below 0.4, the sources were petroleum combustion. The sources were from grass combustion, when the ratio was above 0.5. The Ant/ (Ant + Phe) in BeiSanHe samples were above 0.1, while in LuanHe water samples, the Ant/(Ant + Phe) were below 0.1. In all water samples, Pyr was not detected. All the results indicated PAHs sources of BeiSanHe River or Luanhe River were from combustion processes and fossil fuels burning, respectively.

4. **Conclusions**
The spatial and temporal distribution of PAHs in surface-water in Luanhe River and Beisanhe River has been studied and the results are as follows:
- Concentration of PAHs in several rivers in north China ranges was from n.d. to 1.98 ng/L
• Considering the same sampling period, the low ring PAHs were main component in Beisanhe River. While in Luanhe River the percentage of low ring PAHs was lower than middle ring PAHs.
• The ratios of specific PAHs indicated that the source of PAHs in Beisanhe River and Luanhe River were from combustion processes and fossil fuels burning, respectively.

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