PAHS AND PCBS LEVELS IN SURFACE WATER OF HARBIN, CHINA

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Abstract
Polycyclic aromatic hydrocarbons (PAHs) were measured in water samples collected from five locations along the Songhua River near Harbin, a city at northeast of China. Polychlorinated biphenyls (PCBs) were measured in water samples collected from four locations in four different areas of Harbin. 25 PAHs and 84 PCBs were analyzed using liquid/liquid extraction, gas chromatography and mass spectrometry (GC/MS) with a selected ion monitoring (SIM) mode. Total PAHs concentrations varied from 230 ng/L to 2100 ng/L, the PAHs profiles were dominated by low molecular PAHs (two- and three-ring components) in water samples. Total PCBs concentrations varied from 37 ng/L to 178 ng/L, the PAHs profiles were dominated by low chlorinated biphenyls (di-, tri- and tetra-) in water samples.
Key words: PAHs; PCBs; Water; Concentration; Distribution; Songhua River; Harbin

1. Introduction

The Songhua river is 1,850 km long and its head water is located in the mountains near the North Korean boundary and flows northwest. The River is important to the millions of people located on or near the river because it supplies fresh drinking water, supports local fisheries, provides transportation routes for shipping, and is a source for agricultural irrigation. Harbin is in northeastern China, and is the capital of Heilongjiang Province. It is a port and rail junction on the Songhua River.
POPs are pollutants that are semi-volatile, bioaccumulative, persistent and toxic. Very few studies exist for the determination of PCBs and PAHs in the Songhua river basin. This area has not been studied since 1983. We have decided to revisit the area to assess current levels of these compounds in this region. And conduct source track down investigations to better assess where these chemicals may be originating.

2. Sampling and Methods

Sampling Songhua River southern basin is divided into four areas, as shown in Figure 1. Area A (in blue) is a suburban region, where the effluent flows directly into the Songhua river without treatment. Area B (in yellow), is inhabitancy and sowntown where the domestic sewage is collected treated in the TP sewage treatment plant, The C area is shown in the pink region, iron and steel plants, textile mills, woodcraft plants and printworks. This region's wastewater flows into WC sewage treatment plant. The green portion is D area, chemical, petrochemical and pesticide factories all waste water drains into the Songhua River (Figure 1) without any treatment.
Water samples were collected from 9 sites in 2006, among which, 5 along the Songhua river (Figure 2), for these 5 samples only analyzed the PAHs levels. 4 from TP and WC sewage treatment plants inflow (respectively are S6 and S7) and 2 from A area and D area (respectively are S8 and S9) that flow into the Songhua river, for these 4 samples only analyzed the PCBs levels.
Water samples were collected in clean glass bottles and stored at 4-5 centigrade in darkness.

Methods Samples were treated, extracted, and analyzed according to the methods of the National Laboratory for Environmental Testing (NLET), Environment Canada. Each water sample was accurately measured and transfer the water sample to a pre-cleaned extraction funnel and spiked with a recovery standard containing CB 65 and 155. The samples were then liquid/liquid extracted for 3 times using dichloromethane. Extracts were cleaned and fractionated using silica chromatography. Pre-rinsed the packed column with dichloromethane then use hexane, the sample was added and eluted with mixture of hexane and dichloromethane (DCM, 1:1 v/v). Fractions were blown down to about 1 mL under a gentle stream of UHP nitrogen and solvent-exchanged into isooctane. The internal standards CB 30 and 204 were added to correct for volume difference.

Figure 1. Four areas in the city of Harbin

Figure 2. Sampling sites along the Songhua River.

All PCB calibration and internal standards were purchased from AccuStandard Inc. (New Haven, CT) and the standard solutions including 25 EPA-PAHs were purchased from Supelco Co. (Supelco, USA). PCB congeners and PAHs were determined by gas chromatography-negative ion chemical ionization mass spectrometry (GC-NICIMS) using an Agilent 6890 GC coupled with Agilent 5973 mass spectrometer (GC/MSD) equipped with a split/splitless injector. The purified extracts were analyzed with an a 60m×0.25mm×0.25μm HP-5MS column (Agilent Co., USA). Selected ion monitoring (SIM) mode was adopted.Organic solvents, acetone,hexane, dichloromethane, isooctane, were purchased from Dikma Co. (Dikma, USA). Silica gel (100–200 mesh; Dikma, USA) was activated at 130°C for 16h.

The column temperature program for PCBs was injector and detector temperatures were kept at 250 and 300 °C, respectively and operated with a helium carrier gas with a flow of 1 mL min^{-1}. The GC oven temperature program was as follows: initially held at 70°C for 1 min, 10°C min^{-1} to 160°C, then 2°C min^{-1} to 280°C, held for 10 min. Transfer line, ion source, and quadrupole temperatures were kept at 250°C, 150°C, and 106°C, respectively. The instrument was operated in selected ion mode (SIM). The column temperature program for PAHs was as follows: initially held at 90°C for 1 min, then raised from 90 to 180°C with 10°C min^{-1}, held for 1 min, from 180 to 280°C at 3℃min^{-1}, held for 20 min.

QA/QC All samples were spiked with a labeled recovery standard (CB 65 and 155) prior to extraction. Sample recoveries averaged for CB 65 and CB 155 have been monitored throughout the experimental procedure, the surrogate recovery (extraction efficiency) fall between 71% and 94% in all samples, and they are acceptable for quantitative analysis sample. Blank samples were included at a rate of one for every 8 water samples extracted, blank in whole procedure was analyzed and the blanks levels were all less than third data, and all results were blank corrected.

3. Results and Discussion

PAHs Total PAH concentrations ranged from 230 ng/L~473.8ng/L, except the down stream site of S5 shows the highest concentration 2100 ng/L among the sites along the Songhua River, which is located in an industrial area where lots energy consumption, industries and metal smelting are the main sources for PAHs, especially, nearby S5 has a big cement plant.

The contribution of PAHs by ring size in water along the Songhua River is shown in Fig.3. It is clear that the PAHs in water were mostly predominated by 2-ring PAHs (naphthalene, 2-MethylNaphthalene, 1-MethylNaphthalene, Fluorene and Phenanthrene), ranged from 77%~88% of total PAHs in water. Phenanthrene is one of the most frequently detected compounds in all water samples, which indicated that the souces of PAHs including motor vehicle emissions and incineration. The similar composition pattern of PAHs indicated the same sources of PAHs in water along the Songhua River.

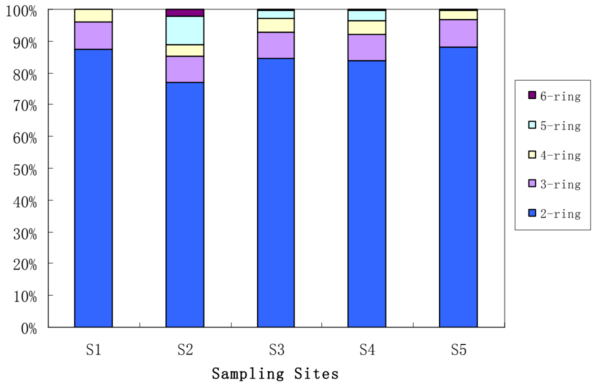

Fig.3.Composition pattern of PAHs by ring size in surface water of Harbin

The concentrations of PAHs in waters exceeding 10,000 ng/L suggested that the water was heavily contaminated by PAHs[1]. It is clear that total PAHs of all samples did not exceeding 10,000ng/L.
The total PAHs in water found in the study are much higher than those found in waters which detected in Tonghui River, Beijing, China (range from 193~2650 ng/L)[2] and in northern Greece (range form 184~856 ng/L)[3], less than the surface water, Tianjin, China (range from 1800~35,000 ng/L)[8]. As there have been rare studies, it is difficult to assess the temporal variation of PAHs in Songhua River of Harbin.

Parent PAHs have both natural sources and anthropogenic sources. For parent PAHs, combustion and/or anthropogenic input is often inferred from an increase in the proportion of the less stable, “kinetic” PAH isomers relative to the more stable, “thermodynamic” isomers and the stability of the lighter PAH isomers has been calculated to support such interpretation[4].
The ratios of fluoranthene/pyrene(Flu/Pyr) were used to differentiate PAHs of different origins. In petroleum-derived PAHs, pyrene is much more than fluoranthene. At higher combustion temperatures a predominance of fluoranthene over pyrene is characteristic. When Flu/Pyr > 1 is classically related to pyrogenic sources[5]. At the same time, discrimination occurs in phenanthrene/anthracene (Phe/Ant) ratio. Phe/Ant < 10 for pyrolytic sources and Phe/Ant > 15 for petrogenic sources. Due to the wide rage of values for this index found in the literature, values between 10 and 15 are considered indeterminate relavive to source[6,7]. Thus, when Flu/Pyr > 1 and Phe/Ant < 10 indicates that PAHs originate from pyrogenic sources[6]. The ratios of Flu/Pyr and Phe/Ant are presented in Table1. As shown in Table 1, All the values of Flu/Pyr were higher than 1, Phe/Ant were lower than 15 but around 10 tended to indicate that PAHs were not coming from petrogenic sources but fuel combustion sources.

Table 1 Ratios of Flu/Pyr and Phe/Ant in Songhua river from Harbin, China

sites	Flu/Pyr	Phe/Ant
S1	1.75	10.9
S2	1.78	12.0
S3	1.62	10.7
S4	1.71	11.0
S5	1.86	11.1

PCBs The total PCBs concentrations ranged from 37 ng/L~178 ng/L in samples with mean value of 120 ng/L. The highest concentration was observed at S7, which is the inflow of WC sewage treatment plant, and this plant collected wastewaters from Area C where there are many iron and steel plants, textile mills, woodcraft plants and printworks. And Site S9 is the next highest, perhaps, its PCB contribution stems from the chemical, petrochemical and pesticide factories which are situated in Area D. While, the lowest concentration was S8 located on the outskirts of Harbin where is mainly is farmland. Total PCBs concentration of S6 is two times more than S8, S6 is the inflow of TP sewage treatment plant, and this plant collected wastewaters from Area B where almost no industry or factory just is inhabitancy and sowntown. That is to say, the total PCBs concentration of four areas is C > D >B >A. It indicated that the total PCBs concentration in industrial estate is much more than less-industrial estate or sowntown, and the city zone is much more than the suburb.
In water, proportion of low chlorinated biphenyls (di-, tri- and tetra-) concentrations were more than 84% in all sampling sites, than high chlorinated (penta- and hexa-) with less 16% (Fig.4). Low chlorinated biphenyls are more water-soluble than high chlorinated biphenyls which might be the reason for elevated levels of di- to

trtrachlorobiphenyls than penta- to hexachlorobiphenyls in water. High-chlorinated PCBs with high K_{ow} are likely to be absorbed to suspended particulate material than low chlorinated PCBs.[9] These materials then probably settle onto the bottom sediment near the source.

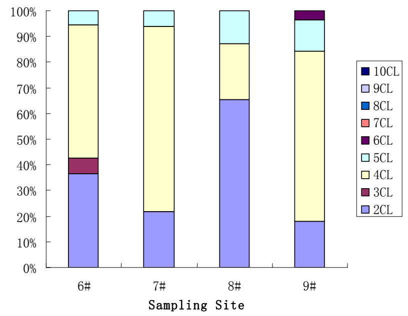

Fig.4.Percentage composition of chlorobiphenyls in water

4. Conclusions

This study has provided data on the levels of PAHs and PCBs in water from Harbin. Due to previous excessive agricultural application, industrial pollutant discharge and difficulty of degradation of these compounds, most of 25 PAHs and 26 PCBs were found at various matrices in water. Of the 25 total PAHs, the predominance of 2-ring PAHs (naphthalene, 2-MethylNaphthalene, 1-MethylNaphthalene, Fluorene and Phenanthrene) in all water. And the sources of PAHs were not petrogenic sources but fuel combustion sources. The congeners of PCBs containing 2-5 chlorines occupied the most pare of PCBs in water. And the total PCBs concentration is less than 1 ug/L—the standard of drinking water of China, and the data of total PCBs concentration indicated that industrial estate is much more than less-industrial estate or sowntown, and the city zone is much more than the suburb.

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