



Polycyclic aromatic hydrocarbons in water, sediment, soil, and plants of the Aojiang River waterway in Wenzhou, China

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ABSTRACT

The town of Shuitou was renowned as the leather capital of China because of its large-scale tanning industry, but the industry's lack of pollution controls has caused severe damage to the local water system. This study determined 15 priority polycyclic aromatic hydrocarbons (PAHs) in water, sediment, soil, and plant samples collected from Aojiang River and its estuary. The total PAHs ranged from 910 to 1520 ng/L in water samples. The total PAH in sediments were moderate to low in comparison with other rivers and estuaries in China, but the relative proportions of PAHs per million people are high when considering the population size associated with each watershed. Ratios of fluoranthene/pyrene and PAHs with low/high molecular weight suggest a petrogenic PAH origin. The PAH composition profile in soil was similar to that in sediment with 4–6 ring PAHs being dominant. The PAHs with 2–3 rings were the dominant species in plant leaves. There were no correlations between PAHs in soils and in plants, suggesting that PAHs accumulate in plant leaves through absorption from the air. The general observation of elevated PAH concentrations in all matrix suggests a possible contribution by the local leather industry on the PAH concentrations in the Aojiang watershed.

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1. Introduction

Polycyclic aromatic hydrocarbons (PAHs) are ubiquitous environmental pollutants that possess carcinogenic and mutagenic properties [1,2]. In addition to natural sources, PAHs are also formed during incomplete combustion, pyrosynthesis, or pyrolysis of hydrocarbons (petrogenesis) and are released into the environment by anthropogenic sources [3–8]. Due to their high toxicity [9] and wide distribution in the environment, including air, water, soils, and sediments, some PAHs have been listed as priority pollutants by the United States Environmental Protection Agency [10]. The determination and monitoring of PAHs in environmental samples is necessary and important to human health.

China has become world's largest manufacturer of goods over the last several decades, and the town of Shuitou, south of Wenzhou in Zhejiang Province, was renowned as the "Leather Capital of the China" for its large-scale tanning industry. According to Asian Times Online [11], at its peak Shuitou employed around 100,000 people in 1200 small workshops occupying more than 36 km²

of land. Because of the lack of pollution controls the local water system (Aojiang River watershed) has been heavily polluted. The leather industry typically uses high volumes of sulfide and lime for hair fade, degreasing, intenerating, and dyeing of pelts. One report revealed that the Aojiang River watershed received a maximum annual wastewater release of 29 million tons, and had a maximum 3952 ton of ammonium nitrogen and 91.9 ton of total germanium in 1998 [12]. Based on the national water quality standards, the water quality in the Aojiang River dropped from Type III in 1992 to lower than Type V in 2003. The impact of the leather industry in Shuitou on the Aojiang River watershed has drawn media attention and it has been named as one of the top 10 major environmental violation cases in China [12].

Shuitou is located at the head waters of the Aojiang River, and the leather industry not only affects the local environment around Shuitou, but also other towns such as Xiaojiang, Aojiang, Longgang and the Aojiang estuary along the Aojiang River (Fig. 1). Complaints from residents in this region include overall deterioration in living environment, black river water, odiferous air, low crop yields, unusual diseases, and fewer young adults who pass the physical exams for National Army admission [12]. Public pressure has forced the local government to downsize the leather industry by organizing large numbers of smaller producers into fewer large manufacturers with better pollution control measures. This has partially mitigated the pollution problems, but the water quality at the Aojiang River remains heavily polluted [12,13]. The

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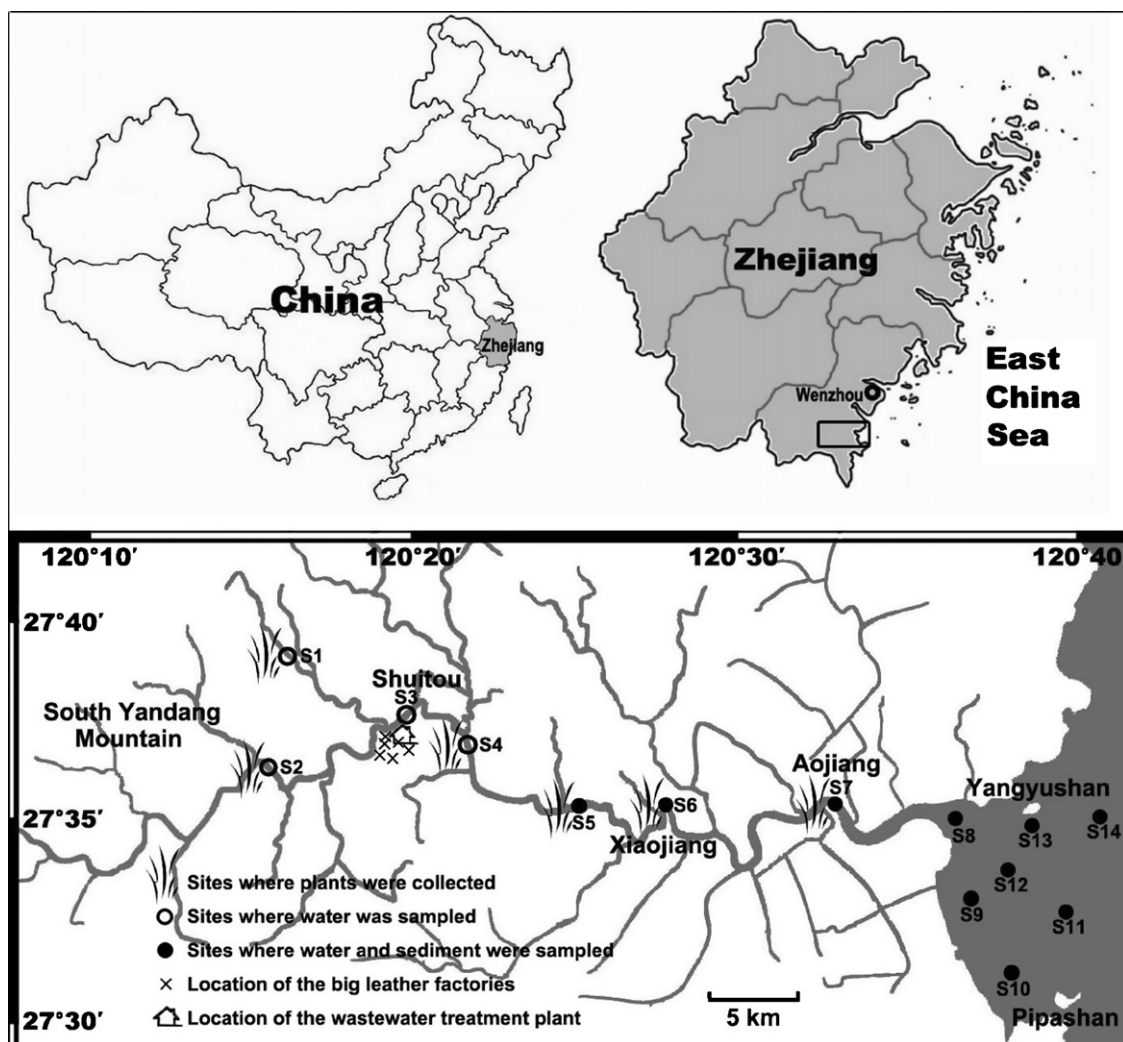


Fig. 1. Map of the Aojiang River and its estuary showing locations of sampling sites.

local Chinese EPA monitoring station has routinely examined many conventional parameters such as biochemical oxygen demand, chemical oxygen demand, and heavy metals, but persistent organic pollutants such as PAHs were not included in the routine surveys. In addition, studies concerning the pollution caused by the leather industry have mainly focused on chemicals such as sulfides, acids, alkalis, and chromium. Few studies have examined organic pollutants such as PAHs even though degreasing, dyeing, decomposing organic matter from raw leather materials such as skin or hide, hair are all significant sources for PAHs. The present study was intended to investigate if the leather industry in Shuitou is associated with the PAH contamination in the Aojiang River and its estuary. Specifically, we quantified the concentration of 15 PAHs (not including acenaphthylene), which are listed as priority pollutants by the United States EPA in water, sediment, soil and plant samples collected from the Aojiang River and its estuary.

2. Materials and methods

2.1. Sampling sites

To evaluate if the leather industry at Shuitou affects the Aojiang River and its estuary, 14 sampling sites were established (Fig. 1). Sites S1, S4–S7 represent major cross-sections along the Aojiang River. Site S2 was located upstream about 4 km away from Shuitou,

and because it is largely unaffected by the leather industry, S2 was used as control site. Site S3 is located at the wastewater treatment plant of Shuitou. The treatment plant receives raw wastewater (S3.1) from leather factories in Shuitou, and discharges the treated wastewater (S3.2) into the Aojiang River. There was a gas station on the river bank near S5. Sites S8–S14 were located in the estuary where S8, S11, S12 represented the main waterway path for traveling boats. Samples were collected in October 2007. The total collection yielded 15 water (S1, S2, S3.1, S3.2, and S4–S14), 10 sediment (S5–S14), one sludge (S3), 7 soil (S1–S7), and six plant samples (S1, S2, 4–7). Soil and plant samples were collected within 0.05 km from the sites for water samples. In particular, soil or plant sampling sites of S3, S5, and S6 were near the main highway, and the rest of the sites were located in farm fields far away from highway.

2.2. Chemicals, sample collection and preparation

Hexane, dichloromethane, acetone and methanol were of high-performance liquid chromatography (HPLC) grade (Baker, Deventer, The Netherlands). Water was purified with a Milli-Q System (Millipore, Bedford, MA, USA). All glasswares were pre-washed and rinsed with distilled solvent (methanol) before use.

Water samples were collected from 5 cm below the water surface using 2 L glass bottles. A solid phase extraction (SPE) cartridge system from Supelco (Bellefonte, PA, USA) was used to extract

Table 1
The detection conditions and composition ($\mu\text{g/mL}$) of the PAH standard mixture.

PAH (abbreviation)	Benzene (and total) rings	Composition ($\mu\text{g/mL}$)	Detection conditions		
			Time (min)	Excitation (nm)	Emission (nm)
Naphthalene (NAP)	2	1000	0	256	441
Fluorene (FLU)	2 (3)	200	0	256	441
Phenanthrene (PHEN)	3	100	0	256	441
Acenaphthene (ACE)	2	1000	0	256	441
Anthracene (ANTH)	3	100	0	256	441
Fluoranthene (FLT)	3 (4)	200	0	256	441
Pyrene (PYR)	4	100	20	270	390
Benzo[a]anthracene (BaA)	4	100	20	270	390
Chrysene (CHRY)	4	100	20	270	390
Benzo[b]fluoranthene (BbF)	4 (5)	200	35	290	410
Benzo[k]fluoranthene (BkF)	4 (5)	100	35	290	410
Benzo[a]pyrene (BaP)	5	100	35	290	410
Dibenzo[a,h]anthracene (dBahAn)	5	200	55–70	290	480
Benzo[ghi]perylene (BghiP)	6	200	55–70	290	480
Indeno (1,2,3-cd)pyrene (INPY)	5 (6)	100	55–70	290	480

PAHs from water. Prior to extraction, the C18 cartridges were pre-conditioned with 5 mL methanol, followed by 10–15 s vacuum drying and wash with 6 mL of HPLC grade ultra pure water. Samples were first passed through 0.7 μm glass-fiber filters (GF/F) (Whatman, Clifton, NJ, USA) to get rid of the particulates. The filters were preheated at 450 °C for 8 h to remove organic compounds. Then 5% methanol (v/v) was added to each water sample (500 mL), and the solution was percolated through the cartridges at a flow rate of 5 mL/min with vacuum pump. The column was then eluted with 10 mL hexane and dichloromethane (1:1, v:v) after centrifugation at 2191 \times g for 10 min.

Samples of sediment were collected with a stainless steel columnar sampler (K-BTM, Cole-Parmer, USA). Three samples of sediment from the top 0–5 cm layer were collected at each sampling site, and were mixed and stored in washed glass bottles. Samples were then transported back to the laboratory on crushed ice in a cooler and stored at 4 °C before processing. Soil and sediment (sludge) samples were extracted based on the ultrasonication method described previously [14,15]. In brief, samples were air dried, and screened through a sieve with 1 mm pore size. Sub-samples of 2.0 g dry mass were placed in 50 mL glass beakers with 10 mL of acetone, 0.2 g copper powder (Merck, Germany), 5 g anhydrous sodium sulfate, and extracted for 15 min in a 30 °C ultrasonic water bath. Procedural blanks and reference controls spiked with 5 μL PAH standard mixture were included for each batch of samples. The mixture was centrifuged at 2191 \times g for 10 min and the supernatant liquid was decanted. Another 10 mL of acetone were added to the residue and the extraction and decant processes were repeated. Extracts were combined and evaporated to dryness in a rotary evaporator. The residue was then dissolved in 2 mL hexane and dichloromethane (1:1, v:v), and solutions were processed through a silica gel column. Samples were eluted with 8 mL hexane and dichloromethane (1:1, v:v).

For plant samples, the leaves of *Artemisia santolina* Schrenk were collected near or at soil sampling sites and fresh leaves were ground into a homogeneous mixture by mortar and pestle. Leave samples of 2 g wet weight were subjected to ultrasonic extraction as described above for soil and sediment samples. For PAHs extracted from water, sediment, soil, and plant, elutes were evaporated to dryness with gentle nitrogen flow after extraction, and the residue was dissolved in 0.5 mL methanol and filtered through a 0.45 μm PTFE membrane filter prior to analysis.

2.3. Sample analyses

Samples were analyzed by the HPLC (Agilent1200 series, USA) on a C18 reverse column (Agilent, Eclipse XDB-18, 4.6 \times 150 mm)

coupled with a fluorescence detector. The native fluorescence of the PAHs was used for their detection and quantification, and PAHs were determined by their retention times calibrated by a mixed guide sample (Supeclo Company, USA) containing 15 individual PAHs (Table 1). Acenaphthylene was not included in this study because of its low fluorescent properties [16]. Our method employs an injection volume of 20 μL , a 40 °C column temperature, a mobile phase of methanol/water (75:25) for 70 min, and a flow rate of 0.8 mL/min. Average recovery rates of PAHs were 64–104% for water samples, 67–96% for sediment, 61–100% for soil samples, and 67–83% for plant samples. Data presented were the averages of two duplicate analyses. PAH concentrations were expressed as ng/L in water samples, and ng/g of dry weight in sediment, sludge, soil, and ng/g of wet weight in plant samples.

3. Results and discussion

3.1. PAHs in water samples

Twelve PAHs were identified in the water samples, among which 2–3 ring PAHs plus pyrene accounted for approximately 98% of total PAHs (\sum PAHs) (Table 2). The low concentrations of 5-ring PAHs and absence of benzo[ghi]perylene (6 rings) were expected as 5–6 ring PAHs are non-volatile, non-biodegradable and less water-soluble, and they are usually adsorbed onto sediment [17]. The concentrations of \sum PAHs in water samples from Aojiang River varied from a minimum of 909.9 ng/L at S10 to a maximum of 1519.8 ng/L at S5 (Table 2), which were much higher than PAH concentrations in water samples from rivers and estuaries elsewhere such as 21.7–138 ng/L in the Xijiang River, a major tributary of the Pearl River, South China [18], 12–130 ng/L in the Susquehanna River, the main tributary of the Chesapeake Bay, USA [19], and 12–430 ng/L in the lower Mississippi River, USA [20]. This indicates that surface water in the Aojiang River and its estuary are heavily contaminated with PAHs. Since the leather industry is the sole commercial pollution source in this region, is typically characterized by large consumption of water, and the population in this region (Pingyang county) is relatively low (\sim 800,000) [12], the high concentrations of PAHs in the Aojiang River may well indicate a significant contribution from the leather industry. The particularly high value observed at S5 could due to the additional PAH contamination from the adjacent gas station.

PAH concentration in a wastewater sample collected prior to treatment (S3.1) was 1444.2 ng/L, indicating that the wastewater from leather factories contained a high concentration of PAHs. However, PAH concentration decreased to 546.0 ng/L for samples collected after treatment (S3.2), resulting in 62% removal of the

Table 2
The PAH concentration (ng/L) in water samples collected from all sites including a wastewater sample from a leather factory (S3.1) and an effluent sample from a wastewater treatment plant (S3.2) at site S3.

PAH	S1	S2	S3.1	S3.2	S4	S5	S6	S7	S8	S9	S10	S11	S12	S13	S14
NAP	388.2	372.6	426.8	–	245.1	492.8	398.1	235.8	193.6	184.8	194.9	216.7	197.9	174.4	175.3
FLU	33.3	26.7	47.5	20.3	74.1	43.6	62.9	82.5	81.9	67.8	66.9	64.7	84.1	93.0	58.3
PHEN	160.9	115.9	466.5	138.1	181.6	239.5	179.8	198.0	219.2	158.0	132.8	206.7	167.3	232.4	174.4
ACE	184.6	139.0	176.6	135.0	184.1	211.1	171.4	209.1	208.6	225.7	180.6	190.6	240.0	260.2	228.2
ANTH	11.5	9.3	8.2	8.3	9.6	117.4	10.3	8.6	15.4	8.5	10.3	14.2	13.6	14.0	11.6
FLT	102.5	88.6	98.2	78.0	122.3	107.7	90.2	96.6	135.2	124.7	88.5	104.8	120.7	141.8	113.2
PYR	232.1	194.2	197.6	163.1	280.4	283.9	214.9	249.4	297.7	442.6	218.3	263.2	280.4	349.4	235.6
BaA	2.5	2.3	2.8	1.7	2.8	3.4	2.3	2.4	6.0	3.9	2.7	3.5	3.0	4.0	3.4
CHRY	2.2	1.9	2.0	1.5	2.6	2.6	1.8	2.1	3.4	2.9	2.4	3.2	2.4	3.3	2.9
BbF	10.5	14.8	14.5	–	9.5	13.5	14.4	17.6	12.8	12.4	9.9	9.2	14.3	9.0	9.4
BkF	0.8	0.6	1.0	–	0.9	1.3	0.6	0.8	2.0	1.0	0.5	1.8	0.9	1.4	1.1
BaP	2.6	2.6	2.5	–	2.7	3.0	2.4	2.9	3.2	2.6	2.1	3.6	2.5	4.3	2.4
Total	1131.7	967.9	1444.2	546.0	1115.7	1519.8	1148.5	1105.8	1179.0	1234.9	909.9	1082.2	1127.1	1287.2	1015.7

Note: The concentrations for dBahAn, BghiP, and INPY were all below the detection limit (–) in all sampling sites, thus omitted from the table.

\sum PAHs and 100% removal for some of the high ring and carcinogenic PAHs such as benzo[b]fluoranthene, benzo[k]fluoranthene, and benzo[a]pyrene (Table 2). A significant reduction of phenanthrene was also observed for samples collected prior to (466.5 ng/L) and after wastewater treatment (138.1 ng/L). The persistently high levels of \sum PAHs throughout the sampling sites could be due to the unregulated waste discharge from individual leather processing plants which release wastewater directly into the Aojiang River without passing through the wastewater treatment plant.

3.2. PAHs in sediment and sludge samples

All 15 PAHs were identified in sediment and sludge samples; among which pyrene was the most dominant PAH species and accounted for approximately 50% of \sum PAHs in each sampling site (Table 3). In particular, the concentration of potentially carcinogenic PAHs (BaA, CHRY, BbF, BkF, BaP, dBahAn, INPY) were high in proportion to the \sum PAHs (12% on average), which is much higher than the same comparison in water samples (2% on average). This confirms previous findings that high ring PAHs are usually adsorbed into sediment [17,21]. This raises concerns about the potential risk to humans and the environment. The absolute values of total PAH in the Aojiang River (490.6–883.4 ng/g) were not high when compared with sediment samples from other rivers in China such as 1168–21,329 ng/g in the Pearl River, Guangdong [22], 0.787–1943 μ g/g in 10 rivers in Tianjin urban/industrial complex [23], 102.9–3419.2 ng/g in the Daliao River, Liaoning [24], 464–2621 ng/g in the Lanzhou Reach of the Yellow River, Gansu [25], and 91.3–1835.2 ng/g in the Qiantang River, Zhejiang [26].

Table 3
The PAHs concentration (ng/g) in sediment samples including a sludge sample (S3) (taking from a wastewater treatment plant).

PAH	S3	S5	S6	S7	S8	S9	S10	S11	S12	S13	S14
NAP	193.1	71.4	70.6	72.8	81.2	72.2	72.9	74.6	77.5	75.7	75.1
FLU	119.8	4.6	5.0	3.4	4.7	5.3	3.5	2.9	5.2	2.8	3.7
PHEN	653.3	74.4	33.4	37.6	40.8	27.8	42.9	27.4	44.8	46.8	30.7
ACE	247.5	82.6	53.5	56.8	39.5	24.6	25.4	21.9	38.2	38.2	39.4
ANTH	51.8	17.5	9.2	14.2	10.3	9.4	12.4	7.7	11.9	10.8	13.1
FLT	125.6	75.4	45.6	69.1	47.0	43.1	61.6	35.0	52.2	53.8	52.3
PYR	1063.6	440.2	210.3	361.9	265.1	252.4	405.5	171.7	319.3	281.0	330.6
BaA	42.7	21.8	10.7	19.7	11.9	12.2	10.5	9.4	12.8	11.5	14.5
CHRY	9.7	13.7	5.5	13.3	7.3	7.1	9.6	5.1	7.3	6.7	7.9
BbF	34.8	22.3	11.7	22.7	13.8	14.7	16.6	12.0	15.4	14.4	15.6
BkF	7.0	11.1	5.0	11.1	5.6	8.6	8.3	4.8	5.6	5.8	7.0
BaP	10.9	19.6	9.0	22.0	10.2	11.5	16.0	8.8	9.8	10.6	12.9
dBahAn	13.6	7.2	6.3	7.5	6.7	6.0	5.5	6.4	6.4	6.2	6.2
BghiP	19.4	7.7	6.9	9.6	6.5	6.4	5.1	6.9	5.9	6.7	7.8
INPY	12.7	13.9	7.9	18.1	9.2	10.6	10.3	9.5	9.5	8.8	11.3
Total	2605.5	883.4	490.6	739.8	559.8	511.9	706.1	404.1	621.8	579.8	628.1

Similarly the absolute values of total PAH in the Aojiang estuary (404.1–706.1 ng/g) were not high when compared to estuaries in China or elsewhere (see Table 3 in [27]). However, when the population size is taken into account, the values reported in the present study are disproportionately high because rivers such as the Pearl River in south China, the Daliao River, rivers in Tianjin, and the Qiantang River in east China, and the Yellow River in north China all have populations ranging from several millions to several hundred millions while the population in the Aojiang watershed is less than one million with approximately 200,000 people inhabiting the surround Aojiang River (mainly from Shuitou and Aojiang Town). For example, calculation of \sum PAHs per million people yielded 4.6–91.8 ng/g in the Qiantang River, 16.7–304.7 ng/g in the Pearl River, but 613.3–1104.2 ng/g in the Aojiang River. Our findings also indirectly reveal the significant contribution of the leather industry in Shuitou on PAH contamination in the local watershed.

The \sum PAH concentration in the sludge sample (2605.5 ng/g) was 2–3 times higher than the average \sum PAHs in sediments (Table 3). This value was in the same range (μ g/g) as PAHs in sludge samples from treatment plants elsewhere [28,29]. The high PAH concentrations associated with wastewater treatment sludge could be due to the absorbency of the high portion of the hydrophobic, low water-soluble PAHs on the suspended matter in water (sludge) [30].

Ratios of fluoranthene to pyrene [26,31] or the low molecular weight (LMW) PAHs to high molecular weight (HMW) PAHs [32] are the two indexes that are most frequently used to assess the origin of PAHs. This is because concentrations of pyrene are much higher in the fossil fuels and their byproducts than the concen-

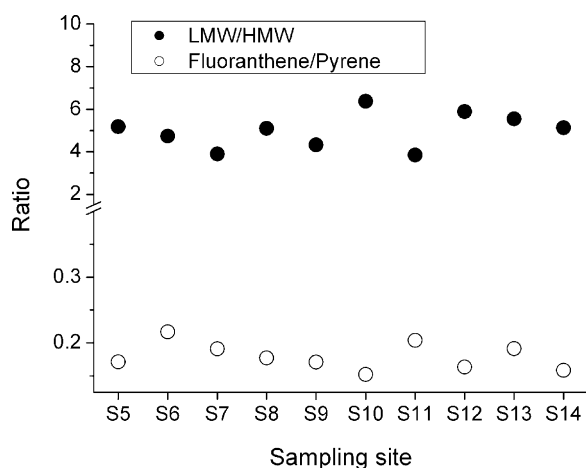


Fig. 2. Ratios of fluoranthene/pyrene and low molecular weight PAHs (LMW) to high molecular weight PAHs (HMW) in sediment samples. The LMW PAHs include PHEN, ANTH, FLT, and PYR, and the HMW include the rest 4–6 ring PAHs.

tration of fluoranthene [33], and the petrogenic contamination are dominated with LMW PAHs [34–36], while the pyrolytic contamination are characterized with HMW PAHs [37]. Therefore, ratios of fluoranthene/pyrene being less than 1 or those of LMW/HMW being greater than 1 indicate petrogenic derived PAH contamination, while the opposite indicates pyrogenic PAH contamination. In all sampling sites, the ratios of fluoranthene/pyrene were less than 1, and the ratios of LMW/HMW were greater than 1 (Fig. 2), suggesting that the source of the PAHs in the sediment are mainly from petroleum pollution originating from industries, domestic waste along the river and oil leakage from ships.

3.3. PAHs in soil samples

All 15 PAHs were detected in soil samples (Table 4) and their composition pattern is similar to that in sediment samples collected from the Aojiang River (Fig. 3). The PAHs with 4–6 rings composed the majority of PAHs in soil samples while PAHs with 2–3 rings only accounted for 24% of \sum PAHs on average. This could be due to the higher biodegradation rate of soil bacteria in utilizing low ring than high ring PAHs as energy [38]. The presence of a considerable amount of naphthalene, however, may be due to its strong association with soil organic matter, thus reducing its losses by volatilization [39]. The \sum PAHs concentration was found to be high at sites S3, S5, and S6, all three of which are located adjacent to the busy highway. It is possible that deposition of particulate

Table 4
The PAH concentration in the soil samples (ng/g).

PAH	S1	S2	S3	S4	S5	S6	S7
NAP	38.3	47.4	45.0	42.9	74.7	135.4	62.3
FLU	4.4	8.7	14.5	3.4	4.6	10.0	6.3
PHEN	48.9	50.6	141.8	52.9	157.8	144.6	79.8
ACE	29.9	25.5	85.6	20.7	96.2	96.4	122.8
ANTH	11.2	8.0	36.9	16.2	48.8	32.0	21.0
FLT	50.4	34.3	248.1	66.6	165.3	134.3	86.2
PYR	385.3	178.4	1103.0	405.6	999.7	1082.7	472.6
BaA	13.3	7.4	47.0	17.9	51.3	38.5	23.4
CHRY	6.0	4.0	25.8	10.5	37.6	23.1	15.1
BbF	14.9	8.9	51.0	20.1	53.8	41.4	26.5
BkF	5.5	3.5	22.4	8.3	23.6	18.2	12.8
BaP	7.0	5.2	40.7	6.2	30.0	31.9	20.3
dBahAn	8.3	5.2	8.7	5.8	13.2	13.4	12.4
BghiP	7.2	5.3	24.2	7.5	9.9	13.1	9.5
INPY	10.3	4.6	40.1	11.7	30.3	26.6	15.4
Total	640.9	397.0	1934.8	696.3	1796.8	1841.6	986.4

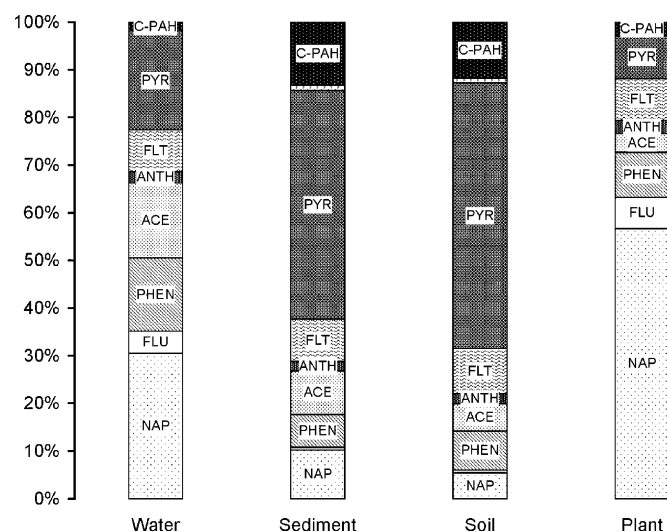


Fig. 3. Mean composition of individual PAHs in water, sediment, soil, and plant of samples collected from the Aojiang River. Data from the Aojiang estuary (S8–S14) were not included. The legends from bottom to top represent naphthalene (NAP), fluorene (FLU), phenanthrene (PHEN), acenaphthene (ACE), anthracene (ANTH), fluoranthene (FLT), pyrene (PYR), benzo[ghi]perylene (BghiP), and the sum of carcinogenic PAHs (C-PAH: benzo[a]anthracene, chrysene, benzo[b]fluoranthene, benzo[k]fluoranthene, benzo[a]pyrene, dibenzo[ah]anthracene, and indeno[1,2,3-cd]pyrene).

associated PAHs emitted from vehicles (e.g., busy traffics associated with the leather industry business) is responsible for the elevated PAH concentration in soils because it has been established that PAH flux to soil correlates significantly with the corresponding levels in air [40] and urban street dust [41]. The lowest PAH concentration (397.0 ng/g) was observed at site S2, located upstream of the Aojiang River and is expected to receive minimal impact from the leather industry in Shuitou. When compared with the control site (S2), background soil values (10 ng/g; [42]) or soil samples from elsewhere (e.g., the mean value in Korean soils is 236 ng/g [43]), the level of PAH in soil samples from the Aojiang River was significantly increased.

When compared to the PAH limit standards in other countries, the PAH concentrations in Aojiang River are 35 times the Dutch standard (0.02–0.05 μ g/g), but were lower than the Mexican (0–6 μ g/g) and Polish standards (0.02–10 μ g/g) [44]. Based on the classification of the Polish standard, the soil in the Aojiang River can be classified as “lightly polluted” with respect to PAH contamination. When PAHs were evaluated for their biological impact on organisms, the majority of PAH species did not exceed the effects range low value (ERL) guidelines established by Long et al. [45]. However, acenaphthene exceeded the ERL cutoff (16 ng/g) at all sampling sites. Pyrene exceeded the ERL (665 ng/g) by 438.0 ng/g at S3, 334.7 ng/g at S5, and 417.7 ng/g at S6. Because these guideline values appeared to be highly accurate for PAHs while concentrations above ERL represent a possible-effects range within which harmful results would occasionally occur [45], findings in this study indicated a possible adverse outcome from PAHs on the biota in the Aojiang River.

3.4. PAHs in plant samples

The PAH concentrations in the leaves of *A. santolina* Schrenk (Table 5) were higher than values reported elsewhere (20–1000 ng/g, [42]). The PAH composition profile in plants largely differs from that in soil samples from the same region with 2–3 ring PAHs accounting for \sim 80% of \sum PAHs (Fig. 3). The composition of total potentially carcinogenic PAHs accounted for \sim 3% of \sum PAHs,

Table 5
The PAH concentration in leaves of *Artemisia santolina* Schrenk (ng/g wet weight).

PAH	S1	S2	S4	S5	S6	S7
NAP	721.8	1501.9	2342.2	1478.2	1065.9	1842.3
FLU	178.6	169.7	174.4	176.8	162.8	168.9
PHEN	218.0	193.7	289.2	314.7	202.7	268.1
ACE	87.4	112.6	89.9	126.4	110.4	92.0
ANTH	35.9	54.9	94.4	85.3	47.1	126.4
FLT	164.6	157.8	198.5	309.0	207.1	351.2
PYR	141.0	210.3	297.2	329.7	183.9	251.7
BaA	16.3	25.6	26.8	41.8	26.7	109.7
CHRY	5.3	9.1	7.1	11.9	7.9	8.1
BbF	10.6	15.2	10.2	21.5	15.6	16.3
BkF	2.3	4.9	3.8	6.7	5.6	8.2
BaP	3	6.4	4.9	7.2	7.5	8.2
Total	1584.8	2462.1	3538.6	2909.2	2043.2	3251.1

Note: The concentrations for dBahAn, BghiP, and INPY were all below the detection limit in all sampling sites, thus omitted from the table.

which was similar to what was measured in water samples. The presence of carcinogenic PAHs in *A. santolina* also suggested potential human health risk associated with the consumption of fruits and vegetables grown in this region as similar accumulation may occur in the leaves of other plant species. Although naphthalene was the most volatile and degradable of the PAHs due to its low ring number [38], it was, on average, the most abundant compound in leaves of *A. santolina*, ranging from 721.8–2342.2 ng/g wet weight. The relatively high concentration of naphthalene in plants could be due to its higher solubility in water, it penetrates the soil profile to the root zone, and is absorbed through the roots of the plants. Although the highest \sum PAH concentration was observed at site S4 (3538.6 ng/g), the corresponding value in soil sample at the same site was 696.3 ng/g. Analysis of \sum PAHs concentrations in soil and plant samples at the same sites failed to show significant correlation between them ($R^2 = 0.1606$), which indirectly suggested that plants could be absorbing PAHs from the air and this mode of transport could be more significant than PAH accumulation through root absorption from soil. Future studies are needed to evaluate PAH concentrations in air of this region, and also to explore the correlations between PAH concentrations in air and plants.

4. Conclusions

Twelve of the 15 PAHs were detected in the water samples collected from the Aojiang River and its estuary. The absence of dibenzo[a,h]anthracene, benzo[ghi]perylene, and indeno(1,2,3-cd)pyrene in water samples may be due to their low solubility in water, and their propensity to irreversibly absorb onto the sediment. The wastewater treatment plant played an important role in reducing PAH concentration in wastewater. The degree to which water was contaminated with PAHs in the Aojiang River and its estuary was higher in comparison with other rivers and estuaries. All 15 PAHs were detected in sediment and soil samples. The PAH composition in sediments and soils shared a similar pattern and was dominated by 4–6 ring PAHs. Analysis of the origin of PAH contamination in sediment suggested a petrogenic source. The \sum PAHs in soil samples were high and in particular acenaphthene exceeded ERL guidelines in all sites and pyrene exceeded ERL guidelines in three sites, suggesting possible adverse effects caused by PAHs on the biota in the Aojiang River. The PAHs with 2–3 rings, especially naphthalene, were the dominant species found in the leaves of *A. santolina*. The lack of correlation between PAH concentration in soil and in plant suggested that plants may absorb PAHs from the air and that this could be a more significant factor than PAH accumulation through root absorption from soil. Given the relatively small population size surrounding the Aojiang River, the elevated concentrations of PAHs in water, sediment, soil, and plant suggested a

possible impact of the local large-scale leather industry in Shuitou on the Aojiang watershed.

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