

Occurrence and removal efficiency of six polycyclic aromatic hydrocarbons in different wastewater treatment plants

Manli Wu, Lili Wang, Huining Xu and Yi Ding

ABSTRACT

Occurrence and removal efficiency of six polycyclic aromatic hydrocarbons (PAHs) (fluoranthene, benzo[b]fluoranthene, benzo[k]fluoranthene, benzo[a]pyrene, benzo[ghi]perylene and indeno [1,2,3-cd]pyrene) in wastewater were monitored at different treatment processes in three wastewater treatment plants (WWTPs) by using ultra performance liquid chromatography-tandem mass spectrometry (UPLC-MS/MS). Chromatographic separation was performed on a Waters Acquity UPLC BEHC18 column (1.7 μm , 2.1 mm \times 50 mm). A 0.2 μm precolumn filter was used to protect the analytical column. The result indicated that (1) the total concentrations of six PAHs were 427, 318, and 220 ng L⁻¹ in the influent of three wastewater treatment plants, respectively. Among six PAHs, the content of fluoranthene was the highest, accounting for 62–66% of total PAHs. (2) Throughout the wastewater treatment process, different treatment units exhibited different removal efficiencies for six PAHs. Biological treatment stage and aerated grit chamber appeared to be necessary for effective removal of six PAHs. The removal efficiencies of six PAHs were 73–83% at biological treatment units, and 24–56% at the aerated grit stage, respectively. The final sedimentation and disinfection for PAH removal was minor.

Key words | polycyclic aromatic hydrocarbons, removal efficiency, ultra performance liquid chromatography-tandem mass spectrometry, wastewater treatment plant

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INTRODUCTION

Polycyclic aromatic hydrocarbons (PAHs) are a well-known group of toxic compounds, which share the same core structure: two or more fused rings consisting of only carbon and hydrogen. PAHs mainly originate from fossil fuel combustion and release of petroleum and petroleum products (Benner *et al.* 1990; Freeman & Cattell 1990). Some of these are considered to be probable or not probable human carcinogens, and endocrine disrupting activities of PAHs have been reported (Clemons *et al.* 1998; Brun *et al.* 2004). Therefore, their distributions in the environment and potential human health risks have become the focus of much attention. Due to their ubiquitous occurrence, high toxicity and suspected carcinogenicity and mutagenicity, PAHs are included in the US Environmental Protection Agency and in the European Union priority lists of pollutants (USEPA 1999; EC 2001). It is also well known that, among the 16 priority PAHs, four, five and six ring PAHs have greater carcinogenic potential

than two, three and seven ring PAHs (Chaloupka *et al.* 1993; Long & Combes 1995).

Wastewater treatment plants (WWTPs), especially those serving both domestic and industrial areas, consistently receive complex mixtures, containing a wide variety of PAHs. In recent years, the occurrence of PAHs in domestic wastewater and its treatment effluent has become a topic of wide concern because of their potential hazardous effects on the water environment and because of health risks related to water reuse (Christian *et al.* 2006; Juan *et al.* 2009; Ma *et al.* 2010; Liu *et al.* 2011). However, few studies have been conducted for investigating PAH distribution in different treatment stages, and there is as yet insufficient information or knowledge on the removal efficiency of PAHs at WWTP applying different types of biological treatments.

Additionally, the routine quantitative analysis of PAHs in wastewater at the low levels fixed by the USEPA and

EU requires the development of analytical methods that both provide efficient extraction and concentration, and permit simple, rapid and low-cost determination of PAHs. A wide number of chromatography techniques were developed for the determination of PAHs in wastewater, such as thin-layer chromatography, gel permeation chromatography, gas chromatography (GC), and high-performance liquid chromatography (HPLC), etc. (China EPA 2002; Martinen *et al.* 2003; Miège *et al.* 2003; Blanchard *et al.* 2004; Sponza & Gök 2010). These traditional LC and GC separation techniques are time-consuming (40–60 min per sample) because of their limited separation performance. In order to reduce reagent consumption and overall analytical time, development of a simple and highly reliable analytical method for the quantification of PAHs in wastewater would be desirable.

The objective of the present study was: (1) to optimize and validate an analytical method to determine six types of high-molecular-weight PAHs in wastewater. PAHs were determined using ultra performance liquid chromatography-tandem mass spectrometry (UPLC-MS/MS) method in this study; (2) to investigate the occurrence of six PAHs using this UPLC-MS/MS method in three WWTPs in Xi'an in China, and to estimate the source and diminution of these PAHs during the treatment process; and (3) to compare the removal efficiency of six PAHs in three WWTPs with different treatment processes and at different treatment stages. This study is also intended to contribute to recent China Water Directives aimed at reducing the discharge of hazardous compounds to the environment.

MATERIALS AND METHODS

Chemicals and reagents

A solution containing six PAHs including fluoranthene (FLT; 100 µg mL⁻¹), benzo[b]fluoranthene (BbF; 100 µg mL⁻¹), benzo[k]fluoranthene (BkF; 100 µg mL⁻¹), benzo[a]pyrene (Bap; 100 µg mL⁻¹), benzo[ghi]perylene (BghiP; 100 µg mL⁻¹) and indeno[1,2,3-cd]pyrene (IND; 100 µg mL⁻¹) (purity > 99%) was purchased from AccuStandard (New Haven, USA). Methanol (HPLC grade), *n*-hexane (HPLC grade), and acetone (AR, distillation) were purchased from Tianjin Kermel Chemical Reagent. All other chemicals used were of analytical reagent grade. The water for chromatographic purposes was purified using an ELGA system (PURE-LAB Option F7, Ultra Genetic, UK).

Sample collection

The three WWTPs received sewage mainly from domestic and industrial sources in the service area. Some details of the three WWTPs are shown in Table 1.

For investigating the occurrence of PAHs in the three WWTPs and removal patterns in wastewater treatment processes, 5-d time-proportional composite samples (from March 8th to March 12th, 2010) were collected from sampling sites in the three WWTPs. Sampling sites are shown in Figure 1. For No.1 WWTP, samples were collected from six locations along the treatment process, namely the plant influent (after coarse and fine screen), effluent from aerated grit chamber, anaerobic tank, oxidation ditch, final sedimentation, and disinfection. For No.2 WWTP, samples were collected from seven locations along the treatment process, namely the plant influent (after coarse and fine screen), effluent from aerated grit chamber, anoxic tank, anaerobic tank, aerobic tank, final sedimentation, and disinfection. For No.3 WWTP, samples were collected from three locations along the treatment process, namely the plant influent (after coarse and fine screen), effluent from aerated grit chamber, and effluent.

The samples were collected and stored in pre-cleaned amber glass containers at -4 °C before filtration and extraction.

Sample pretreatment

1.0 L wastewater samples were centrifuged for 10 min at 7,000 rpm using a high speed freezing centrifuge (Allegra™ X-22R, Beckman Company, USA) and filtered through a 0.45 µm micro porous filter membrane. Then, samples were loaded onto a pear shaped separatory funnel and

Table 1 | Operational details of the three wastewater treatment plants (WWTPs)

WWTP	Type of treatment	Treatment capacity (m ³ /d)	The percentage of industrial waste/domestic waste
No.1	Coarse and fine screens; primary settler; Orbal Oxidation ditch; secondary settler	100,000	45%/55%
No.2	Coarse and fine screens; primary settler; inverted A2/O; secondary settler	250,000	70%/30%
No.3	Coarse and fine screens; primary settler; CASS	200,000	10%/90%

CASS, Cyclic Activated Sludge System.

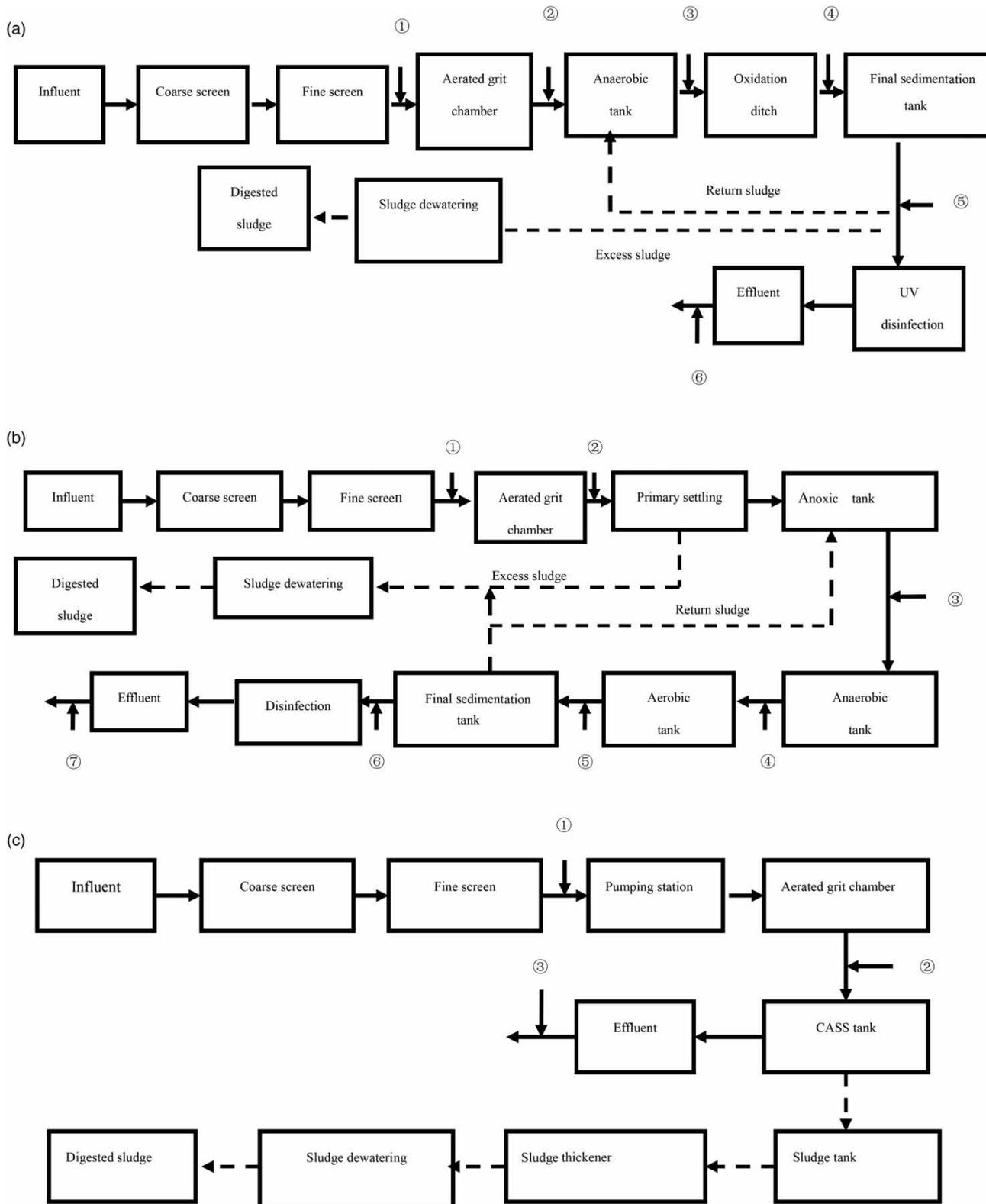


Figure 1 | Flowchart and sampling points at three WWTPs in Xi'an, China. (a) Sampling points in No.1 WWTP of Xi'an. ① Influent; ② Aerated grit chamber; ③ Anaerobic tank; ④ Oxidation ditch; ⑤ Final sedimentation tank; ⑥ Effluent. (b) Sampling points in No.2 WWTP of Xi'an. ① Influent; ② Aerated grit chamber; ③ Anoxic tank; ④ Anaerobic tank; ⑤ Aerobic tank; ⑥ Final sedimentation tank; ⑦ Effluent. (c) Sampling points distribution in No.3 WWTP of Xi'an. ① Influent; ② Aerated grit chamber; ③ Effluent.

extracted three times with 50 mL *n*-hexane. The combined organic phase was dried over anhydrous sodium sulfate (China EPA 2009). The final solution was carefully evaporated to dryness with a vacuum evaporator (water bath at 40 °C), and then fixed to a volume of 100 µL using methanol as a solvent. 5 µL of the reconstituted solution was then injected into UPLC-MS/MS for analysis.

PAH analysis

The UPLC-MS/MS (Waters, USA) used was Waters Acquity UPLC-TQD equipped with Atmospheric Pressure Chemical Ionization source (APCI). Chromatographic separation was performed on a Waters Acquity UPLC BEHC18 column (1.7 µm, 2.1 mm × 50 mm) at 32 °C. A 0.2 µm precolumn filter was used to protect the analytical column. A 5 µL sample was injected for UPLC analysis. Mobile phase A was methanol with phase B ultra-pure water. The flow rate was 0.15 mL min⁻¹. The time program for the multi-step gradient was 0–2.5 min: 80/20 (A/B, v/v) to 95/5; 2.5–7.0 min: 95/5 to 100/0; 7.0–8.0 min: 100/0 to 80/20; 8.0–11.0 min: 80/20 to 80/20. Total run time was 11 min per sample.

The MS/MS equipment consisted of a Waters Micro-mass Quattro Micro triple–quadrupole system. Analysis was performed using multi-reaction monitoring (MRM). The parameters such as MRM transition (precursor ion > daughter ion), cone voltage, and collision energy were optimized using the IntelliStart program of the Acquity UPLC console (Zhu et al. 2008; Cai et al. 2009).

Calibration and recovery

An amount of 10 µg mL⁻¹ of calibration standard mix was prepared from stock solutions described in the above Chemicals and Reagents section. This standard mix was diluted further using methanol through the series dilution

method, resulting in the following calibration standard solutions: 100.0, 50.0, 20.0, 10.0, 5.0, 2.0, and 1.0 µg L⁻¹. An amount of 5 µL of each standard solution was injected onto the column five times. The calibration standards were analyzed using water/methanol as a binary mobile phase in an injection sequence starting from 1.0 to 100.0 µg L⁻¹.

For the recovery test, 1 L of wastewater was spiked with six PAHs using the working solutions to yield fortified water samples containing 200 ng L⁻¹ PAHs. The fortified samples were shaken vigorously to enable sufficient distribution of the target compounds within the sample matrix. The spiked samples were homogenized by shaking and then extracted by liquid–liquid extraction with *n*-hexane. Unspiked samples (i.e. ‘blank’ samples) were also processed, in an identical manner to the spiked samples. Then, they were determined by UPLC-MS/MS. Recoveries were calculated by using Equation (1).

$$R = \frac{A_3 - A_1}{A_2} \times 100\% \quad (1)$$

In Equation (1) A_3 , A_1 , and A_2 are peak areas for 1 L wastewater sample containing 200 ng L⁻¹ PAHs, 1 L blank samples, 200 ng L⁻¹ PAHs working solution, respectively.

RESULTS AND DISCUSSION

Identification and quantification of target compounds

Table 2 lists MRM data acquisition parameters, calibration, correlation coefficients (R^2) and recovery for each target compound. All plots were linear, and R^2 was >0.990 throughout the method validation. There was a small,

Table 2 | UPLC-MS/MS acquisition parameters and method validation for six PAHs

Compound	t_R (min)	Selected ions for MS quantification		Cone voltage (V)	Collision energy (eV)	Calibration		
		Precursor ion	Daughter ion			Correlation equation	R^2	Recovery (%)
FLT	3.32	202.3	200.2	90	48	$y = 0.5037x + 0.1253$	0.997	75 ± 7
BbF	4.77	252.3	250.4	96	50	$y = 0.6527x - 0.06964$	0.997	76 ± 7
BkF	5.07	252.4	250.2	95	50	$y = 0.5906x - 0.3923$	0.995	76 ± 7
Bap	5.21	252.5	250.4	96	50	$y = 3.064x - 1.3354$	0.992	86 ± 9
IND	6.00	276.5	274.3	100	56	$y = 0.3605x - 0.1066$	0.992	74 ± 9
BghiP	6.21	276.3	274.4	100	55	$y = 0.2307x - 0.08241$	0.991	74 ± 6

positive or negative intercept for each analyte. The recovery varied from 74 to 86% for all target compounds.

Occurrence and source of PAHs in the three WWTPs

The optimized analytical method for the determination of six PAHs was applied to the analysis of the three WWTPs wastewater samples in Xi'an, China. Tables 3–5 are the concentrations of six PAHs determined in the three WWTPs water sampled in March 2010. The results show that, from the influent of the three WWTPs, six target compounds, namely FLT, BbF, BkF, Bap, BghiP and IND, were all detected. For six PAHs in wastewater, the concentrations of the sum of six PAHs in the three WWTPs were 427 ng L⁻¹ in No.1 WWTP, 318 ng L⁻¹ in No.2 WWTP, and 220 ng L⁻¹ in No.3 WWTP. Among the six PAHs, the content of FLT was the highest, which was 146–281 ng L⁻¹, occupying 62–66% of total

concentrations of six PAHs (Figure 2). However, the concentrations of the five other PAHs were relatively low, ranging from 13.4 (BkF in No.1 WWTP) to 46.8 ng L⁻¹ (BbF in No.1 WWTP), with rates ranging from 3 to 11% (Figure 2).

The concentration range of six PAHs was found comparable to those in several water bodies in the WWTP that have been reported. For example, Busetti reported the total concentration of six PAHs was 202 ng L⁻¹ in an Italian wastewater treatment plant (Busetti *et al.* 2006). In a wastewater treatment plant in Norway, the total concentration of six PAHs was 390 ng L⁻¹ (Christian *et al.* 2006). A similar concentration of 429 ng L⁻¹ was reported for the Mataró's WWTP in Spain (Juan *et al.* 2009). Similarly, six PAHs were found at comparable levels (552 ng L⁻¹) in WWTP in China as reported by Ma *et al.* (2010).

Among six PAHs, the most potent of the carcinogenic PAHs, benzo(a)pyrene (BaP), was detected in the influent

Table 3 | PAHs detected from the influent, effluent, and different treatment stages in No.1 WWTP of Xi'an ($n=3$, average \pm standard deviation)

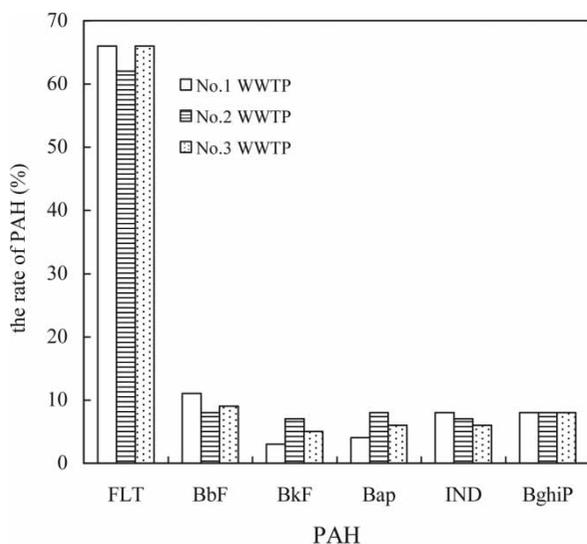
No.1 WWTP (ng L ⁻¹)						
Compound	Influent	Aerated grit chamber	Biological treatment stage			Effluent
			Anaerobic pond	Oxidation ditch	Final sedimentation tank	
FLT	281 \pm 18	123 \pm 11	36.7 \pm 1.7	35.2 \pm 2.3	30.0 \pm 2.4	29.4 \pm 1.3
BbF	46.8 \pm 5.1	14 \pm 2.1	9.1 \pm 1.6	4.1 \pm 0.9	5 \pm 0.4	3.3 \pm 0.2
BkF	13.4 \pm 1.2	4.5 \pm 0.6	3.3 \pm 0.6	2.2 \pm 0.2	1.4 \pm 0.2	1.5 \pm 0.4
Bap	15.1 \pm 1.9	5.4 \pm 0.8	4.4 \pm 0.9	2.6 \pm 0.5	1.6 \pm 0.3	1.6 \pm 0.1
IND	34.7 \pm 2.8	23.1 \pm 1.3	14.3 \pm 1.1	3.1 \pm 0.6	1.7 \pm 0.6	1.2 \pm 0.5
BghiP	36.3 \pm 1.2	17.2 \pm 2.3	3.5 \pm 0.6	3.3 \pm 0.7	2.7 \pm 0.3	2.8 \pm 0.8
Total PAHs	427	188	71.4	50.5	42.5	39.9

Table 4 | PAHs detected from the influent, effluent, and different treatment stages in No.2 WWTP of Xi'an ($n=3$, average \pm standard deviation)

No.2 WWTP (ng L ⁻¹)							
Compound	Influent	Aerated grit chamber	Biological treatment stage			Final sedimentation tank	Effluent
			Anoxic pond	Anaerobic pond	Aerobic pond		
FLT	198 \pm 11	100 \pm 10	26.1 \pm 2.1	17.4 \pm 1.8	14.3 \pm 3.2	12.3 \pm 2.4	13.6 \pm 1.2
BbF	25.9 \pm 2.6	17.1 \pm 1.8	5.2 \pm 1.2	2.2 \pm 0.9	1.8 \pm 0.1	1.9 \pm 0.5	2.6 \pm 0.2
BkF	21.2 \pm 3.2	3.5 \pm 0.6	2.6 \pm 0.8	2 \pm 0.6	1.9 \pm 0.3	1.6 \pm 0.1	1.1 \pm 0.1
Bap	24.0 \pm 1.8	5.1 \pm 1.4	3.7 \pm 0.3	2 \pm 0.6	2.1 \pm 0.3	1.8 \pm 0.2	1.2 \pm 0.3
IND	23.2 \pm 3	13.1 \pm 1.3	6.1 \pm 0.6	4.5 \pm 0.9	2.6 \pm 0.2	1.7 \pm 0.3	1.7 \pm 0.8
BghiP	25.1 \pm 3.2	13.8 \pm 2.5	4.2 \pm 0.7	4.4 \pm 0.8	3.9 \pm 0.8	2 \pm 0.4	1.6 \pm 0.5
Total PAHs	318	153	47.9	32.5	26.6	21.2	21.8

Table 5 | PAHs detected from the influent, effluent, and different treatment stages in No.3 WWTP of Xi'an ($n = 3$, average \pm standard deviation)

Compound	No.3 WWTP (ng L ⁻¹)		
	Influent	Aerated grit chamber	Effluent
FLT	146 \pm 13	115 \pm 13	24.3 \pm 3.6
BbF	19.2 \pm 2.4	13.6 \pm 3.3	1.3 \pm 0.6
BkF	11.3 \pm 3.6	6.1 \pm 1.1	1.1 \pm 0.3
Bap	12.8 \pm 2.5	6.3 \pm 1.1	1.2 \pm 0.1
IND	12.6 \pm 2.5	10.3 \pm 2	2.3 \pm 0.3
BghiP	18.3 \pm 2.8	14.3 \pm 1.9	2.7 \pm 0.5
Total PAHs	220	167	32.8

**Figure 2** | The ratio of individual PAH to total PAHs in three WWTPs.

of three WWTPs, with concentrations varying from 12.8 to 24.0 ng L⁻¹. The observed BaP levels were in the low range of earlier reported influent levels: 77 ng L⁻¹ for the WWTP in Montreal (Pham & Proulx 1997). Similar concentrations of Bap were reported for the Seine Aval treatment plant in Paris (Blanchard *et al.* 2004) at 21.4 ng L⁻¹; for the Thessaloniki sewage treatment plant in Greece (Manoli & Samar 1999) at 22 ng L⁻¹; and for the Fusina WWTP in Venice at 19.3 ng L⁻¹ (Busetti *et al.* 2006).

In recent years, the indeno[1,2,3-cd]pyrene/(indeno[1,2,3-cd]pyrene + benzo[ghi]perylene) (IND/(IND + BghiP)) concentration ratio has been used to identify the sources of PAHs (Lai *et al.* 2009). Yunker (Yunker *et al.* 2002) demonstrated that IND/(IND + BghiP) was ≤ 0.2 in unburned petroleum (petrogenic), 0.2–0.5 in petroleum combustion, and ≥ 0.5 in grass/wood/coal combustion. To

evaluate the sources of PAHs found in the three WWTPs, the PAH concentration ratios of IND/(IND + BghiP) were calculated. Based on the average PAH data determined in the three WWTPs, the IND/(IND + BghiP) ratios were calculated to be 0.49, 0.48, and 0.41 for WWTP Nos. 1, 2, and 3, respectively. These results are close to 0.5, indicating the dominant sources of PAHs in the three WWTPs were petroleum and grass/wood/coal combustion.

Removal efficiency of six PAHs in the three WWTPs

Figure 3(a) compares the removal efficiency of six PAHs in the three WWTPs. The removal of each of these PAHs was between 81% (IND in No.3 WWTP) and 97% (IND in No.1 WWTP). The total removal efficiency of six PAHs was 91% in No.1 WWTP, 93% in No.2 WWTP, and 85% in No.3 WWTP. According to the results, the No.2 WWTP had the greatest removal efficiency for six PAHs and the No.3 WWTP had the lowest.

For PAHs with a greater number of fused rings, volatilization is insignificant and adsorption onto organic matter is the prevalent removal mechanism (Lazzari *et al.* 1999). An important process for these compounds is a preferential adsorption to particles, which are fairly well removed by decantation. In addition, two other elimination pathways must be taken into account: evaporation from the different basins in relation to the high PAH vapor pressure and biodegradation processes (aerobic and anaerobic) (Blanchard *et al.* 2004).

Six PAHs removal along the treatment process

To investigate six PAHs removal along the treatment process, the samples were collected at different sampling sites (Figure 1) and the concentrations of six PAHs along treatment process were determined. The results are shown in Figure 3(b). It was found that the aerated grit chamber exhibited significant removal for six PAHs, and the removal efficiency of six PAHs was 56% in No.1 WWTP, 52% in No.2 WWTP, and 24% in No.3 WWTP. Removal was further achieved during the biological treatment stage in three WWTPs, in which removal efficiency of six PAHs was 73% in No.1 WWTP, 83% in No.2 WWTP, and 80% in No.3 WWTP.

Although the final sedimentation should be important for the final solid/liquid separation in the WWTP, its function for PAHs removal was minor and the removal efficiency of six PAHs was 16% in No.1 WWTP and 20% in No.2 WWTP. Disinfection had nearly no effect on six PAHs removal.

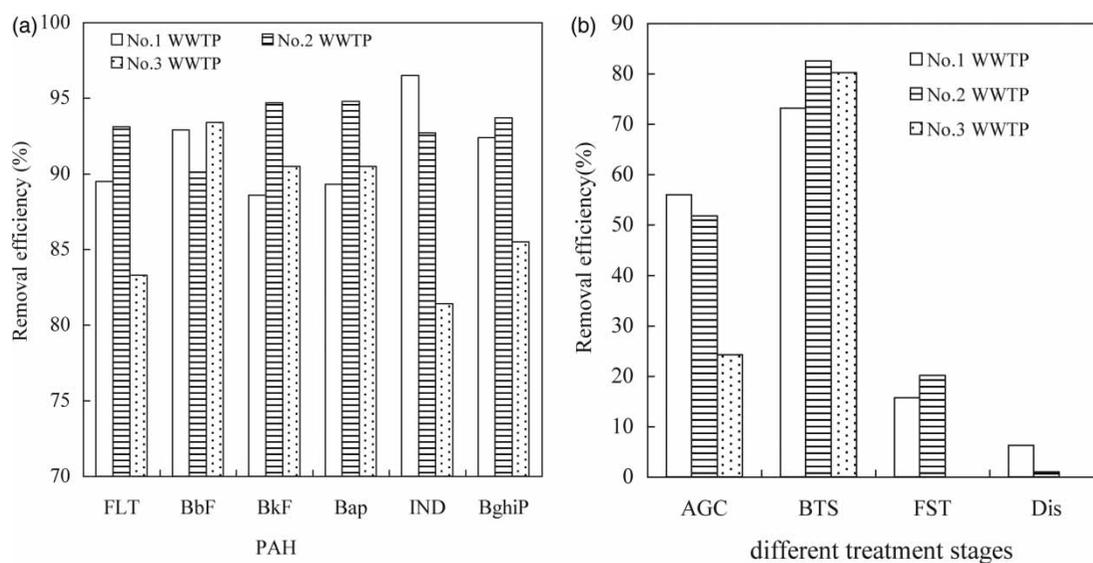


Figure 3 | Six PAHs removal efficiencies and removal ratios in different treatment stages. (a) The removal efficiency of each of six PAHs in three WWTPs. (b) Removal ratios in different treatment stages. AGC – aerated grit chamber; BTS – biological treatment stage; FST – final sedimentation treatment; Dis – disinfection.

CONCLUSIONS

A new method of UPLC-MS/MS for fast and sensitive detection of six PAHs in wastewater was developed and validated in this study. Compared with the conventional PAH determination methods, this method saves time and solvent and improves instrument sample throughput by two- to five-fold. The analytical method described in this study was shown to be reliable for the determination of six PAHs in wastewater with good recoveries varying in the range of 74–86%. The method has been used to determine the concentrations of six PAHs in wastewater samples taken from three WWTPs in Xi'an, China.

PAH concentration ranges (as ng L^{-1}) in the raw wastewaters in three WWTPs were: for FLT, 146 to 281 (mean: 208); for BbF, 19 to 47 (mean: 31); for BkF, 11 to 21 (mean: 15); for Bap, 13 to 24 (mean: 17); for IND, 13 to 35 (mean: 24); for BghiP, 18 to 36 (mean: 26). The total concentrations of six PAHs ranged from 220 to 427 ng L^{-1} in the three WWTPs. Among six PAHs, the content of FLT was the highest, occupying 62–66% of total concentrations of six PAHs. The concentration of Bap varied from 12.8 to 24.0 ng L^{-1} in raw wastewater. Pham & Proulx (1997) in wastewaters to the Montreal treatment plant found concentration values for FLT and Bap ranging respectively from 83 to 216 ng L^{-1} and from 20 to 77 ng L^{-1} , which were similar to our results.

Differences in ability of different treatment types to remove six PAHs were evident. The best results were

obtained by No.2 WWTP, where the A2/O acted as a biological disposal process with 93% removal efficiency for six PAHs. The other two WWTPs effectively reduced six PAHs load by 85% (No.3 WWTP with Cyclic Activated Sludge System (CASS) process) and 91% (No.1 WWTP with oxidation ditch process).

Biological treatment stage and aerated grit chamber appeared to be necessary for effective removal of six PAHs. But the role of final sedimentation and disinfection for PAHs removal was minor.

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