

Identification and removal of polycyclic aromatic hydrocarbons in wastewater treatment processes from coke production plants

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Abstract Identification and removal of polycyclic aromatic hydrocarbons (PAHs) were investigated at two coke plants located in Shaoguan, Guangdong Province of China. Samples of raw coking wastewaters and wastewaters from subunits of a coke production plant were analyzed using gas chromatography–mass spectrometry (GC/MS) to provide a detailed chemical characterization of PAHs. The identification and characterization of PAH isomers was based on a positive match of mass spectral data of sample peaks with those for PAH isomers in mass spectra databases with electron impact ionization mass spectra and retention times of internal reference compounds. In total, 270 PAH compounds including numerous nitrogen, oxygen, and sulfur heteroatomic derivatives were positively identified for the first time. Quantitative analysis of target PAHs revealed that total PAH concentrations in coking wastewaters were in the range of 98.5 ± 8.9 to 216 ± 20.2 $\mu\text{g/L}$, with 3-4-ring PAHs as dominant compounds. Calculation of daily PAH output from four plant subunits indicated that PAHs in the coking wastewater came mainly from ammonia stripping wastewater.

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Coking wastewater treatment processes played an important role in removing PAHs in coking wastewater, successfully removing 92 % of the target compounds. However, 69 weakly polar compounds, including PAH isomers, were still discharged in the final effluent, producing 8.8 ± 2.7 to 31.9 ± 6.8 g/day of PAHs with potential toxicity to environmental waters. The study of coking wastewater herein proposed can be used to better predict improvement of coke production facilities and treatment conditions according to the identification and removal of PAHs in the coke plant as well as to assess risks associated with continuous discharge of these contaminants to receiving waters.

Keywords Coking wastewater · Coke plant · Polycyclic aromatic hydrocarbons · Chemical identification · Pollutant removal

Introduction

Polycyclic aromatic hydrocarbons (PAHs) are a class of diverse organic compounds made up of two or more fused aromatic rings. They have received immense attention because of their presence in the environment and adverse impacts on ecosystems and human health (Matsuzawa et al. 2001; Motelay-Massei et al. 2006; Guo et al. 2007; Fatone et al. 2011). These compounds are among the most carcinogenic, mutagenic, and toxic contaminants (Arfsten et al. 1996; Petry et al. 1996) and are classified among the so-called persistent organic pollutants, some of which are listed as U.S Environmental Protection Agency (US-EPA) and European Union (EU) priority pollutants. PAHs are ubiquitous in industrial and municipal wastewater (Dai et al. 2007; Manoli and Samara 2008; Fatone et al. 2011), as they can be generated from both natural processes and anthropogenic

activities such as industrial production, transformation, and waste incineration (Omar et al. 2006). Coke production is one of the major sources in China that contributes 16 % of total PAH (Xu et al. 2006). It has been reported that 1,602 t of benzo[a]pyrene was discharged to wastewater in Chinese coking wastewater in 2005 alone (NDRC 2006). Therefore, it is essential to identify and remove these toxic pollutants in coking wastewater to reduce their hazard to aquatic organisms and humans.

PAHs in coking wastewater originate not only from processes of coke production but also from purification processes of industrial by-products, such as ammonium, benzene, and tar. Thus, a better understanding of the distribution of PAHs in the subunits of the coke production will be helpful to optimize coke production facilities for controlling and minimizing the amount of PAHs released from this source. It can also help alleviate treatment loads on coking wastewater treatment plants (WWTPs). Most PAHs can be removed in coking WWTPs before wastewater is discharged to the environment. Physical, biological, and chemical methods are usually applied in wastewater treatment to achieve the maximum possible removal of target pollutants (Byrns 2001; Katsoyiannis and Samara 2005). For example, biological wastewater treatment facilities are designed for optimal biotransformation activity by providing high density of active microorganisms and a variety of carbon, nutrient, and energy sources to promote cometabolism of recalcitrant pollutants (Heidler et al. 2006). Combination of anoxic, oxic, and hydrolytic zones favors anaerobic and aerobic metabolisms (Zhang et al. 2012). A better understanding of the removal of PAHs during wastewater treatment process will be helpful to optimize the WWTPs for minimizing the amount of PAHs discharged to the environment.

Previously, very limited studies have been reported regarding the identification and quantification of PAHs in coking wastewater (Miller 1980; Walters and Luthy 1984), which is much more complicated than municipal wastewaters, containing considerable amounts of phenols, polycyclic nitrogen-containing aromatics, and oxygen- and sulfur-containing heterocyclic and acyclic compounds (Zhang et al. 1998; Blanchard et al. 2004). Among these available studies, the focuses were mainly on the quantification of 16 PAHs in the wastewater, not including the distribution of these compounds in coke production. It has become increasingly evident in recent years that hundreds of PAHs between naphthalene (molecular weight (MW), 128) and coronene (MW, 302) are present in environmental matrices (Barron and Holder 2003; Zhang et al. 2012). Thus, analysis of just 16 PAHs in coking wastewater may be inadequate for comprehensive identification of PAH sources and characterization of PAH removal. Limitation on the study of PAHs in coking wastewater can be ascribed to many factors,

including: (1) distribution of coking plants mainly in developing countries, which limits the study of representative wastewater samples; (b) economic and social conditions that do not allow developing countries to fully address pollutants from coking wastewater; and (c) technically difficult collection, extraction, and separation of target organic compounds from the complex matrix (Busetti et al. 2006; Poster et al. 2006). As economic development has proceeded and public health awareness has increased, recent research has begun to focus on coking wastewater (Zhu et al. 2009; Bai et al. 2011; Chu et al. 2012). In recent years, many efforts have been made to develop effective analytical techniques for PAHs in complex matrices (Chen et al. 2005; Busetti et al. 2006; Guo et al. 2007), which make the identification and quantitative analyses possible for PAHs in coking wastewater.

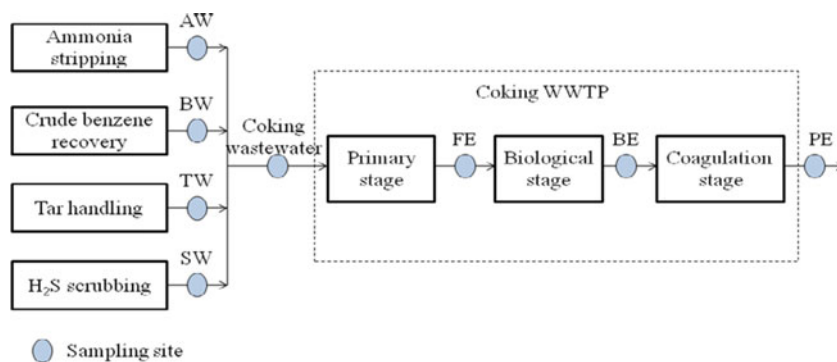
The aim of the present study was to identify PAHs in the wastewaters of a coke plant and examine PAH concentrations at numerous sites within the plant. The specific objectives were (1) to determine if coke plants were an important discharge source of PAHs to environmental waters by identifying various PAHs and measuring the concentrations of 18 PAHs in coking wastewaters from two plants, (2) to judge the PAH source during coke production by qualitatively and quantitatively analyzing PAHs in the subunits of coke production, and (3) to evaluate the removal of PAHs during wastewater treatment processes.

Materials and methods

Chemicals and materials

An analytical standard solution containing 18 PAH compounds, each at 2,000 $\mu\text{g/mL}$, and five deuterated surrogates, each at 4,000 $\mu\text{g/mL}$, was obtained from Supelco (Bellefonte, PA, USA). The 18 PAHs included naphthalene (Naph), 1-methynaphthalene (1-M-Naph), 2-methynaphthalene (2-M-Naph), acenaphthylene (Acy), acenaphthene (Ace), fluorene (Fle), phenanthrene (Phen), anthracene (Ant), fluoranthene (Flu), pyrene (Pyr), benzo[a]anthracene (BaA), chrysene (Chr), benzo[b]fluoranthene (BbF), benzo[k]fluoranthene (BkF), benzo[a]pyrene (BaP), indeno[1,2,3-cd]pyrene (Inp), dibenzo[a,h]anthracene (DBA), and benzo[g,h,i]perylene (BgP); the deuterated surrogates were naphthene-d8, acenaphthene-d10, phenanthrene-d10, chrysene-d12, and perylene-d12. Hexamethylbenzene used as an internal standard for gas chromatography (GC) analyses was obtained from Sigma-Aldrich (Gillingham, Dorset, VT, USA). All solvents used for sample processing and analysis (dichloromethane, hexane, acetone, and methanol) were of High Performance Liquid Chromatography

Fig. 1 Production processes at coke plant B and flow chart of the coking WWTP. *BW* crude benzene recovery wastewater, *TW* tar handling wastewater, *AW* ammonia stripping wastewater, *SW* H₂S scrubbing wastewater, *PE* primary effluent, *BE* biological effluent, *FE* final effluent



(HPLC) grade from Merck (Darmstadt, Germany). Deionized water was produced by a Milli-Q system (Millipore, USA).

Samples

Coking wastewater samples were taken from two coke industrial sites (designated as A and B) located in the Guangdong province of China. The companies responsible for the sites produce industrial coke for the steel industry as well as tar, crude benzene, ammonia, and naphthalene derivatives. Coking wastewater samples from the outflow of both sites were collected from May 14, 2010 to September 30, 2010. Sampling at site B was also carried out within the industrial complex. In particular, wastewater samples from ammonia stripping, crude benzene recovery, tar handling, and H₂S scrubber

as well as the effluent of various stages in the coking WWTP were collected from October 10 to 20, 2010. The scheme of sampling sites is shown in Fig. 1.

Extraction and separation

Water samples were filtered with glass filters (GF/F, 0.7 μm) to partition liquid and particle phases. Based on preliminary analysis of the organic compound content, subsamples of 50 mL for wastewaters from the subunits of coke production, 100 mL for coking wastewaters, or 500 mL for WWTP effluent were extracted onto C18 cartridges. Twenty microliters of surrogate standards (80 μg/mL) was added to the aqueous samples to correct losses along the extraction process and provide efficiency of the extract.

Fig. 2 Total ion chromatograms from GC/MS of weak polar fraction for identification of PAHs in coking wastewater from coke plant A (**a**) and coke plant B (**b**)

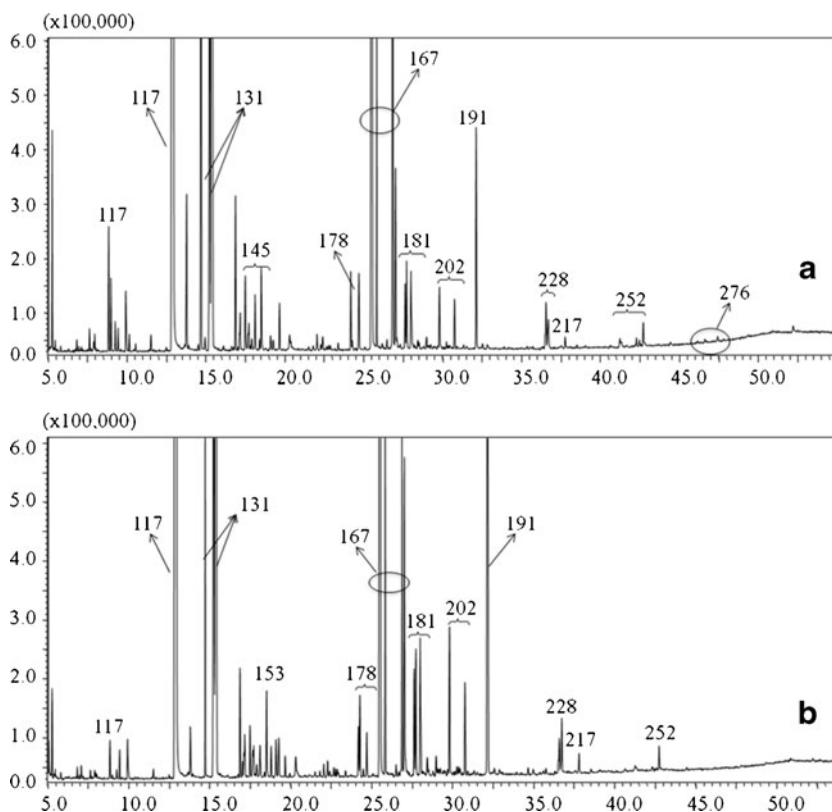
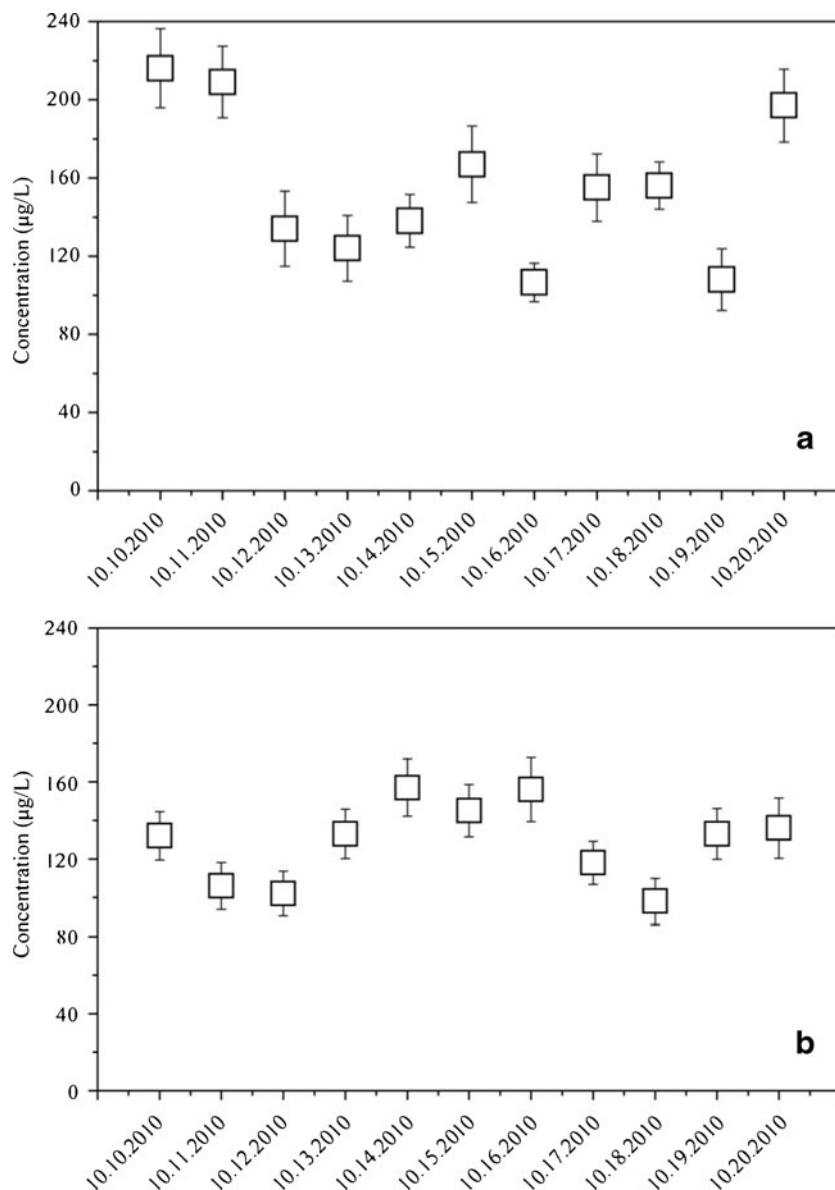


Fig. 3 Total PAH concentrations in coking wastewater from coke plant A (a) and coke plant B (b) on Oct 10–20, 2010



The extract was loaded onto a 1:2 alumina/silica gel glass column with 1 g of anhydrous sodium sulfate overlaying the silica gel for clean up and fractionation. First, 15 mL of hexane was applied to remove aliphatic hydrocarbons. Then, the weakly polar compounds containing PAHs were collected by eluting 70 mL of dichloromethane/hexane (3:7, v:v) and concentrated to 0.5 mL under a gentle stream of purified N₂. The internal standard (100 µg/mL, 5 µL) was added to the sample prior to GC–mass spectrometry (GC/MS) analysis.

Instrumental analysis

Identification and quantification of PAHs was performed using a GC/MS (Shimadzu, QP2010 Plus) with a 30 m × 0.25 mm id × 0.25 µm film thickness DB-5 ms column

(J&W Scientific, USA). The GC/MS conditions for sample analysis were as follows: the injection port, interface line, and ion source temperature were maintained at 280, 290, and 250 °C, respectively. The column temperature was programmed from 60 to 310 °C at 5 °C/min and held for 10 min. Helium was the carrier gas at a flow of 1.2 mL/min with a linear velocity of 42.4 cm/s. The mass spectrometer was operated in electron impact ionization mode (EI⁺, 70 eV). One microliter of volume of each sample was injected in the split mode, with the split ratio of 10:1.

Identification and quantification of PAHs by GC/MS

Identification of PAHs was based on a positive match of mass spectral data of the PAH isomers with mass spectra databases or based on a comparison of electron

Fig. 4 Total ion chromatograms from GC/MS of the weak polar fraction for identification of PAHs in wastewater from ammonia stripping (a), crude benzene recovery (b), tar handling (c), and H₂S scrubbing (d)

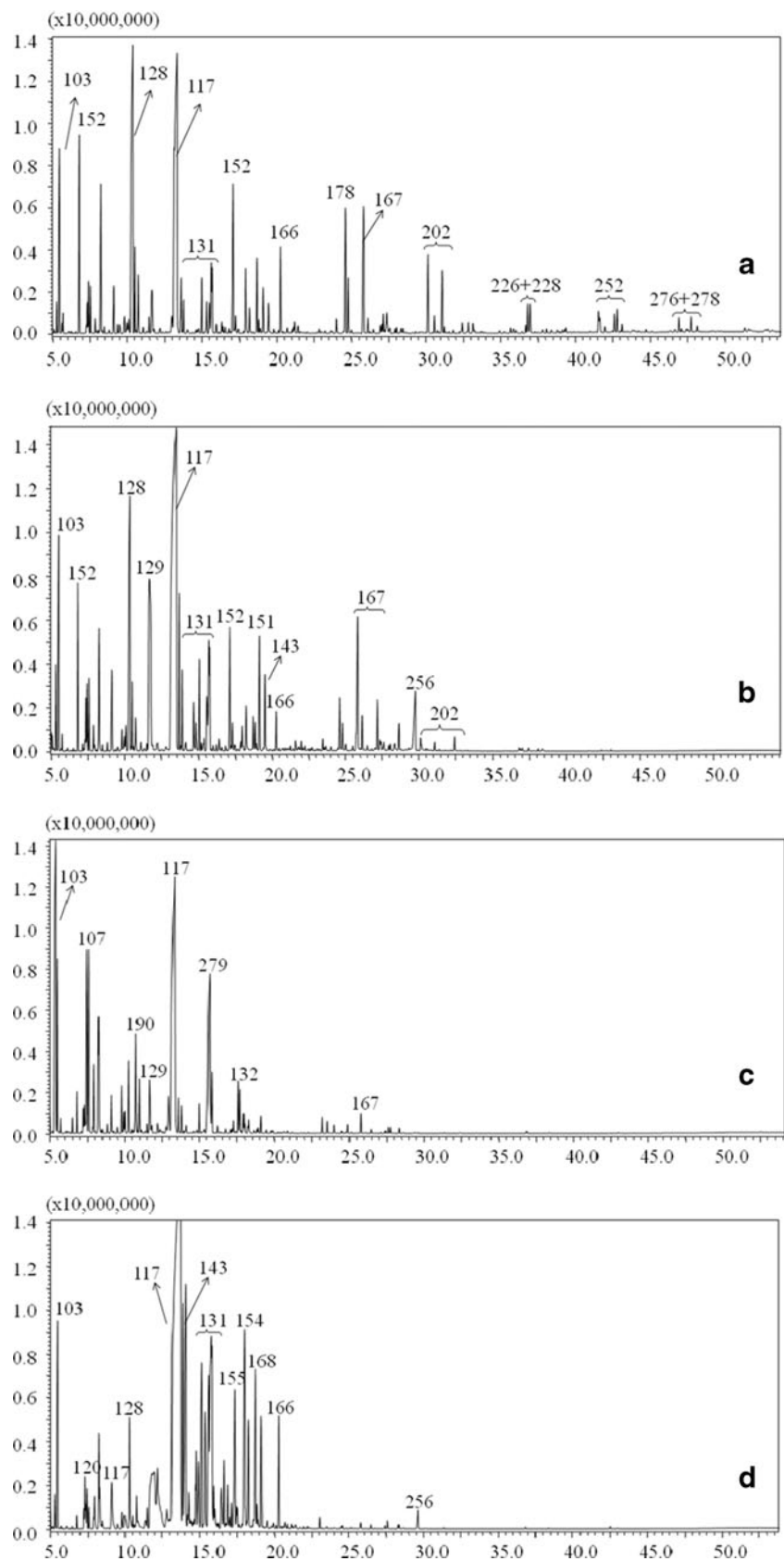


Table 1 Mean PAH concentrations (\pm SD) in the wastewater from the coking processes

PAH compound	Selected wastewater sample ($\mu\text{g/L}$)			
	BW ($n=6$)	TW ($n=6$)	AW ($n=6$)	SW ($n=6$)
Naph	278 \pm 38.0	3,770 \pm 415	2,140 \pm 710	616 \pm 62
1-M-naph	12.2 \pm 1.62	388 \pm 51.2	101 \pm 53.7	357 \pm 76.6
2-M-naph	8.94 \pm 1.69	998 \pm 89.3	0.72 \pm 0.26	257 \pm 87.1
Acy	13.0 \pm 0.54	246 \pm 33.5	629 \pm 145	31.4 \pm 6.12
Ace	5.46 \pm 1.34	422 \pm 62.2	65.3 \pm 23.5	1,270 \pm 335
Fle	3.64 \pm 0.35	671 \pm 115	140 \pm 39.2	645 \pm 151
Phen	5.11 \pm 1.16	216 \pm 92.9	188 \pm 32.2	13.3 \pm 2.15
Ant	2.52 \pm 0.42	8.5 \pm 0.6	46.5 \pm 12.6	2.60 \pm 0.24
Flu	1.65 \pm 0.33	469 \pm 92.2	54.3 \pm 15.4	4.21 \pm 1.13
Pyr	1.41 \pm 0.18	320 \pm 95.4	32.4 \pm 8.96	2.82 \pm 0.42
BaA	1.61 \pm 0.23	160 \pm 90.8	7.67 \pm 1.06	2.26 \pm 0.27
Chr	1.11 \pm 0.30	126 \pm 50.6	5.91 \pm 1.11	1.82 \pm 0.33
BbF	1.35 \pm 0.43	144 \pm 80.0	4.38 \pm 0.53	1.67 \pm 0.11
BkF	2.79 \pm 0.51	124.8 \pm 70.7	5.61 \pm 0.93	3.13 \pm 0.21
BaP	1.67 \pm 0.29	160.5 \pm 90.3	4.80 \pm 0.90	1.94 \pm 0.99
DBA	1.68 \pm 0.49	19.8 \pm 5.16	1.94 \pm 0.61	1.69 \pm 0.51
InP	1.63 \pm 0.17	102 \pm 30.3	3.31 \pm 0.87	1.68 \pm 0.22
BgP	1.08 \pm 0.12	83.6 \pm 10.3	2.57 \pm 0.97	1.11 \pm 0.32
Total PAHs	345 \pm 45.8	8,710 \pm 950	3,430 \pm 342	3,220 \pm 725

impact ionization mass spectra and retention times of targeted compounds with those of internal reference compounds. For correction of inaccuracies of retention time, the retention time of the surrogate standards was used.

Quantification was performed using a seven-point calibration curve established using hexane-based internal standard for each individual PAH. The R^2 values of the PAH calibration curves were all greater than 0.99. Detection limits of the method ranged from 0.01 to 0.58 $\mu\text{g/L}$. The average recoveries for all the sludge samples were 64 \pm 11, 86 \pm 11, 92 \pm 10, 89 \pm 9, and 96 \pm 10 % for naphthalene-d8, acenaphthene-d10, phenanthrene-d10, chrysene-d12, and perylene-d12, respectively.

Results and discussion

Identification and quantification of PAHs in coking wastewater

The total ion chromatograms (TIC) from GC/MS analyses of coking wastewater samples collected from two coking plants in the Guangdong province of China are presented in Fig. 2. In total, 358 weakly polar organic compounds were positively identified in the two coking wastewater samples, of which 270 were PAHs or their derivatives. As is clearly visible in Fig. 2, the whole chromatograms were dominated

by compounds in the MW range of 117–252. Some differences in the amounts and types of weakly polar compounds in the wastewater samples were observed between the two coking sites, which might be due to the different coke production processes applied in the two plants. Isomers of MW 117, 131, 167, 181, 191, 202, and 252 were, nevertheless, the dominant compounds in both samples. PAHs with low MW have a large number of possible isomers with the same MW, as evident from the seven isomers of MW 181, four isomers of MW 202, six isomers of MW 206, and four isomers of MW 252 found in the samples. In addition to the major PAH constituents, the wastewater samples also contained numerous heteroatomic PAH derivatives, including N-heterocycles, O-heterocycles, and S-heterocycles. These compounds were present in strong association with PAHs in the wastewaters. In coking wastewaters, 4-azafluorene series (MW 167), indole (MW, 117), and its alkylated derivatives (MW, 131) were the main N-containing PAHs, while 4-azafluorene accounted for a significant proportion in the coking wastewaters (Fig. 2). The dominant O-containing and S-containing heterocycles were 1-ethyl-3-isocyanatobenzene and benzo[b]naphtho[2,1-d]thiophene, respectively (Table S1). The appreciable levels of organic nitrogen, oxygen, and sulfur in Chinese coal (Bi et al. 2008) are believed to be responsible for the presence of heteroatomic PAHs in coking wastewaters upon incomplete combustion of coal (Osborne et al. 1997). As PAHs in coking wastewater originated from the coke production

Table 2 Identification of the selected PAHs and derivatives in the treated wastewater from the WWTP of coke plant B

Retention time	Compound	Influent	Primary effluent	Biological effluent	Final effluent
5.05	1-Chloro-1,2,3-trimethylcyclopropane	+			
5.15	2-Methyl-1,3-dithiacyclopentane	+	+		
5.24	5-Methyl-3-heptanone	+			+
5.25	6-Methyl-5-heptene-2-one			+	
5.26	Benzonitrile	+	+		
5.33	2,2,4-Trimethylheptane	+			+
5.50	Undecane	+			+
5.51	Tridecane	+		+	
5.58	Octanal	+	+		+
5.87	1,7-Dioxaspiro[5.5]undecane	+		+	
6.28	3-Methyl-5-propylnonane			+	
6.29	2,3,8-Trimethyldecane				+
6.80	5-Isobutylnonane	+	+	+	+
6.17	2-(4-Methyl-3-cyclohexen-1-yl)-1-propanol	+	+		
6.27	2,3,5,8-Tetramethyldecane	+	+		
6.63	3,7-Dimethylnonane	+			+
6.64	5-Butylnonane	+		+	
6.73	3,4-Dimethyldecane	+		+	+
6.74	3,7-Dimethylnonane	+	+		
6.79	3-Ethyl-3-methylheptane	+	+		
6.92	2-Methyl-5-propylnonane	+	+		
6.93	2,6,11-Trimethyldodecane	+		+	
6.94	2,7,10-Trimethyldodecane	+			+
6.95	4,6-Dimethyldodecane	+			
7.04	Acetophenone		+	+	+
7.05	1,2-Dichlorocyclohexane	+			
7.17	4-Nonanone			+	
7.18	4-Methylheptane	+			+
7.30	1-Undecanethiol		+		
7.63	2-Methylhexanal			+	
7.71	5-Butylnonane	+		+	+
7.81	Undecane				+
7.87	3,7-Dimethyldecane	+	+	+	
7.88	5-Isobutylnonane	+	+	+	+
7.93	Nonanal		+	+	+
7.95	2,4,6-Cycloheptatriene-1-carbonitrile	+			
8.02	3,3-Dimethylhexane		+		
8.03	5-Isobutylnonane	+	+	+	+
8.11	2,6-Dimethyl-2,5-Heptadien-4-one		+	+	
8.19	2,3,4-Trimethyldecane	+		+	
8.19	3-Methyl-4-heptanone	+	+		
8.26	2,2-Bis(<i>p</i> -methoxyphenyl)-1,1-dichloroethylene	+		+	
8.33	3,5-Dimethylanisole	+		+	
8.83	Benzeneacetonitrile	+	+		
8.96	2,6-Dimethyl-6-nitro-2-hepten-4-one				+
8.98	4-Methyl-3-penten-2-one	+	+	+	
9.24	Cyclopentasiloxane, decamethyl-		+		
9.43	Naphthalene, 1,2,3,4-tetrahydro-	+	+	+	+
9.98	Azulene	+			+

Table 2 (continued)

Retention time	Compound	Influent	Primary effluent	Biological effluent	Final effluent
10.26	Naphthalene	+	+	+	+
10.38	Tridecane	+			+
10.54	Decanal	+	+	+	+
11.40	3-Methylbenzyl cyanide	+			
11.51	Isoquinoline	+	+		
11.52	Cinnamitrile	+			+
12.48	Nonane, 5-methyl-5-propyl-			+	
12.49	4,6-Dimethyldodecane				+
12.50	2-Bromododecane		+		
12.51	5-Isobutylnonane	+		+	+
12.96	Indole	+	+	+	+
13.13	1-Methylnaphthalene	+	+	+	+
13.30	Benzocycloheptatriene		+		
13.57	2-Methylnaphthalene	+	+	+	+
13.68	3-Ethyl-3-methylheptane		+		+
13.69	1-Chlorooctadecane			+	
13.93	Indole-2-carboxylic acid		+		
14.72	2-Methylindol	+	+	+	
15.24	3-Methylindole	+	+	+	+
15.35	4-Methylindole	+	+	+	+
15.41	5-Methylindole	+	+		
16.74	Biphenylene			+	
16.76	Acenaphthylene	+	+		+
17.03	2,3-Dimethylindole	+	+		
17.12	5,7-Dimethylindole	+	+		
17.17	4,7-Dimethyl-2H-isoindole	+		+	
17.67	1,3-Dimethylindole	+	+		
17.72	2,4,6-Trimethylbenzonitrile	+			
17.81	6-Ethyl-2-methylindolizine	+			
17.88	1-Naphthalenecarbonitrile		+		
17.91	2-Methyl-5-(butyn-1-yl)pyridine	+			
17.92	Acenaphthene	+	+	+	+
17.94	2,6,10,15-Tetramethylheptadecane				+
18.39	Menadione			+	+
18.40	7-Acenaphthenone	+	+		
18.50	2-Naphthalenecarbonitrile				+
18.52	1-Naphthalenecarbonitrile	+	+	+	+
18.80	6-Chloro-1H-indole	+	+		
19.01	Heptadecane				+
19.10	3-Methylisoquinoline	+	+	+	
19.27	3-Methylquinoline	+	+		
19.66	2,6-Ditert-butyl-4-(hydroxymethylene)-2,5-cyclohexadie	+	+	+	+
19.95	Fluorene	+	+	+	+
20.32	Diethyl phthalate	+	+	+	+
20.37	2-(Methylmercapto)benzothiazole	+		+	+
20.38	6,8-Dioxapentadecane	+	+		
20.86	<i>N,N</i> -diphenyl-hydrazinecarboxamide	+		+	+
20.99	5-Nitroisoquinoline	+		+	
21.15	2-Ethyl-1,4-naphthoquinone	+		+	

Table 2 (continued)

Retention time	Compound	Influent	Primary effluent	Biological effluent	Final effluent
21.51	Benzo[g]quinoline	+	+	+	+
21.81	4-Quinolinecarboxaldehyde	+	+		
22.29	3-Phenylpyridine	+			
22.39	2-Naphthylacetonitrile			+	+
22.42	2-Phenylpyridine	+			
22.66	3-Phenylpyridine	+			
22.78	4-Phenylpyridine	+			
22.86	2-Ethyl-2-methyldecanol				+
22.89	3-Phenylpyridine	+			
22.96	1-Chloro-2-naphthalenamine	+	+		
23.39	Benzo[h]cinnoline	+	+	+	+
23.69	Naphtho[2,3-b]thiophene		+		
23.79	1-Iodohexadecane				+
24.28	Phenanthrene	+	+	+	
24.47	Benzo[g]quinoline			+	
24.49	Anthracene	+	+	+	+
24.68	Benzo[g]quinoline				+
24.70	6b,8a-Dihydrocyclobut[a]acenaphthylene	+	+	+	+
25.11	Tridecanal				+
25.51	4-Azafluorene	+	+	+	+
25.81	2-Naphthylacetonitrile			+	+
26.64	1-Methylanthracene			+	
26.49	Thianaphthene-3-acetonitrile	+	+	+	
26.63	1-Methylanthracene		+		+
26.64	4-Methylphenanthrene				+
26.84	2-Naphthylacetonitrile				+
26.85	1-Naphthaleneacetonitrile			+	
27.03	9-Methyl-9H-carbazole	+	+		
27.14	2-Methoxy-3-nitromethyl benzoate				+
27.64	3-Methylcarbazole	+	+	+	+
27.74	1-Aminofluorene	+	+		+
28.01	2-Methylcarbazole	+	+	+	+
28.11	9,10-Anthracenedione			+	+
28.23	1,8-Dimethylcarbazole		+		
28.44	3-Methylcarbazole			+	
28.45	2-Fluorenamine	+	+	+	
28.81	2-Nonadecanone				+
29.09	3-Methylcarbazole	+	+		
29.10	3,4-Dimethyl-9H-carbazole	+	+		
29.14	2-Hexadecyloxirane	+			+
29.15	1,8-Dimethylcarbazole	+	+		
29.44	3,4-Dimethyl-9H-carbazole	+	+		
29.50	1,8-Dimethylcarbazole	+	+		
29.55	3-Methylcarbazole	+	+		
29.69	10,11-Dihydrocarbamazepine	+	+		
29.80	Benzo[def]phenanthrene	+	+		
29.88	10,11-Dihydrocarbamazepine	+	+		
30.15	1,1'-Biphenyl, 4-(1-azido-1-methylethyl)-	+	+		
30.26	Fluoranthene	+	+	+	+

Table 2 (continued)

Retention time	Compound	Influent	Primary effluent	Biological effluent	Final effluent
30.37	1-Chloro-4-(chlorophenylmethyl)benzene	+	+		
30.47	2-Acetylfluorene	+	+		
30.61	Acenaphtho(1,2-B)pyridine	+			
30.77	Pyrene	+	+	+	+
32.14	9H-Fluorene-9-carbonitrile	+	+	+	+
34.63	1-Chloropyrene	+			
35.74	Benz[c]acridine	+			
35.91	1-Heneicosanol				+
36.50	Benz[a]anthracene	+			
36.69	Benzo(b)carbazole			+	
36.71	11H-Indeno[1,2-b]quinoline	+			+
36.96	Chrysene	+	+	+	+
37.11	9-Anthracenecarboxaldehyde				+
37.76	Benzo[a]carbazole	+		+	
37.77	3-Fluoranthanamine		+		
37.77	1-Aminopyrene	+	+		
41.53	Benzo[b]fluoranthene	+	+	+	+
41.63	Benzo[j]fluoranthene	+	+	+	+
42.59	Benzo[k]fluoranthene	+	+	+	+
42.77	Benzo[a]pyrene	+	+	+	+
46.93	Indeno[1,2,3-cd]pyrene	+	+	+	+
47.09	Dibenz[a,h]anthracene	+	+	+	+
47.73	Benzo[ghi]perylene	+	+	+	+

processes, the composition of PAHs in the coking wastewater was likely influenced here by the source coal's organic composition and coking processes. Coal is a complex, heterogeneous mixture of organic and inorganic constituents of allothigenic or authigenic origin, in which PAHs are present as the most abundant constituents, particularly with less than five rings and their methyl derivatives (Zhao et al. 2000; Bi et al. 2008). During pyrolysis of raw coal, PAHs with two or three rings can evaporate from the solid phase. Besides volatilization, the PAHs can be formed during coke production by pyrolysis and pyrosynthesis (Liu et al. 2008). The identification of hundreds of PAHs in coking wastewater demonstrated that coking wastewater was the important source of these compounds in the aquatic environment.

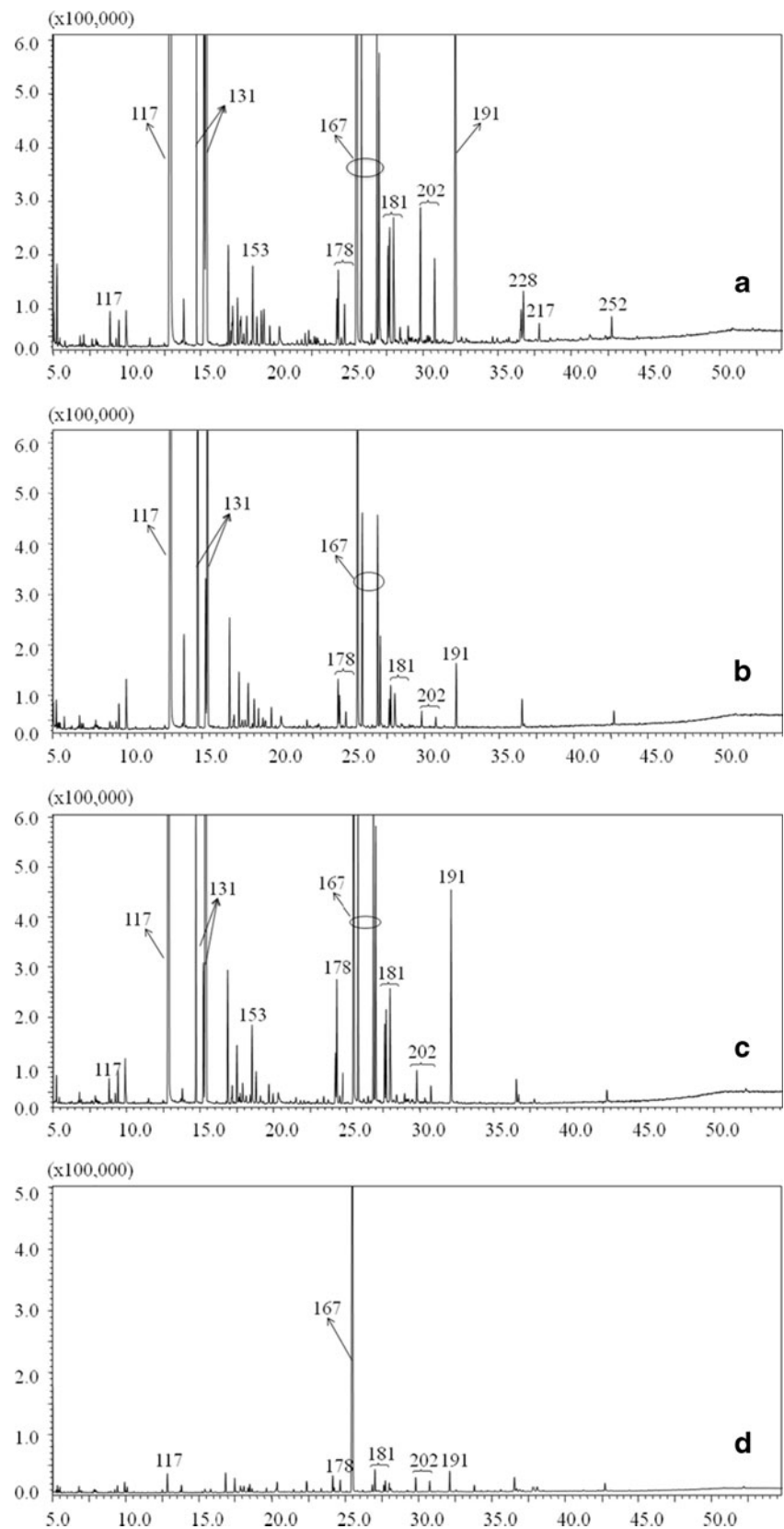
Levels of contamination in the coking wastewater were assessed by quantitative determination of 18 PAHs over 11 consecutive days, as shown in Fig. 3. The total PAH concentrations of these coking wastewater samples ranged from 107±10.2 to 216±20.2 µg/L for coke plant A and from 98.5±8.9 to 157±14.9 µg/L for plant B, which were much higher than their concentrations in other countries (Walters and Luthy 1984). Compounds with medium MW were the dominant PAHs in these two coking wastewaters, in which Phen, Flu, and Pyr represented 17, 29, and 18 % of the total PAH load,

respectively. Other PAH species such as Naph, BaA, Chr, and BaP also contributed a notable proportion. The PAH concentrations measured here were much higher than those measured in other countries (Walters and Luthy 1984) or in urban and urban/industrial wastewater (Pham and Proulx 1997; Fatone et al. 2011; Manoli and Samara 2008). Considering the higher concentrations and variety of PAH derivatives identified here, these results indicated that coking wastewater was a clear source of PAHs. To minimize PAH discharge to the environment, it was, therefore, necessary to trace the source of these compounds during coke production processes and to treat coking wastewater by WWTP before discharge.

Distribution of PAHs over coking processes

Identification and quantitative analysis of the wastewater from separate production subunits within coke plant B allowed the evaluation of the contribution of selected individual production processes to the total coking outflow, which could also provide basic information on the wastewater composition for designing the treatment method. In the coke plant, coking wastewater originated from the processes of tar handling, crude benzene

Fig. 5 Total ion chromatograms from GC/MS of the weak polar fraction in the influent (**a**) and treated wastewater from the WWTP of coke plant B. **b** Primary effluent; **c** biological effluent; **d** final effluent



recovery, ammonia stripping, and H_2S scrubbing. Thus, the PAHs in coking wastewater were produced mainly

during coke production and/or the by-product production and purification.

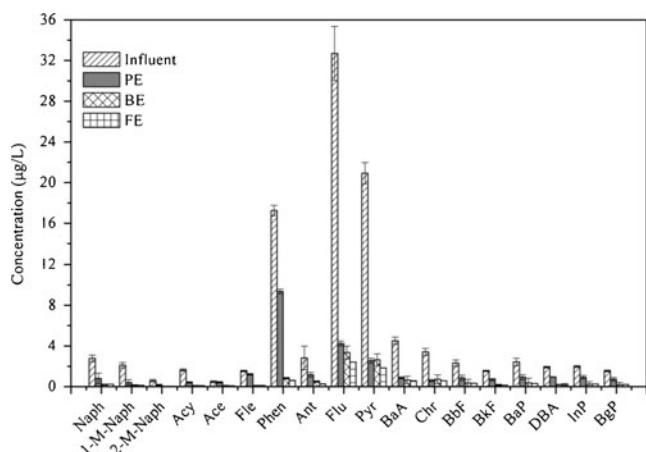


Fig. 6 PAH concentrations in treated effluent of the coking WWTP

The TICs from GC/MS analyses of wastewater samples collected from four subunits in coke plant B are presented in Fig. 4, with detailed information on the identified compounds listed in Table S2. As a whole, the total amount and variety of PAHs in these four wastewaters were almost identical to those seen in raw coking wastewater, indicating that PAHs in the latter mainly originated from these four subunits in the plant. Although the four chromatograms were dominated by compounds having MW of 103 and 117, the compositions of the four wastewaters had big differences. For the tar scrubber sample, the chromatogram was dominated by 2-4-ring PAHs in the MW range of 128–202, with some smaller peaks for several nitrogen-heteroatomic compounds (MW, 103, 117, 131, and 167) and 1-chloroindane (MW, 152). Among the main PAHs, three isomers of MW 154, four isomers of MW 156, six isomers of MW 166, six isomers of MW 192, and four isomers of MW 202 were identified, with the isomers of MW 128, 166, 178, and 202 being abundant. For the ammonium stripping sample, 167 weakly polar compounds

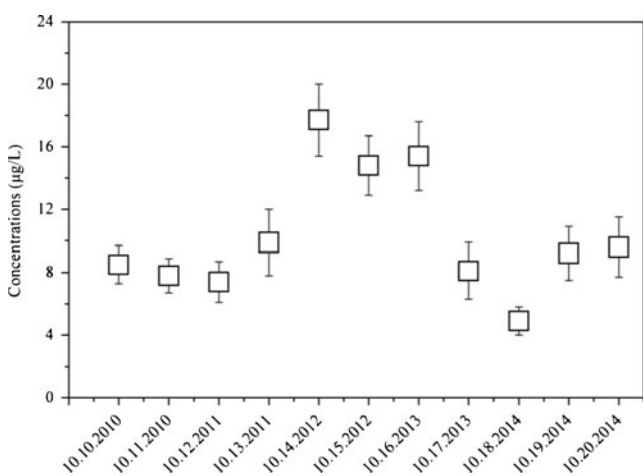


Fig. 7 Total PAH concentrations in the final effluent from coke plant B on Oct. 10–20, 2010

were identified, with compounds in the MW range of 128 to 166 representing the dominant PAHs. Similar to the tar scrubber sample, this chromatogram also contained nitrogen-heteroatomic compounds; however, compounds with MW of 129, 143, and 151 accounted for a greater proportion of the total PAH derivatives here. Samples from crude benzene recovery (Fig. 4b) and H₂S scrubbing (Fig. 4d) had much lower abundances of weakly polar compounds, and their chromatograms were dominated by compounds with lower MW (MW of 103 to 168). The heteroatomic compounds with nitrogen, oxygen, or both were the representative compounds in both benzene recovery wastewater (MW, 107, 132, 190, and 279) and H₂S scrubbing wastewater (MW, 120, 155, and 168). After these nitrogen- and/or oxygen-heteroatomic compounds, 2-3-ring PAHs were the next most abundant compounds in these two wastewater samples.

As shown in Table 1, the total PAH concentrations in wastewater samples from the four plant subunits were between 345±45.8 and 8,702±519 µg/L, with the highest concentration in tar handling wastewater. The total PAH concentration in crude benzene recovery wastewater was the lowest, but this was still much higher than PAH concentrations in raw coking wastewater. Concentrations of individual PAHs in wastewater from the four subunits roughly ranged from 1.1±0.1 to 3,770±410 µg/L. Two- and three-ring compounds, dominated by Naph, 2-M-Naph, Acy, Ace, Fle, and Phen, contributed 80–99 % to the total PAHs in all the subunit wastewaters. In particular, Naph contributed most strongly to wastewaters from tar handling, ammonia stripping, and crude benzene recovery processes, making up 43, 62, and 81 % of the total PAH load, respectively, at concentrations of 3,770±410, 2,140±324, and 278±38 µg/L, respectively. In contrast, Naph contributed 19 % to the PAH load in wastewater from the H₂S scrubbing; instead, Ace was the dominant compound, with a contribution of 40 %, followed by Fle. The presence of individual PAHs with high concentrations in subunit wastewaters suggested that removal at their source within various subunits would potentially be a better control method for these compounds during coke production.

Based on the concentrations of PAHs determined in subunit wastewaters and on the wastewater volume from various processes in the coking plant, the daily output of PAHs from subunit wastewaters was calculated. The results indicated that compounds in the coking wastewater came mainly from ammonia stripping wastewater, which contributed 98 % of the total PAHs detected. Although the wastewater from tar handling and H₂S scrubbing had larger concentrations of PAHs, their respective contributions of 0.5 and 1.3 % to the total coking wastewater PAHs were much lower than that of ammonia stripping wastewater due to their lower wastewater volumes (3.6 and

24 m³/day, respectively) compared that for ammonia stripping (1,680 m³/day).

Removal of PAHs during wastewater treatment processes

WWTPs play an important role in removing pollutants from wastewater, using physical, chemical, and biological methods for optimal removal. In removal processes, pollutants would undergo separation, air stripping, transformation, and adsorption (Zhang et al. 2012), and the amounts and concentration were reduced after these treatment processes. In the coking WWTP, the amounts and varieties were reduced from 358 in the coking wastewater (influent) to 69 in the final effluent (Table 2). As shown in Fig. 5, the chromatograms of coking wastewater and pretreatment effluent had similar compositions, both being dominated by N-heteroatomic compounds (MW, 117 to 181) and the major PAHs with medium MW (MW, 178 to 202). This indicated little change in water quality at the pretreatment stage. In this stage, volatilization and separation from tar were expected to allow removal of low MW and high MW PAHs, respectively (Zhang et al. 2012). In the biological effluent, 73 weakly polar compounds were found, and the chromatogram was dominated by one N-heteroatomic compound, 4-azafluorene (MW, 167). This indicated that most of the PAHs were removed in the biological unit, with possible mechanisms of chemical transformation, biodegradation, and adsorption to sludge (Shiaris 1989; Sigman et al. 1998; Heidler et al. 2006; Zhang et al. 2012). Similar to that for the biological effluent, the final effluent chromatogram was still dominated by 4-azafluorene (MW, 167), and 69 weakly polar compounds were still present. This suggested that coagulation did not play an effective role in removing these organic pollutants and that advanced treatment was necessary for the most effective control of PAHs.

To determine the behaviors of PAHs during coking wastewater treatment processes, 18 PAHs in the liquid phase at different treatment stages were quantified. The total concentration of these 18 PAHs was reduced from 103±24.5 µg/L in the influent to 8.5±3.1 µg/L in the final effluent (Fig. 6) for a removal rate of 92 %. The removal of aqueous PAHs in the pretreatment stage was distinct, as the total PAH concentration in pretreatment effluent was no larger than 27.4±2.5 µg/L. This large reduction can be ascribed to several possible mechanisms: (1) recirculated flow may have diluted target compounds in the pretreatment effluent, (2) the separation of tar using air flotation may have removed these hydrophobic compounds with the tar phase, or (3) the ammonium stripping process could release these semivolatile organic compounds to the atmosphere. Biological treatment played an important role in removing PAHs, as the total concentration of target PAHs was reduced to below 3.4±0.3 µg/L in the biological effluent. As

expected, the biological treatment provided satisfactory removal of PAHs, reaching greater than 60 % removal for most of the target compounds. Mechanisms that can remove PAHs during biological treatment were volatilization, air stripping, adsorption, and biodegradation/biotransformation (Katsoyiannis and Samara 2005). Volatilization and air stripping were facilitated by the forced injection of air into the aeration tanks; thus, they played a role in removing these compounds that had relatively high Henry's law constants (Rogers 1996; Byrns 2001; Katsoyiannis and Samara 2005) and significant distribution in the aqueous phase. Therefore, removal of PAHs with low MW in the biological treatment process might be partially attributed to volatilization and air stripping. However, the high boiling point (217 to 550 °C) and strong sorption potential (log K_{ow} of 3.37 to 6.84) of other PAHs suggested these processes did not contribute as strongly to their removal. As hydrophobic compounds, PAHs tended to accumulate to particles and sludge, and mass losses would be mainly due to the adsorption to sludge for PAHs, which had been proved in the previous study (Zhang et al. 2012). Concerning biotransformation, it was important for compounds with moderate log K_{ow} (3–3.5), while it was drastically reduced for compounds with log K_{ow} >6 (Byrns 2001). Thus, PAHs with log K_{ow} value of 3.37 to 6.84 in the current study were likely removed during biological treatment, in part, through biotransformation, including complete microbially mediated mineralization and cometabolism with other carbon sources. In the aqueous phase of secondary clarifier effluent, concentrations of all individual PAHs were below 5 µg/L. Although Ant and Pyr were reduced to 30 % of their levels before this process, the concentrations of some PAHs, such as Naph, Acy, Fle, Inp, and BgP, increased by 1–23 %. The phenomenon of increased concentrations also happened in the biological treatment stage, which might occur as a result of sampling methods, analytic technology, or fluctuation of water quality; however, the most significant factor would be the inclusion of nonsettleable small particles.

PAH loads and potential environmental implications

After the treatment composed of physical, biological, and float facilities, 84–96 % of the individual PAHs were removed from the aqueous phase of coking wastewater. However, PAHs were still present in the final effluent from coking plant B, with total PAH concentrations ranging from 4.9±1.5 to 17.7±3.8 µg/L over 5 months of sampling (Fig. 7). Considering the wastewater volume for the coke plant (1,800 m³/day), the total PAH loads in WWTP final effluent were 8.8±2.7 to 31.9±6.8 g/day from this plant alone. As PAHs tended to be adsorbed onto particles, the true environmental PAH load from this plant was greater than the above values. For China as a whole, the total environmental PAH inputs from all treated coking wastewater

would be relatively higher due to over 1,300 coking wastewater treatment facilities that are in operation today.

The marked persistence of PAHs in coking wastewater was noteworthy and potentially problematic, given the compounds' high production volume and established human toxicity (Nisbet and Lagoy 1992). In particular, PAHs in aqueous water were much more bioavailable and toxic than those adsorbed to particles (Gustafsson et al. 1997). Given the negative impact of these industrial contaminants, many countries have started to take action for environmental protection. Under Chinese law (GB8978-1996), only BaP has, so far, been restricted, with a maximum allowable concentration of 0.03 $\mu\text{g/L}$. Under EU law, maximum allowable concentrations are 2.4 $\mu\text{g/L}$ for Naph, 0.4 $\mu\text{g/L}$ for Ant, and 1.0 $\mu\text{g/L}$ for Flu (Sanchez-Avila et al. 2009). In the final effluent studied here, concentrations of Flu and BaP were 2.4 and 0.3 $\mu\text{g/L}$, respectively, over the European and Chinese limits, respectively. Since PAHs are highly hydrophobic and can be adsorbed to and accumulate in suspended particles, higher concentrations of PAHs were present in the coking WWTP final effluents, which contain particles, than found in the aqueous phase alone. However, in this case, the coking WWTP effluents were discharged to the river and diluted therein, and the potential impact was likely lower and localized to the outfall discharge area.

Conclusions

In this study, coke plants were found to be the important source of aquatic PAHs. Two hundred seventy PAHs were identified in coking wastewater and coking production subunit wastewaters, with 3-4-ring PAHs as the dominant compounds. Total PAH concentrations in coking wastewater ranged from 98.5 ± 8.9 to 216 ± 20.2 $\mu\text{g/L}$ and were between 345 ± 45.8 and $8,702 \pm 519$ $\mu\text{g/L}$ in subunit wastewaters. Two- and three-ring compounds predominated in these subunit wastewaters, in which Naph, 2-M-Naph, Acy, Ace, Fle, and Phen were the dominant compounds. The calculation of daily PAH output from the four subunits indicated that PAHs in the coking wastewater came mainly from ammonia stripping wastewater. WWTP played an important role in removing PAHs in coking wastewater, from which 92 % of the target compounds was removed and only 69 weakly polar compounds were found in the final effluent. However, 8.8 ± 2.7 to 31.9 ± 6.8 g/day of PAHs with toxic potential were discharged to environmental waters, suggesting that implementation of tertiary treatments in this WWTP was still needed to reduce the continuous input of these contaminants to the environment.

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