Coking wastewater treatment plant as a source of polycyclic aromatic hydrocarbons (PAHs) to the atmosphere and health-risk assessment for workers

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ABSTRACT

PAHs were identified and some of them were determined in the air around a coking wastewater treatment plant (WWTP) using passive air samplers. Seventy seven PAHs were found in the emissions from the degreasing tanks, the aeration tanks and the secondary clarifiers. $\sum$ PAH concentrations within the plant (373.3 ± 27.3–12959.5 ± 685.9 ng/m^3) were 3–41 times higher compared to the reference sites (315.7 ± 50.2–363.4 ± 77.5 ng/m^3). The identification of numerous PAHs and high concentrations of these selected ones in the air of the studied sites indicated that the coking WWTP was a new source of atmospheric PAHs. Variations in the PAH pattern were observed in air within the coking WWTP. For example, Flu and Pyr accounted for 35–46% of the total contents at the degreasing tanks, but less than 10% at the hydrolytic tanks. The calculation of the diagnostic ratios suggested that PAHs in the emissions had the source characters of coal combustion. Furthermore, highly elevated PAH concentrations were determined at the degreasing tanks compared to the other tanks (i.e., aeration tanks and secondary clarifiers) and likely associated with their high concentrations in the coking wastewater and increased volatilization at high water temperature. Health risk assessments were carried out by evaluating the inhalation PAH exposure data. The resultant inhalation exposure levels due to TEQ$_{BaP}$ for workers ranged from 1.6 ± 0.6 to 71.2 ± 8.2 ng/m^3, and the estimated lung cancer risks were between $0.1 \times 10^{-3} \pm 0.1 \times 10^{-4}$ and $5.2 \times 10^{-3} \pm 0.5 \times 10^{-3}$, indicating PAHs in the air around the degreasing tanks and the aerobic tanks would have potential lung cancer risk for the operating workers.

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1. Introduction

The development of industry production and the increase of urban population cause a dramatic increase of industrial and municipal wastewaters which must be treated in a safe and environmentally friendly manner before they are discharged to the aqueous environment. However, the common used wastewater treatment plant (WWTP) can not achieve the complete removal of pollutants, thus appearing the point sources of water pollution (Pham and Proulx, 1997). Also, WWTPs can become the atmospheric sources of some organic pollutants, such as volatile organic compounds (Simonich et al., 2000; Escalasa et al., 2003; Wu et al., 2006), perfluorooctanoic acid (Webster et al., 2010), polyfluoroalkyl compounds (Ahrens et al., 2011) and PAHs (Byrns, 2001; Seth et al., 2008). Recently, intense attention has been paid on PAHs in the atmosphere (Simcik et al., 1999; Park et al., 2002; Omar et al., 2006; Zhang et al., 2011a), as the most carcinogenic, mutagenic and toxic contaminants (Deng et al., 2006).

PAHs are a class of diverse organic compounds made up of two or more fused aromatic rings with carbon and hydrogen atoms. There are many sources of atmospheric PAHs, most of which are generated from anthropogenic emissions such as industrial production, transportation and waste incineration (Omar et al., 2006). In many cities, the dominant source of PAHs in the atmosphere has been found to be vehicular emissions (Simoneit et al., 1991; Simcik et al., 1999; Park et al., 2002). Other important sources of PAHs that are not originated from fossil fuels include the combustion of domestic, garden and electric wastes (Omar et al., 2006; Zhang et al., 2011a), and the smoke from regional forest fire. Tobacco smoking as well as use of heating devices can also increase the indoor contents of PAHs in the air (WHO, 1987). As the semi-volatile organic compounds, PAHs can volatilize or be air-stripped to the atmosphere due to the forced injection of air into the mixed liquid during wastewater treatment processes (Byrns, 2001; Seth et al., 2008).

Industrial and municipal WWTPs are mostly discussed as point sources for PAHs released into the aquatic environment (Pham and Proulx, 1997; Manoli and Samara, 2008; Vogelsang et al., 2006; Fatone et al., 2011); however, field studies of PAHs in the representative atmosphere from WWTPs are limited. It is mainly because of the difficulties in collecting air samples and analyzing these compounds,

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so there are no data available on the emissions of PAHs to atmosphere from this potential source. Since 2000, numerous efforts have been made to develop the effective sampling and/or analytical techniques for PAHs in the gas-phase samples (Bi et al., 2003; Chen et al., 2005; Klanova et al., 2008; Tao et al., 2009). These newly developed techniques make the identification and characterization possible for PAHs in the emissions from WWTPs. Because the emissions from wastewater come into direct contact with the operating workers in WWTPs, PAHs in these emissions may be inhaled by them. As it is well known, PAHs may create toxicity in organisms, by interfering with cellular membrane function and the coupled enzyme system (Nisbet and Lagoy, 1992; Orecchio, 2010), thus it is essential to make the health-risk of these compounds to the workers in WWTPs.

The aim of this study was to identify PAHs in the emissions of a coking WWTP and examine atmospheric PAH concentrations at numerous sites on and around the WWTP. The specific objectives were (i) to determine if coking WWTPs were important emission sources of PAHs to air by identifying various PAHs and measuring the concentrations of 18 PAHs in the atmosphere at the coking WWTP, (ii) to characterize the composition of PAHs in these samples in order to identify sector specific differences, and (iii) to evaluate the health-risk of PAHs in the air of the coking WWTP.

2. Materials and methods

2.1. Chemicals and materials

The standard solution PAHs that containing 18 compounds, each at 2000 μg/mL, i.e., 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), bnzo[g,h,i]perylene (BgP), and deuterated surrogate (each at 4000 μg/mL) containing naphthene-d8, acenaphthene-d10, phenanthrene-d10, chrysene-d12 and perylene-d12 were obtained from Supelco (Bellefonte, PA, USA). Hexamethylbenzene used as an internal standard for GC analyses was obtained from Aldrich Chemicals (Gillingham, Dorset, USA). All solvents used for sample processing and analysis (dichloromethane, hexane, acetone and methanol) were HPLC grade from Merck (Darmstad, Germany). Deionized water was produced by a Milli-Q system (Millipore Co., USA).

2.2. Coking WWTP and sampling

The investigated coking WWTP was located in Shaoguan Steel Company, Guangdong province of China, with an average treatment capacity of 2000 m^3/d. The ammonia still effluent and cleaning wastewater were the influent of the coking WWTP. The influent was first floated to remove oil stick at the degreasing tanks. From there, the liquid effluent went through an aeration stage where anoxic-oxic-hydrolytic-oxic system coupled with biological fluidized-bed was applied to degrade the organic matter. Forced air was injected into aeration tanks through the bottom to enhance microbial activity, which introduced turbulence to water surface and bubbling/aqueous PAHs emission. The biological effluent then went through secondary clarifiers, where the bacteria and remaining particles were coagulated and removed from the wastewater. Finally, the secondary clarifier effluent was discharged to drainage of the steel company.

To assess emissions of PAHs to air from the coking WWTP, passive air samplers (PAS) equipped with glass filters (GFFs, 140 mm diameter) and polyurethane foam (PUF) disks (140 mm diameter × 13.5 mm thick, density 0.021 g/m^{-3}) were deployed for 28 days (Oct 2–29, 2010) around the WWTP. Before sampling, the PUF disks were previously by Soxhlet extracted with dichloromethane for 72 h, and the GFFs were preconditioned by heating in a furnace at 450 °C for 6 h. The air samples were operated at the degreasing tanks (sites 1–3), anaerobic tanks (sites 4–6), aerobic 1 tanks (sites 7–9), hydrolytic tanks (sites 10–12), aerobic 2 tanks (sites 13–15), secondary clarifiers (sites 16 and 17), which were all open to the atmosphere, and at two reference sites (sites 18 and 19) (Fig. 1). During sampling, the climatic of this region was a moderately warm with a mean temperature of 23 °C, and prevailing southeast wind.

2.3. Sample preparation

Air sampling medias including GFFs and PUFs were spiked 20 μL surrogate standards (80 μg/mL) and Soxhlet extracted with 200 mL dichloromethane for 48 h in a water bath maintained at 46 °C. The extract passed to a 1:2 alumina/silica gel glass column with 1 g anhydrous sodium sulfate overlaying the silica gel for clean-up and fraction. First, 15 mL of hexane was applied to remove aliphatic hydrocarbons. Then, the eluents containing PAHs were collected by eluting 70 mL of dichloromethane/hexane (3:7, v:v), and were concentrated to 0.5 mL under a gentle purified N_2 stream. 5 μL internal standards (100 μg/mL) was added to the sample prior to GC/MS analysis.
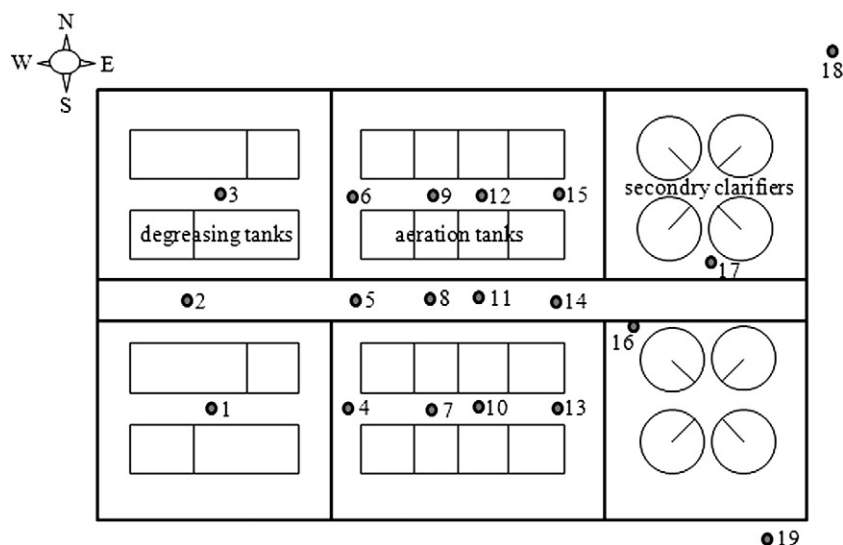

Fig. 1. Sampling sites on and around the coking wastewater treatment plant.

2.4. Instrumental analysis

PAHs were analyzed 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 (70 eV). 1 μL volume of each sample was injected in the split mode, the split ratio was 10:1.

2.5. Identification and quantification

Identification of PAHs was based on a positive match of mass spectral data of the PAH isomers with mass spectra databases or comparison of EI$^+$-mass spectra with those reference compounds and gas chromatographic retention times. For correction of inaccuracies of retention time, the retention time of the surrogate standards were 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. Duplicate measurements (site 7 and 8) and field blank were evaluated. Field blank concentrations (n = 5) were <1% of the concentrations measured in the samples. Method detection limits were calculated as 3 times signal to noise for each compound in the actual air samples and ranged from 0.02 to 0.98 ng/m^3. The average recoveries for air samples were 58.7 ± 8.7% for naphthalene-d8, 74.6 ± 9.1% for acenaphthene-d10, 86.7 ± 8.7% for phenanthrene-d10, 96.8 ± 10.1% for chrysene-d12 and 96.0 ± 9.7% for perylene-d12.

3. Results and discussion

3.1. Identification of PAHs in the emissions from the coking WWTP

The total ion chromatograms (TICs) from GC/MS analysis of six air samples collected from the coking WWTP are presented in Fig. 2, and the GC retention time, molecular formula and molecular weight (MW) for the constituents of PAHs are listed in Table 1. It was revealed that there were seventy seven PAHs in these air samples,
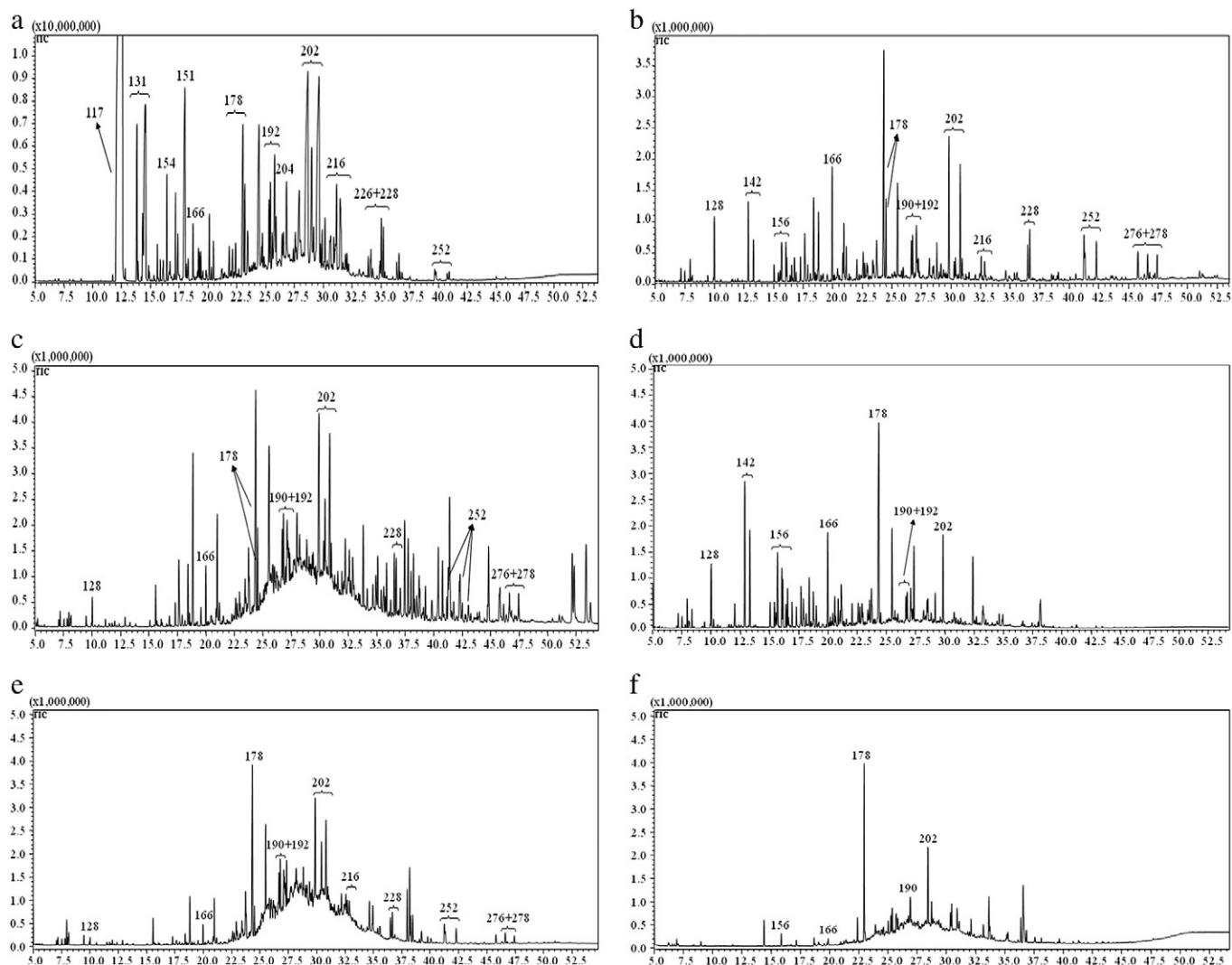

Fig. 2. The scan GC/MS chromatogram of weakly polar fraction for identification of PAHs in the emissions from the degreasing tanks (a), the anaerobic tanks (b), the aerobic 1 tanks (c), the hydrolytic tanks (d), the aerobic 2 tanks (e) and the secondary clarifiers (f).

Table 1
Identification of PAHs in the emissions from the coking WWTP.

No.	Compound	Retention time (min)	Molecular weight	Molecular formula	Degreasing tanks	Anaerobic tanks	Aerobic 1 tanks	Hydrolytic tanks	Aerobic 2 tanks	Secondary clarifiers
1	Naphthalene	9.01	128	$C_{10}H_8$	0	+	++	+	+	+
2	1-Methylnaphthalene	11.71	142	$C_{11}H_{10}$	+	+	+	++	+	0
3	2-Methylnaphthalene	12.82	142	$C_{11}H_{10}$	+	0	+	++	0	0
4	Biphenyl	13.94	154	$C_{12}H_{10}$	+	0	+	+	0	0
5	1-Ethylnaphthalene	14.21	156	$C_{12}H_{12}$	0	0	0	0	0	0
6	1,2-Dimethyl naphthalene	14.85	156	$C_{12}H_{12}$	+	0	0	+	0	0
7	2-Ethylnaphthalene	15.10	156	$C_{12}H_{12}$	0	0	0	0	0	0
8	Diphenylmethane	15.21	168	$C_{13}H_{12}$	0	0	0	+	0	0
9	1,3-Dimethylnaphthalene	15.30	156	$C_{12}H_{12}$	+	0	0	0	0	0
10	2,4-Dimethylnaphthalene	15.39	156	$C_{12}H_{12}$	0	0	0	0	0	0
11	Acenaphthylene	15.61	152	$C_{12}H_8$	++	0	0	0	0	0
12	2,6-Dimethylnaphthalene	15.68	156	$C_{12}H_{12}$	0	0	0	+	0	0
13	Acenaphthene	16.43	154	$C_{12}H_{10}$	++	0	+	0	+	+
14	2-Methyl-1,1'-biphenyl	16.63	168	$C_{13}H_{12}$	0	0	++	0	0	0
15	1-Isopropenylnaphthalene	17.04	168	$C_{13}H_{12}$	+	0	0	0	0	0
16	1-Methyl-4-(phenylmethyl)- Benzene	17.69	182	$C_{14}H_{14}$	0	0	0	0	0	0
17	Fluorene	18.70	166	$C_{13}H_{10}$	++	+	++	++	+	++
18	2,4'-Dimethyl-1,1'-bipheny	18.76	182	$C_{14}H_{14}$	0	0	0	+	0	0
19	3,4'-Dimethyl-1,1'-bipheny	18.85	182	$C_{14}H_{14}$	0	0	0	+	0	0
20	1-Isopropenylnaphthalene	18.97	168	$C_{13}H_{12}$	0	0	0	0	0	0
21	2-Ethyl-1,1'-biphenyl	19.08	182	$C_{14}H_{14}$	0	0	0	+	0	0
22	1-Methylfluorene	19.17	180	$C_{14}H_{12}$	+	0	0	0	0	0
23	Phenalene	19.49	166	$C_{13}H_{10}$	0	0	0	+	0	0
24	2-Methylfluorene	21.21	180	$C_{14}H_{12}$	+	+	+	+	+	+
25	3-Methylfluorene	21.35	180	$C_{14}H_{12}$	0	0	+	+	0	0
26	4-Methylfluorene	21.60	180	$C_{14}H_{12}$	0	0	+	+	0	0
27	9-Methylenefluorene	21.83	180	$C_{14}H_{12}$	+	++	0	0	0	0
28	Phenanthrene	22.88	178	$C_{14}H_{10}$	0	++	++	++	++	++
29	Anthracene	23.02	178	$C_{14}H_{10}$	++	++	0	++	++	+
30	Diphenylethyne	23.18	178	$C_{14}H_{10}$	++	+	0	++	++	++
31	9,10-Dihydro-2-methylanthracene	23.61	194	$C_{15}H_{14}$	+	0	0	0	+	+
32	9,9-Dimethyl-9H-fluorene	23.72	194	$C_{15}H_{14}$	+	0	0	0	+	0
33	3,3',4,4'-Tetramethyl-1,1'-biphenyl	23.79	210	$C_{16}H_{18}$	0	0	+	0	+	+
34	9-Ethenylanthracene	24.62	204	$C_{16}H_{12}$	+	0	+	+	+	++
35	2-Methylphenanthrene	25.28	192	$C_{15}H_{12}$	++	+	++	++	++	+
36	3-Methylphenanthrene	25.40	192	$C_{15}H_{12}$	++	0	++	+	0	0
37	9-Methylanthracene	25.55	192	$C_{15}H_{12}$	++	0	+		0	0
38	4 H-Cyclopenta[def]phenanthrene	25.76	190	$C_{15}H_{10}$	++	0	+	0	+	++
39	4-Methylphenanthrene	25.88	192	$C_{15}H_{12}$	++	+	+	+	++	+
40	2-Phenylnaphthalene	26.80	204	$C_{16}H_{12}$	++	0	0	0	0	0
41	2,3-Dimethylphenanthrene	27.40	206	$C_{16}H_{14}$	+	0	+		+	0
42	2,5-Dimethylphenanthrene	27.56	206	$C_{16}H_{14}$	+	0	+	0	+	0
43	3,6-Dimethylphenanthrene	27.64	206	$C_{16}H_{14}$	+	0	+	0	+	+
44	Fluoranthene	28.65	202	$C_{16}H_{10}$	++	++	0	0	++	++
45	4,5-Dihydropyrene	28.98	204	$C_{16}H_{12}$	++	0	+	0	++	0
46	Pyrene	29.28	202	$C_{16}H_{10}$	++	++	++	++	++	+
47	11H-Benzo[b]fluorene	31.15	216	$C_{17}H_{12}$	++	+	++	+	++	+
48	2-Methylfluoranthene	31.45	216	$C_{17}H_{12}$	++	0	+	0	+	+
49	1-Methylpyrene	31.49	216	$C_{17}H_{12}$	+	0	+	0	+	+
50	4-Methylpyrene	31.91	216	$C_{17}H_{12}$	+	0	0	0	+	0
51	2-Methylpyrene	32.03	216	$C_{17}H_{12}$	+	0	0	0	+	0
52	7H-Benzo[c]fluorene	32.17	216	$C_{17}H_{12}$	0	0	0	0	+	0
53	o-Terphenyl	33.10	230	$C_{18}H_{14}$	0	0	0	0	+	0
54	1,8-Diethynylanthracene	34.05	226	$C_{18}H_{10}$	+	0	+	0	+	0
55	Benzo[c]phenanthrene	34.10	228	$C_{18}H_{12}$	+	0	+	0	0	0
56	Cyclopenta[cd]pyrene	34.90	226	$C_{18}H_{10}$	+	0	+	0	+	0
57	Benz[a]anthracene	35.00	228	$C_{18}H_{12}$	++	0	++	0	++	0
58	Chrysene	35.18	228	$C_{18}H_{12}$	++	0	++	+	++	0
59	Cyclopentano(cd)pyrene	35.47	228	$C_{18}H_{12}$	0	0	0	0	0	0
60	7-Methylbenz[a]anthracene	36.91	242	$C_{19}H_{14}$	+	0	+	0	+	+
61	6-Methylchrysene	37.09	242	$C_{19}H_{14}$	0	0	+	0	+	+
62	9H-Cyclopenta[a]pyrene	37.26	240	$C_{19}H_{12}$	0	0	+	0	+	0
63	1,12-Dimethylbenz[c]anthracene	37.51	240	$C_{19}H_{12}$	0	0	+	0	+	0
64	Benzo[b]fluoranthene	39.65	252	$C_{20}H_{12}$	+	+	++	+	++	+
65	Benzo[j]fluoranthene	39.74	252	$C_{20}H_{12}$	+	+	++	+	++	0
66	Benzo[e]pyrene	40.08	252	$C_{20}H_{12}$	0	0	0	0	0	0
67	Benzo[k]fluoranthene	40.71	252	$C_{20}H_{12}$	+	+	+	+	++	+
68	Benzo[a]pyrene	40.90	252	$C_{20}H_{12}$	+	0	0	0	++	0
69	Benzo[e]pyrene	41.25	252	$C_{20}H_{12}$	0	0	0	0	0	0
70	3-Methylbenz[j]aceanthrylene	42.26	266	$C_{21}H_{14}$	0	0	0	0	0	0
71	1,2:7,8-Dibenzophenanthrene	44.70	278	$C_{22}H_{14}$	0	0	0	0	0	+

Table 1 (*continued*)

No.	Compound	Retention time (min)	Molecular weight	Molecular formula	Degreasing tanks	Anaerobic tanks	Aerobic 1 tanks	Hydrolytic tanks	Aerobic 2 tanks	Secondary clarifiers
72	Indeno[1,2,3-cd]pyrene	44.98	276	$C_{22}H_{12}$	+	+	++	+	++	+
73	Dibenz[a,h]anthracene	45.14	278	$C_{22}H_{14}$	0	0	0	0	0	+
74	Dibenzo[a,c]anthracene	45.45	278	$C_{22}H_{14}$	0	0	+	0	+	0
75	Pentacene	45.57	278	$C_{22}H_{14}$	0	0	+	0	+	0
76	Benzo[ghi]perylene	45.80	276	$C_{22}H_{12}$	+	+	+	0	+	0
77	Dibenzo(a,h)pyrene	49.46	302	$C_{24}H_{14}$	+	0	+	0	+	0

with TICs dominated by alkyl-substituted ones. For the sample from the degreasing tanks, except some nitrogen-heteroatomic compounds such as indole (MW, 117) and methyl indoles (MW, 131), the whole chromatogram was dominated by 3–5 ring PAHs in the molecular weight (MW) rang of 154–252. Among these PAHs, six isomers of MW 156, three isomers of MW 178, five isomers of MW 180, four isomers of MW 192, three isomers of MW 204, six isomers of MW 216, four isomers of 228 and six isomers of MW 252 PAHs were found, with the isomers of MW 178, 192, 202, 216, and 228 being the abundant. From Fig. 1b to f, it can be seen that air samples from the aeration tanks and the secondary clarifiers demonstrated similar chemical compositions but with much lower abundances of PAHs than the sample from the degreasing tanks. The high MW PAHs (MW 252, 276 and 278) contributed more obvious proportion in the samples from the anaerobic tanks and the aerobic tanks, as a result of the injection of forced air. It has been previously reported that the main sources of PAHs in the atmosphere were the burning of organic materials such as coal, oil, petrol gas, wood and the smoking of tobacco (Chang et al., 2006; WHO, 1987). The identification of kinds of PAHs in these emissions demonstrated that the coking WWTP would be a new source of these compounds in the atmosphere.

3.2. Distribution of atmospheric PAHs within the coking WWTP

Concentrations of PAHs in the air around the coking WWTP are shown in Fig. 3. Air concentrations of PAHs at reference sites (sites 18 and 19) were in the range as reported for the urban areas (Chang et al., 2006). However, $\sum$PAH concentrations at the site 19 (363.5 ± 56.6 ng/m³) were about 3 times higher compared to previous measurements in South China (Yang et al., 2010; Zhang et al., 2011a). $\sum$PAH concentrations at the more distant reference site (site 18) were lower in comparison to site 19. Site 18 was approximately 500 m from the perimeter of the WWTP and not downwind,

Fig. 3. The concentrations of total PAHs on and around the coking wastewater treatment plant.

therefore unlikely impacted by the emissions from the WWTP. In contrast, the other reference site (site 19), which was much closer (within 100 m of the treatment tanks), was able to detect the emissions from the coking WWTP.

Air concentrations of $\sum$PAH concentrations within the plant (sites 4–17) were 3–41 times higher compared to the reference locations (sites 18 and 19). This observation further indicated that the coking WWTP was a source of PAHs to the atmosphere. It was found that $\sum$PAH concentrations at the degreasing tanks were 3–35 times higher in comparison to the aeration tanks (sites 4–15) and the secondary clarifiers (sites 16 and 17). The higher concentrations at the degreasing tanks were likely due to the evaporation of these semi-volatile organic compounds into the atmosphere as the concentrations of individual PAH in wastewater can reach to 4809.5 ± 534.6 µg/L (Zhang et al., 2012), and the temperature of coking wastewater was high (about 50 °C). $\sum$PAH concentrations at the aeration tanks varied from 976.3 to 3173.8 ng/m³, higher than those at the secondary clarifiers (373.8 to 727.6 ng/m³). This was attributed to higher aqueous PAHs concentrations in these tanks and enhanced volatilization associated with air stripping in the aeration process. $\sum$PAH concentration of site 16 was about 2 times higher than that at site 17, although both sites were located at the secondary clarifiers. It should be noticed that site 16 was closer to the aeration tanks and therefore it might receive a substantial proportion of PAHs in the emissions from the aeration tanks.

As shown in Table 2, the $\sum$PAH concentrations in the air of the degreasing tanks (sites 1–3) were higher than the averaged concentrations of PAHs at the carbon black manufacturing industry (2770.0 ng/m³) (Tsai et al., 2001), the e-waste recycling regions (313.4–1040.7 ng/m³) (Zhang et al., 2011a) and the cook rooms (30.0–597.0 ng/m³) (See et al., 2006), but lower than those at the coke plant (299,910.0 ng/m³) (Petry et al., 1996), the sinter plant (30,400.0 ng/m³) (Lin et al., 2008), the fastener manufacturing industry (88,300.0 ng/m³) (Chen et al., 2008), and the road intersection (12,999.0 ng/m³) (Tsai et al., 2004). The $\sum$PAH concentrations in the air of the anaerobic tanks and the hydrolytic tanks were comparable with those in the air of the e-waste recycling regions, while they at the aerobic tanks were a little lower than those at the carbon black manufacturing industry. It was reported that PAH exposure levels for the workers at the black carbons manufacturing industries were higher than the corresponding lifetime lung cancer risks. (Tsai et al., 2001). For this study, PAH concentrations in the air of most of the selected sites were higher or comparable with those in the air of the carbons black manufacturing industry, suggesting that PAHs in the air around the coking WWTP would have potential health-risk for operating workers exposed to these organic compounds.

3.3. Composition profiles and diagnostic ratios of PAHs in the air of the coking WWTP

As shown in Fig. 4, 3 and 4-ring PAHs predominated within the coking WWTP, in which Phen, Ant, Flu and Pyr were the dominant compounds. Proportions of these compounds in the selected sampling sites were higher than those at the reference sites. The elevated level of 3–4 ring PAHs in the air was possibly caused by their
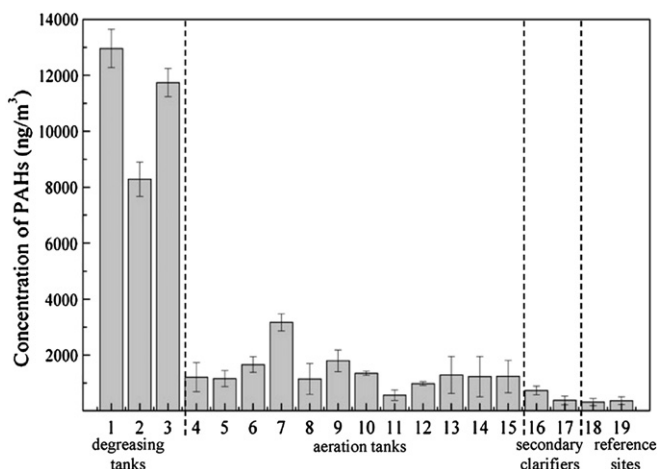
Table 2
Comparison of $\sum$ PAH concentrations and TEQ$_{BaP}$ calculated for various samples from different occupational environments.

Occupational environment	Sample type/place	$\sum$ PAH concentrations (ng/m^3)	TEQ$_{BaP}$ (ng/m^3)	Reference
Coke plant	Atmosphere/Switzerland	299,910.0	11857.2	Petry et al., 1996
Fastener manufacturing industry	Oil mists/France	88,300.0	234.0	Chen et al., 2008
Sinter plant	Sintering grate/Taiwan	30,400.0	160.0	Lin et al., 2008
Road intersection	Atmosphere/Tianjin, China	12,999.0	530.0	Tsai et al., 2004
Carbon black manufacturing industry	Packaging/Taiwan	2770.0	766.0	Tsai et al., 2001
E-waste recycling regions	Atmosphere/Guiyu, China	1040.7	13.7	Zhang et al., 2011a,b
Cook rooms	Airborne particles/Malay	597.0	54.0	See et al., 2006
	Airborne particles/China	135.0	14.0	
	Airborne particles/India	30.0	2.5	
Sites 1–3	Degreasing tanks	8286.6–12,959.5	37.6–71.2	This study
Sites 4–6	Anaerobic tanks	1056.1–1206.1	11.7–15.0	
Sites 7–9	Aerobic 1 tanks	1142.8–3173.8	12.1–51.7	
Sites 10–12	Hydrolytic tanks	972.1–1347.2	1.6–8.0	
Sites 13–15	Aerobic 2 tanks	1224.9–1286.8	19.7–24.9	
Sites 16–17	Secondary clarifiers	373.8–727.6	13.8–26.8	

dominance in the coking wastewater compared to 2-ring and 5–6 ring ones. Despite the higher evaporation rate, the low concentrations of 2-ring PAHs available in the coking wastewater resulted in their lower contribution in the air. Being as hydrophobic chemicals, high MW PAHs (5–6 ring PAHs) tended to be adsorbed onto the particles in wastewater, thus their aqueous concentrations would be decreased as they became associated with particles that were removed as sludge from the wastewater, and resulted in lower levels in air. Furthermore, it was found that 3-ring PAHs predominated at the anaerobic tanks and the hydrolytic tanks, while 4-ring ones were the dominated compounds at the degreasing tanks, the aerobic 1 tanks, the aerobic 2 tanks and the secondary clarifiers. These results were likely due to different behaviors of these compounds in the coking wastewater (Zhang et al., 2012) combined with the difference in their volatilization potentials from wastewater. For example, Flu and Pyr accounted for 42–46% of the total PAH content at the degreasing tanks, but less than 10% at the hydrolytic tanks. Interestingly, their air concentrations increased from anaerobic tanks and hydrolytic tanks to aerobic tanks, which were induced not only by the different emissions for individual compounds but also by the increased concentrations of these two compounds in the wastewater of the aerobic tanks. There is significant evidence that Flu and Pyr can be produced biologically under the anaerobic conditions through microbial metabolism (Tsai et al., 2001; Bakhtiari et al., 2009).

The diagnostic ratios of PAHs have recently been examined as a useful tool for evaluating and distinguishing the sources of PAHs. For example, the abundance ration of low molecular weight (2–3 rings) hydrocarbons to high molecular weight (4–6 rings) hydrocarbons, Ant/(Ant + Phen), Flu/(Flu + Pyr), BaA/(BaA + Chr) and InP/(InP + BgP) were applied to distinguish the petrogenic and pyrolytic sources of PAHs in the environment (Yunker et al., 2002; Doong and Lin, 2004; Deng et al., 2006; Guo et al., 2007). An Ant/(Ant + Phen) ratio >0.1 indicates that combustion is a dominant source of PAHs (Budzinski et al., 1997), and the Flu/(Flu + Pyr) ratio of >0.5 denotes combustion (Budzinski et al., 1997; Yunker et al., 2002). For BaA/(BaA + Chr), the ratio of >0.35 is the characteristic of combustion (Budzinski et al., 1997). InP/(InP + BgP) ratio of >0.5 indicates wood and coal combustion, while between 0.2 and 0.5 is considered as the source of fuel petro-chemical fuel combustion (Budzinski et al., 1997).

The values of isomeric ratios for different air samples around the coking WWTP are listed in Table 3. The Flu/(Flu + Pyr) ratio ranged from 0.54 to 1.01, and the BaA/(BaA + Chr) ratios were from 0.20 to 0.61. Although the Ant/(Ant + Phen) ratio of sites 9, 10, 13 and 14 were lower than 0.1, all of the InP/(InP + BgP) ratios were higher than 0.2. Taking into consideration that these air samples were collected around the coking WWTP, PAHs in the emissions stemmed mainly from the coking wastewater, produced during the coking processes and/or correlative production processes. The results of isomeric ratios suggested that atmospheric PAHs from the coking wastewater still had the source characteristics of coal combustion, despite of that the wastewater was treated by physical, biological and chemical processes.

3.4. Health risk assessment for workers exposed to PAHs

It was well recognized that PAHs could create toxicity in organisms, by interfering with cellular membrane function and the coupled enzyme system, and metabolites of PAHs may bind to DNA which causes biochemical disruptions and cell damage in organisms (Nisbet and Lagoy, 1992; Orecchio, 2010). Several PAH species have been classified into probable (2A) or possible (2B) human carcinogens by the International Agency for Research on Cancer (IARC, 1987). The carcinogenic potency associated with exposure of a given PAH compound can be obtained by calculating its BaP toxic equivalent concentration (TEQ$_{BaP}$) according to the toxic equivalent factor (TEF) (Norramit et al., 2005). The list of TEF$_{BaP}$ compiled by Tsai et al. (2004) was adopted in this study (Table 4). To assess the carcinogenic potencies associated with the total PAH concentrations in the emissions from the coking WWTP, sum of each individual TEQ$_{BaP}$ was calculated. (Table 5). The calculated total TEQ$_{BaP}$ concentrations at different sampling sites varied from 1.6 ± 0.1 ng/m^3 (site 11) to 71.2 ± 8.2 ng/m^3 (site 3). The occupational exposure level in this research were lower than those in the fastener manufacturing industry, the sinter plant, the coke plant, the carbon black manufacturing industry and the road intersection. The calculated total TEQ$_{BaP}$ concentrations at the degreasing tanks and the aerobic tanks were higher than those at the e-waste recycling regions and the cook rooms of China and India. The above results can be explained by the fact that total PAHs

Table 3
The isomeric ratios of selected PAHs at different sampling sites.

| Isomeric ratios/stations	Site 1	Site 2	Site 3	Site 4	Site 5	Site 6	Site 7	Site 8	Site 9	Site 10	Site 11	Site 12	Site 13	Site 14	Site 15	Site 16	Site 17
Ant/(Ant + Phen)	0.19	0.17	0.21	0.10	0.10	0.11	0.10	0.50	0.04	0.06	0.19	0.49	0.03	0.05	0.20	0.15	0.39
Flu/(Flu + Pyr)	0.56	0.54	0.55	0.57	0.63	0.60	0.58	0.70	0.60	0.74	0.94	1.01	0.70	0.64	0.67	0.59	0.80
BaA/(BaA + Chy)	0.59	0.54	0.59	0.43	0.43	0.34	0.50	0.20	0.41	0.14	0.13	0.61	0.30	0.39	0.37	0.35	0.44
Inp/(Inp + BgP)	0.48	0.48	0.51	0.57	0.52	0.45	0.56	0.70	0.53	0.66	0.45	0.44	0.64	0.58	0.61	0.50	0.29
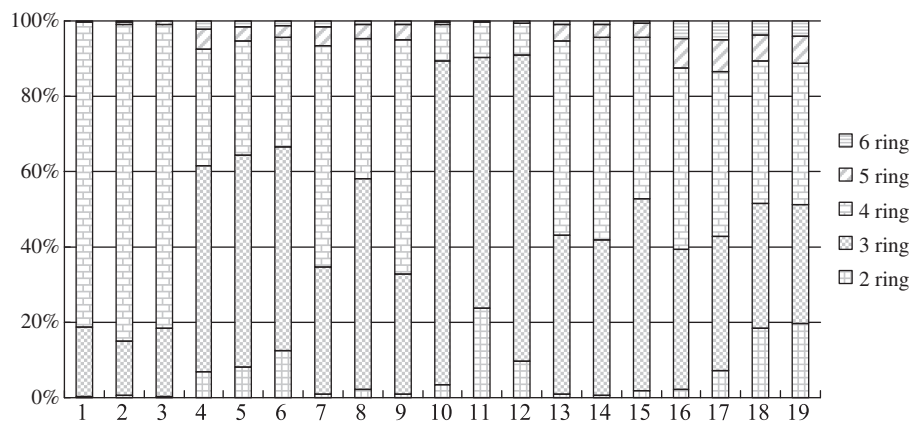
Fig. 4. The PAH profiles distributions at different sampling sites.

in these emissions were dominated by low MW PAHs which are known with lower TEFs.

Health risk assessments were carried out by inhalation PAH exposure data in order to quantify lung cancer risk. Regarding the lung cancer risk via the inhalation route, the sum of TEQ_{BaP} for PAHs was used to estimate the corresponding lifetime lung cancer risks for workers. Pott (1985) estimated a relationship between the BaP

Table 4
Toxic equivalency factors (TEF_{BaP}).

Compounds	TEF_{BaP}
Naph	0.001
Acy	0.001
Ace	0.001
Fle	0.001
Phen	0.001
Ant	0.01
Flu	0.001
Pyr	0.001
BaA	0.1
Chr	0.01
BbF	0.1
BkF	0.1
BaP	1
DBA	1
InP	0.1
BgP	0.01

Table 5
The calculated total TEQ_{BaP} concentrations and cancer risk estimates from exposure to PAHs via inhalation PAH exposure in the coking WWTP.

Site	TEQ_{BaP} (ng/m^3)	Cancer risk
1	37.6 ± 6.2	$2.6 \times 10^{-3} \pm 0.4 \times 10^{-3}$
2	45.3 ± 5.6	$3.3 \times 10^{-3} \pm 0.3 \times 10^{-3}$
3	71.2 ± 8.2	$5.2 \times 10^{-3} \pm 0.5 \times 10^{-3}$
4	15.0 ± 4.2	$0.9 \times 10^{-3} \pm 0.3 \times 10^{-3}$
5	11.7 ± 6.2	$0.8 \times 10^{-3} \pm 0.4 \times 10^{-3}$
6	14.9 ± 7.3	$0.9 \times 10^{-3} \pm 0.4 \times 10^{-3}$
7	51.6 ± 12.4	$3.6 \times 10^{-3} \pm 0.8 \times 10^{-3}$
8	12.1 ± 6.5	$0.7 \times 10^{-3} \pm 0.4 \times 10^{-3}$
9	34.5 ± 8.5	$2.4 \times 10^{-3} \pm 0.5 \times 10^{-3}$
10	8.0 ± 2.4	$0.6 \times 10^{-3} \pm 0.2 \times 10^{-3}$
11	1.6 ± 0.6	$0.1 \times 10^{-3} \pm 0.1 \times 10^{-4}$
12	6.1 ± 0.5	$0.4 \times 10^{-3} \pm 0.1 \times 10^{-4}$
13	25.0 ± 9.1	$1.7 \times 10^{-3} \pm 0.6 \times 10^{-3}$
14	20.8 ± 5.4	$1.5 \times 10^{-3} \pm 0.3 \times 10^{-3}$
15	19.7 ± 3.8	$1.4 \times 10^{-3} \pm 0.2 \times 10^{-3}$
16	15.8 ± 6.9	$0.9 \times 10^{-3} \pm 0.4 \times 10^{-3}$
17	13.8 ± 7.5	$0.8 \times 10^{-3} \pm 0.4 \times 10^{3}$

exposure and the lung cancer risk for occupational exposure, based on a data bank provided by an epidemiological study conducted by Redmond et al. (1976). It was suggested the unit risk of 7.0×10^{-5} $(ng/m^3)^{-1}$ for a 25-year occupational PAH exposure was corresponded with the averaged BaP concentration of 1 μg/m^3 (Tsai et al., 2001). The unit risk was proposed to estimate the lung cancer risk caused by the lifetime exposure, therefore, it has been adopted by a recent study for assessing the lung cancer risks of general adults exposure to the ambient atmospheric PAHs (Tsai et al., 2001; Lin et al., 2008; Zhang et al., 2011a). However, for PAH exposure, the US Environmental Protection Administration suggested a different unit risk of 6.4×10^{-7} $(ng/m^3)^{-1}$ by using the same data bank based on its total PAH content (US EPA, 1984). Since recent studies have indicated BaP can be a better indicator than total PAH content on characterizing the carcinogenic potency of PAHs (Petry et al., 1996; Zhang et al., 2011b), the unit risk suggested by Pott was used in this study. As shown in Table 5, the resultant lifetime lung cancer risks of emissions from the coking WWTP were between $0.1 \times 10^{-3} \pm 0.1 \times 10^{-4}$ and $5.2 \times 10^{-3} \pm 0.5 \times 10^{-3}$. The highest value was found at the degreasing tanks (sites 1–3), followed by the aerobic 1 tanks (sites 7 and 9) and the aerobic 2 tanks (sites 13–15), and the cancer risks of these sites were higher than the significant risk level of 10^{-3} defined by a 1980 US Supreme Court (Rodricks et al., 1987). Currently, the Occupational Safety and Health Administration is guided by US Supreme Court taking 10^{-3} as the significant risk level in setting permissible limits (PELs) for carcinogens. From this view, the inhalation exposures of PAHs to workers of the coking WWTP should be acceptable at the anaerobic tanks (sites 4–6), the hydrolytic tanks (sites 10–12) and the secondary clarifiers (sites 16 and 17), with lower cancer risks ($0.1 \times 10^{-3} \pm 0.1 \times 10^{-4}$ and $0.9 \times 10^{-3} \pm 0.1 \times 10^{-3}$), but the cancer risks for the degreasing tanks and the aerobic tanks were obviously unacceptable. However, it should be noted that PAHs levels in these sites were much lower than the recommended exposure limit of 100 μg/m^3 for total PAH content that was recommended by the US National Institute for Occupational Safety and Health in 1978 (Tsai et al., 2001). Therefore, the estimated high lung cancer risks for these exposure groups required further confirmation.

4. Conclusions

A coking WWTP was found to be a new source of atmospheric PAHs. Seventy seven PAHs were identified in the emissions from the coking WWTP, in which 2–5 ring PAHs were the dominant compounds. The total concentrations of selected PAHs in these sites were in the range between 373.3 ± 27.3 and 12959.5 ± 685.9 ng/m^3, and the highest concentration was detected at the degreasing tanks. 3–4 ring PAHs predominated in all these emissions, in which Phen, Ant, Flu and Pyr were the dominant compounds. The compounds in

these emissions had specific PAH composition files and isomer ratios. The degreasing tanks and the aerobic tanks had potential lung cancer risk for the operating workers, thus it was suggested that they should wear protective equipments to avoid inhaling these atmospheric PAHs. The findings in this study suggested that the mechanical seals for the wastewater treatment equipments should be installed to reduce these emissions released into to the ambient atmosphere.

Acknowledgments

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