



Characterization of PAHs in the atmosphere of carbon black manufacturing workplaces

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Abstract

The objective of this study was set out to characterize the polycyclic aromatic hydrocarbon (PAH) content in the atmosphere of an oil furnace carbon black manufacturing plant located in southern Taiwan. A standard semi-volatile sampling train, the PS-1 sampler, was used to collect samples from eight areas, including the feedstock oil unloading, furnace, filtering/micro-pulverization, pelletizing, packaging, office/outside, office/inside, and boundary area, respectively. For each area, side-by-side static samples were collected simultaneously and a total of 16 samples were obtained. For each collected sample, the adsorbent-retained PAH content and the filter-retained PAH content were used directly to determine the concentrations of gaseous-phase PAHs and particle-bound PAHs, respectively. The gas chromatograph/mass spectrometer (GC/MS) technique was used for PAH analyses, and a total of 21 PAH species were determined. Results show the gaseous-phase PAHs accounted for only 69.2% of the total PAH content for samples collected from the packaging area, which was significantly lower than those samples collected from the rest of seven areas (ranging from 96.3 to 99.7%). The result is not so surprising since the packaging area had the highest dust concentration due to the releasing of carbon black dusts during the packaging process. In this study, we further examine the contribution of gaseous-phase PAHs to the total benzo[*a*]pyrene equivalent (BaP_{eq}) content from the health-risk assessment view of point. It can be found the contribution of gaseous-phase PAHs to the total BaP_{eq} content (63.1%) was quite comparable to the corresponding contribution to the total PAH content for samples collected from the packaging area. However, a different trend can be found for samples collected from the other seven areas, where the contributions of gaseous-phase PAHs to the total BaP_{eq}

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content (ranging from 67.7 to 93.4%) were lower than the corresponding contributions to the total PAH content. The above results can be explained by PAH homologues that contained in both gaseous-phase and particle-bound PAHs. It was found the gaseous-phase PAHs contained higher fractions of less carcinogenic low molecular weight PAH homologues, whereas particle-bound PAHs contained higher fractions of more carcinogenic high molecular weight PAH homologues. Considering the contributions of gaseous-phase PAHs to both total PAH content and total BaP_{eq} content were well above 50% for the eight studied areas, it is concluded that both particle-bound and gaseous-phase PAHs should be included for assessing the exposures of carbon black workers. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Carbon black manufacturing; Particle-bound PAHs; Gaseous-phase PAHs; Static sampling

1. Introduction

Carbon blacks [CAS #1333-86-4] are very fine powdered forms of elemental carbon, which can be obtained from the process of partial combustion or thermal decomposition of hydrocarbons. For centuries, carbon black has been used as one of pigments in printing ink, paint, and lacquer manufacturing industries, however, over the past 50 years, it has been used mainly as one of reinforcing fillers in the rubber industry, particularly, for the manufacturing of vehicle tires. In 1999, the annual consumption of carbon black was about 113,000 t in Taiwan area, where 90% (about 100,000 t) was produced domestically. The historical aspects of the manufacture of carbon blacks have been documented and summarized by Gardiner et al. [1]. They concluded that the oil furnace process had been adopted for over 95% of carbon black manufacturing processes worldwide [1]. Based on the Taiwan governmental labor statistics in 1995, about 18,500 workers were exposed to carbon black dusts, including workers in rubber, ink, paint, ceramics, carbon electrode, battery, and carbon black manufacturing industries. A recent study has shown that workers in the carbon black manufacturing industry tended to have the highest exposure level of air-borne carbon black dusts, particularly for those at the filtering, pelletization, packaging, and stacking areas [2].

The manufacture of carbon black involves the combustion of vapor-phase hydrocarbons, semi-volatile organic compounds, such as polycyclic aromatic hydrocarbons (PAHs), are expected to be formed due to the free radical reaction resulting from the cracking of the feedstock oil [3]. It also can be expected that the generated PAHs, including both those adsorbed on the surface of carbon blacks (i.e. particle-bound PAHs), and those remaining in gaseous-phase (i.e. gaseous-phase PAHs), might release to the workplace atmosphere. To date, a number of PAH species have been known to be animal and/or human carcinogenic [4]. Since several studies have shown that the bio-availabilities of the particle-bound PAHs were very low [5–7], it is not so surprising that almost all known standards for assessing workers' carbon black exposures are based on total dust determinations, regardless to their PAH content. Currently, occupational exposure limit values for carbon black dust exposures differ to some extents. For example, both the American Conference for Governmental Industrial Hygienists (ACGIH) and the Occupational Safety and Health Administration (OSHA) of the United States adopt the value of 3.5 mg/m³ as its time-weighted-average threshold limit value (TLV-TWA) and time-weighted-average permissible exposure limit

(PEL-TWA), respectively [8,9]. Cook summarized the occupational exposure limits (OELs) for nine countries in addition to the United States [10]. He has found seven countries selected 3.5 mg/m^3 as their OEL-TWA, but two countries, the Switzerland and the Venezuela, selected 6 and 7 mg/m^3 as their limit values for OEL-TWA, respectively. It should be noted the above limit values might be feasible for the carbon black using industries, such as tire and paint manufacturing industries, since workers are directly exposed to carbon black dusts and PAHs adsorbed by carbon blacks could be tightly bounded. However, it might need further considerations for carbon black manufacturing workers. First, air-borne carbon black dusts occurring in the workplace atmosphere could be more 'fluffy' (or have less surface area of volume ratio) than, and so might contain less tightly adsorbed PAHs. The argument has been supported by a recent study conducted by Gardiner et al. [11]. In their study, they used the urinary 1-hydroxypyrene as an indicator in assessing PAHs exposures of carbon black warehouse workers, although only PAHs adsorbed in the air-borne carbon black dusts were evaluated, they suggested that the bio-availability of PAHs might not be negligible. Second, in addition to particle-bound PAHs, gaseous-phase PAHs might play important roles on the workers' exposures, particularly, for workers at the process area. However, it still remains unclear regarding the extent of gaseous-phase PAHs contributing to the total PAH content (gaseous-phase PAHs + particle-bound PAHs) for samples collected from the atmosphere of the carbon black manufacturing industry.

Considering a number of the PAH species are known to be animal and/or human carcinogenic, thus, it is important to evaluate the contributions of both particle-bound PAHs and gaseous-phase PAHs to the health-risk that associated with the exposure of the total PAH content. In principle, health-risk assessment associated with the exposure of air-borne PAHs can be estimated in two ways. The first approach involves the use of the individual benzo[*a*]pyrene (BaP) concentration in air as a surrogate indicator to estimate the lung cancer risk for a lifetime PAHs exposures. For example, the US EPA has suggested the unit risk of $6.4 \times 10^{-4} (\mu\text{g/m}^3)^{-1}$ for PAHs exposures [12], based on an epidemiological study conducted by Redmond et al. [13]. The second approach involves the use of toxic equivalent factors (TEFs) to characterize more precisely the carcinogenic properties of PAH mixtures. The feasibility of using these two methods in assessing occupational health-risk associated with the worker's exposure to air-borne PAH mixtures has been conducted recently by Petry et al., they have concluded that the TEFs approach would be more feasible for samples with various PAH compositions [14]. To date, only a few proposals for TEFs for PAHs are available. Among them, a new list of TEFs completed by Nisbet and LaGoy, by using the BaP as a reference compound, seems to better reflect the actual state of knowledge on the relative potency of each individual PAH species [15]. Considering that different PAH compositions might be occurred in different workplace atmospheres in a carbon black manufacturing plant, the list of TEFs that suggested by Nisbet and LaGoy was used in this study.

The objective of this study was set out to characterize atmospheric PAH content for samples collected from various workplaces of an oil furnace carbon black manufacturing plant located in southern Taiwan. For each collected sample, beside the total dust concentration, both particle-bound PAH content and gaseous-phase PAH content were also analyzed. The resultant concentrations of both particle-bound and gaseous-phase PAHs were first used to assess their contributions to the total PAH content, then used to assess their contributions to the total benzo[*a*]pyrene equivalent (BaP_{eq}) content from the health-risk assessment view

of point. The results obtained from this study will be useful to assess the roles of both particle-bound and gaseous-phase PAHs on workers' exposures, and thus, will be helpful for the carbon black manufacturing industry to initiate an effective sampling strategy in the future.

2. Methods and materials

2.1. Subjects

An oil furnace carbon black manufacturing plant located in southern Taiwan was chosen in this study. The manufacturing of carbon blacks involves first the preheating of feedstock oil, air, and gas, then partial combustion at temperatures ranging from 1780 to 1950 °C in the furnace depends on the grade of carbon blacks to be produced. The carbon-rich products are then quenched with water and pass through heat exchangers to recycle the heat for preheating the combustion air. After secondary quenching, the light and fluffy carbon blacks are separated in the bag filter, then sent through micro-pulverizers to a surge tank. Finally, the carbon blacks are wet pelletized followed by a drying process to produce pelletized products, and then packaging for shipment. Detailed manufacturing processes, plant layout, and all sampling sites are illustrated in Fig. 1. In this study, the combustion temperature during the sampling day was specified at 1780 °C, and three types of the carbon black products, N-550, N-660, and N-774, were produced. Eight areas, including the feedstock unloading, furnace, bag filtering and micro-pulverization, pelletizing, packaging, office building/inside, office building/outside, and the boundary of the plant, were chosen for sampling.

2.2. Sampling strategy

In this study, side-by-side samples were collected at each selected area, and a total of 16 samples were obtained. A standard semi-volatile sampling train (General Metal Works PS-1) was used to collect air samples. The Whatman glass fiber filter (diameter = 10.2 cm, pore size = 0.8 µm), first cleaned by heating to 450 °C, was used as the particulate collecting medium for the sampling train. Dusts retained on the glass fiber filter were used directly to determine the total dust concentration, and then further analyzed to determine the concentration of particle-bound PAHs. A glass cartridge (Andersen DPS-4), containing a 5 cm polyurethane foam (PUF) plug, followed by 2.5 cm of XAD-2 resins, and finally facilitated with a 2.5 cm PUF plug, was used to the concentration of gaseous-phase PAHs. The PS-1 sampling flowrate was specified at about 120 l/min. The accurate flowrate was determined by using a critical orifice flow calibrator (General Metal Work GMW-25) measured at the beginning and the end of the sampling period. To ensure sufficient amounts of material were collected, the sampling period was specified to about 24 h. The problems that associated with the use of PS-1 sampler to collect semi-volatile organic carbons (such as PAHs) have been discussed by many authors. For example, some authors have addressed that the use of the filter-retained PAHs might lead to an underestimation of particle-bound PAHs because of the "blow-off effect" [16,17]. On the other hand, particles

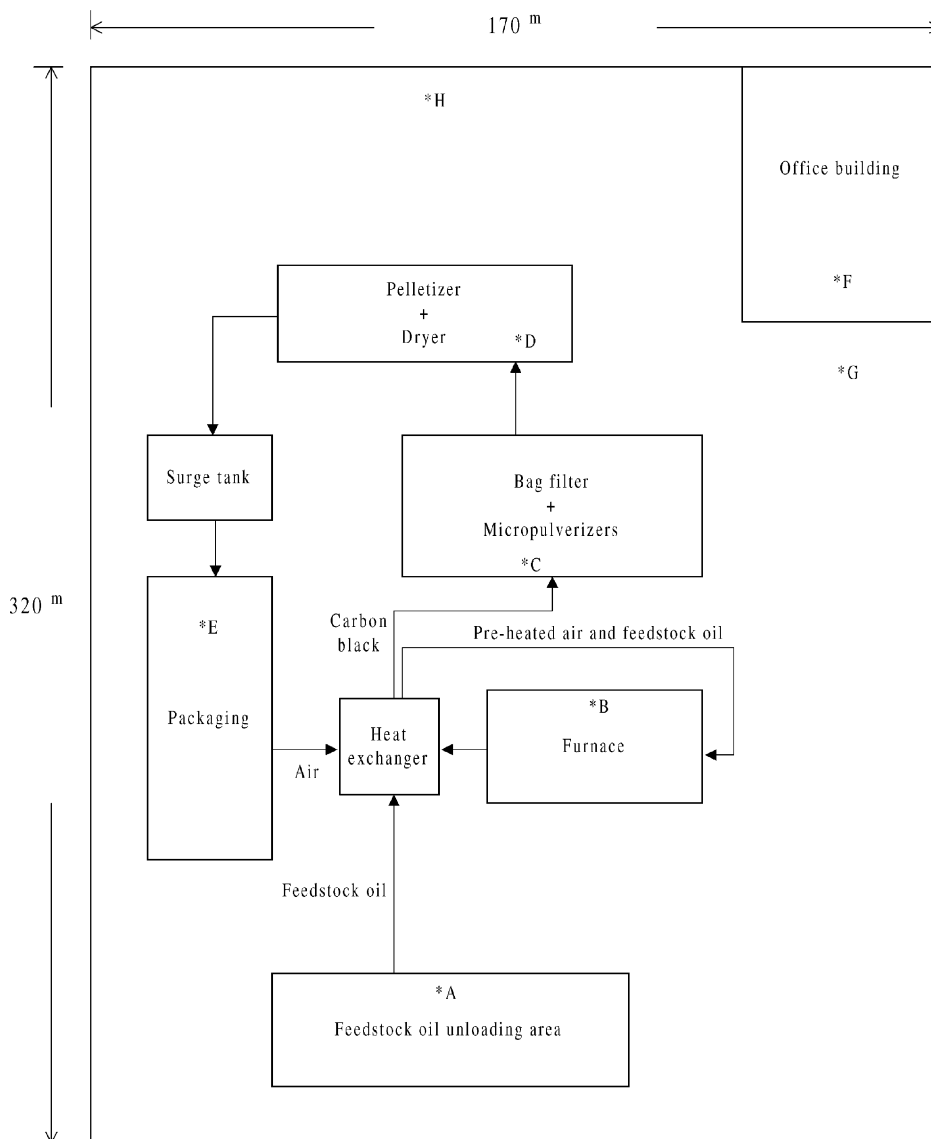


Fig. 1. The layout and flow-chart of the studied carbon black manufacturing plant. Eight workplace were selected for conducting PS-1 sampling, including: (A) feedstock oil unloading area, (B) furnace area, (C) filtering/micro-pulverization area, (D) pelletizing area, (E) packaging area, (F) office/outside, (G) office/inside, and (H) boundary of the plant.

collected on the filter might act as an adsorbent, and thus, might lead to the under-estimation of gaseous-phase PAHs [18,19]. Considering new samplers which can fully correct above sampling problems are still unavailable in the marketplace, therefore, for simplicity, the concentrations of the gaseous-phase PAHs and particle-bound PAHs were determined directly

by using the concentrations of the adsorbent-retained PAHs and the filter-retained PAHs, respectively.

2.3. Sample analysis

For each collected sample, the glass fiber filter was weighed before and after sampling to determine the amount of total suspended particulate (TSP) by using an electrical balance (Sartorius MP 8-6, ± 0.01 mg). For PAHs analysis, samples were placed in a solvent solution (mixture of *n*-hexane and dichloromethane, v:v = 1:1), and extracted in a Soxhlet extractor for 24 h. The extract was then concentrated, cleaned up and re-concentrated to exactly 1.0 or 0.5 ml. Since PAHs are thermally stable (they mostly originate from combustion processes) and exhibit low polarity, they can be detected and positively identified by using gas chromatograph/mass spectrometer (GC/MS) techniques. The mass-selective detection method that used in this study has been evaluated by Gautschi and Mandel [20]. They have concluded the method was sensitive for PAHs analysis. The identification and quantification of PAHs was accomplished by using a GC (Hewlett-Packard 5890) with a mass selectivity detector (MSD) (Hewlett-Packard 5972A). This GC/MS was controlled by a computer workstation and was equipped with a Hewlett-Packard capillary column (HP Ultra 2: 50 m \times 0.32 mm \times 0.17 μ m) and a HP-7673A automatic sampler. The injection volume was 1 μ l, and the splitless injection was specified at 300 °C. The ion source temperature was set at 310 °C, and oven temperatures were set from 50 to 100 °C at 20 °C/min; 100 to 290 °C at 3 °C/min; and 290 °C for 40 min. The primary and secondary ion numbers of PAHs were determined by using the scan mode for pure PAH standards, and the quantification of PAHs was performed by using the selective ion monitoring (SIM) mode.

In this study, a total of 21 PAH species were analyzed, including naphthalene (Nap), acenaphthylene (AcPy), acenaphthene (Acp), fluorene (Flu), phenanthrene (PA), anthracene (Ant), fluoranthene (FL), pyrene (Pyr), cyclopenta[*c,d*]pyrene (CYC), benzo[*a*]anthracene (BaA), chrysene (CHR), benzo[*b*]fluoranthene (BbF), benzo[*k*]-fluoranthene (BkF), benzo[*e*]pyrene (BeP), benzo[*a*]pyrene (BaP), perylene (PER), indeno[1,2,3-*c,d*]pyrene (IND), dibenz[*a,h*]anthracene (DBA), benzo[*b*]chrysene (BbC), benzo[*g,h,i*]perylene (BghiP) and coronene (COR). The above PAH homologues were classified into seven categories based on their numbers of aromatic rings, including: (1) 2-ringed PAH, Nap; (2) 3-ringed PAHs, AcPy, Acp, Flu, PA and Ant; (3) 4-ringed PAHs, FL, Pyr, BaA and CHR; (4) 5-ringed PAHs, CYC, BbF, BkF, BeP, BaP and PER; (5) 6-ringed PAHs, IND, DBA, BbC and BghiP; and (6) 7-ringed PAH, COR. In principle, PAH homologues with high molecular weights are often more carcinogenic than those with low molecular weight PAH homologues [21]. Therefore, PAHs were also further classified into three categories based on their molecular weights, including: low molecular weight (LMW, containing 2- to 3-ringed PAHs), middle molecular weight (MMW, containing 4-ringed PAHs), and high molecular weight (HMW, containing 5-, 6-, and 7-ringed PAHs).

The GC/MSD was calibrated with a diluted standard solution of 16 PAH compounds (PAH Mixture-610M from Supelco) and five individual PAH compounds (from Merck). Analysis of serial dilutions of PAH standards showed that the limit of detection for individual PAH compound was between 39 and 613 pg. The limit of quantification (LOQ) was defined as the limit of detection divided by the sampling volume for the PS-1. The LOQ for individual

PAHs was between 0.23 and 3.54 $\mu\text{g}/\text{m}^3$. Ten consecutive injections of a PAH 610M standard yielded an averaged relative standard deviation of the GC/MSD integration area of 6.3%, with a range of 4.5–9.8%.

In this study, five internal standards (Nap-d8, Acp-d10, PA-d10, CHR-d12, and PER-d12) were used to check the response factors and the recovery efficiencies for PAHs analysis. The recovery efficiencies of 21 individual PAHs and these five internal standards were determined by processing a solution containing known PAH concentrations through the same experimental procedure that used for the analyzing samples. This study showed that the recovery-efficiency of 21 individual PAHs varied between 75.9 and 99.9% and averaged 92.7%. The recovery efficiencies of five internal standards were between 80.4 and 99.7% and were fairly constant. The blank tests for PAHs were accomplished by using the same procedure as the recovery-efficiency tests without adding the known standard solution before extraction. Analysis of field blanks, including glass fiber filters and PUF/resin cartridges, showed no significant contamination (GC/MS integrated area below the detection limit). Analysis of duplicate experiments yielded differences in total-PAH concentration ranging from 7.7 to 13.3% and averaging 9.7% for ambient air samples.

Breakthrough tests were investigated by using two layers of XAD-2 cartridge. Both upper and lower layers of XAD-2 resin were analyzed individually and compared for the PAH mass collected in each layer. Three breakthrough tests were investigated in this study for samples collected from the packaging area, and no significant PAH mass (i.e. <5%) was found in the lower layer of XAD-2 resin.

3. Results and discussion

3.1. Total dust concentrations

Table 1 shows the averaged total dust concentrations that obtained from eight sampling sites. The experimental data reveal the total dust concentrations in sequence were: the packaging (2.04 mg/m^3), pelletizing (0.23 mg/m^3), office/outside (0.12 mg/m^3), furnace (0.09 mg/m^3), office/inside (0.08 mg/m^3), filtering/micro-pulverization (0.07 mg/m^3), and boundary (0.05 mg/m^3). The highest concentration found at the packaging area was due to the releasing of carbon black dusts during the packaging process, since non-enclosure systems were used in the process area. On the other hand, lower concentrations found at the other areas were due to either the use of enclosure systems at the given process areas (such as the pelletizing, filtering/micro-pulverization and furnace), or the studied area were away from the process area (such as the feedstock oil unloading, office/inside, office/outside, and boundary). The concentrations obtained from this study shared the similar trend with a study conducted by Smith and Musch at 24 oil furnace carbon black manufacturing plants [22]. In their study, personal samplings were conducted by using the 37 mm filter cassette. The geometric mean of total dust concentration for workers at the material handling (i.e. the packaging and shipping) area was 1.45 mg/m^3 , which was significantly higher than the concentrations at other areas (<0.59 mg/m^3). However, it should be noted that even for the highest concentration found at the packaging area, both studies revealed its concentration was still below the current PEL-TWA value of 3.5 mg/m^3 [9].

Table 1
Averaged total dusts and total PAHs concentrations for samples collected from the eight studied areas of the carbon black manufacturing plant^a

Compounds	Feedstock unloading	Furnace	Filtering/micro-pulverization	Pelletizing	Packaging	Office/ outside	Office/ inside	Boundary
Total dust	0.06	0.09	0.07	0.23	2.04	0.12	0.08	0.05
Total PAHs	7878.88	3216.84	1646.49	1856.04	1990.02	370.76	1450.35	334.32
Nap	2820.58	2801.16	1402.42	1555.54	1522.70	264.24	1176.94	278.91
2-Ring	2820.58	2801.16	1402.42	1555.54	1522.70	264.24	1176.94	278.91
AcPy	122.86	48.66	102.14	42.80	82.10	40.81	94.16	6.20
Acp	1316.17	96.25	22.59	53.52	182.04	32.08	87.62	7.87
Flu	883.53	57.81	17.25	26.25	61.67	27.47	45.19	8.71
Ant	1976.34	146.02	42.71	137.80	86.45	4.72	1.23	18.51
PA	2.59	11.56	4.59	9.63	8.90	35.43	24.84	1.50
3-Ring	4301.48	360.30	189.28	270.00	421.17	140.51	253.04	42.80
FL	432.57	28.53	12.63	8.74	13.87	11.56	8.26	4.79
Pyr	314.41	20.37	33.05	14.32	20.87	8.63	7.30	4.03
BaA	1.45	0.57	0.55	0.65	0.68	0.60	0.32	0.03
CHR	2.63	0.64	0.25	0.29	0.30	0.10	0.31	0.04
4-Ring	751.05	50.12	46.48	24.00	35.71	21.69	16.19	8.89
CYC	0.42	0.21	0.37	1.47	1.73	0.09	0.27	0.16
BbF	0.53	0.43	0.53	0.52	0.91	0.32	0.30	0.26
BkF	0.04	0.18	0.08	0.04	0.21	0.11	0.15	0.14
BeP	0.53	0.52	0.72	0.31	1.11	0.31	0.32	0.38
BaP	0.33	0.30	0.28	0.51	0.33	0.43	0.05	0.18
PER	0.24	0.43	0.99	0.25	0.85	0.23	0.24	0.46
5-Ring	2.09	2.06	2.98	3.10	5.15	1.48	1.33	1.58
IND	0.53	0.68	0.90	1.17	1.30	0.69	0.63	0.09
DBA	0.30	0.53	0.61	0.24	0.61	0.59	0.64	0.21
BbC	0.57	0.84	1.75	1.08	1.10	1.03	0.96	0.89
BghiP	0.35	0.50	0.96	0.31	0.70	0.27	0.27	0.63
6-Ring	1.74	2.55	4.22	2.80	3.72	2.58	2.50	1.82
COR	1.93	0.65	1.11	0.61	1.58	0.26	0.36	0.31
7-Ring	1.93	0.65	1.11	0.61	1.58	0.26	0.36	0.31

^a Unit: mg/m³ (dust); ng/m³ (PAHs).

More recently, Gardiner et al. [1] have conducted personal samplings at 18 oil furnace carbon black manufacturing plants by using the IOM personal inhalable aerosol sampler. All these plants located in seven European countries (two in Britain, three in France, two in The Netherlands, three in Italy, two in Spain, five in Germany and one in Sweden) and owned by four companies (the Cabot, Degussa, Columbia Chemical and Repsol Quimica). In that study, a total of 1317 the personal inhalable samples were collected from 13 job titles workers, including 151 samples from the warehouse packers. They concluded

that the geometric mean of the total inhalable exposure concentration for warehouse was about 1.96 mg/m^3 , and about 30% of samples were in excess of 3.5 mg/m^3 . Considering no personal sample was collected in this study, therefore, it might be necessary to assess the exposures of packaging workers for the studied plant. For this, a comprehensive personal exposure assessment is being conducted and will be presented in another paper in the future.

3.2. Total PAH content and the distributions of PAH homologues

Table 1 also shows the total PAH content (particle-bound PAHs + gaseous-phase PAHs) and PAH homologues (categorized according to their aromatic rings) obtained from the atmosphere of the eight studied areas. The experimental data reveal that the total PAH content collected from feedstock unloading area ($7.88 \text{ } \mu\text{g/m}^3$) was higher than those collected from process area (ranging from 1.65 (at filtering/micro-pulverization) to $3.22 \text{ } \mu\text{g/m}^3$ (at furnace)). The lower concentration occurring at the process area could be due to the degradation of PAHs that originally containing in the feedstock oil during the combustion process. Above inference has been confirmed by our earlier study conducted at the same carbon black manufacturing plant [23]. In that study, the total PAH content that containing in the feedstock oil (i.e. the input mass), carbon black products, and stack flue gas (i.e. the output masses) during 1 h carbon black manufacturing were about 34,900, 1090, and 91.0 g, respectively. The experimental data revealed that about 96.6% ((input mass – output mass)/input mass) of the total PAHs that originally containing in the feedstock oil had been thermally decomposed. In addition, the concentrations obtained from the office building/inside ($1.45 \text{ } \mu\text{g/m}^3$) was much higher than that obtained from the office building/outside ($0.37 \text{ } \mu\text{g/m}^3$), which was mainly due to cigarette consumption in the office building. In addition, the concentration obtained from the office building/outside was similar to that from the boundary of the plant ($0.33 \text{ } \mu\text{g/m}^3$), which suggests PAHs that released from the manufacturing process might have a limiting effect on the concentrations occurred at the outside of the process area.

Table 1 also shows the distribution of PAH homologues. For feedstock unloading area, PAH content was dominated in sequence by low molecular weight PAHs (LMW-PAHs, including 2- to 3-ringed PAHs), middle molecular weight PAHs (MMW-PAHs, including 4-ringed PAHs), and high molecular weight PAHs (HMW-PAHs, including 5- to 7-ringed PAHs). The similar trend could also be found at the process area. But it can be seen that instead of the 3-ringed PAHs which were the dominant species for LMW-PAHs at the feedstock oil unloading area, the 2-ringed PAH was dominant at the process area. Moreover, it also should be noted that for both LMW- and MMW-PAHs occurred at the feedstock unloading area were still significantly higher than both occurred at the process area (see Table 1). This implies that thermal combustion process might result in the decomposition of both 2- and 3-ringed PAHs originally contained in the feedstock oil. However, whether the 3-ringed PAHs originally contained in the feedstock oil have been partly converted to the 2-ringed PAH, and thus, leads to the domination of 2-ringed PAH occurred at the process area required further investigations. In this study, we also find the HMW-PAHs concentrations occurring at the feedstock unloading area and the process related areas were very low in common. Whether it indicates the involved combustion temperature ($1780 \text{ } ^\circ\text{C}$) was high enough to prohibit the generation of HMW-PAHs, or the generated HMW-PAHs have been further decomposed still remains unknown. Finally, as we examine the fractions

of both LMW-PAHs and MMW-PAHs occurred at the office/outside and boundary of the plant, we find that the trend was generally similar to that occurred at the process area rather than the feedstock unloading area. This might be due to the fact that above two sampling sites were closer to the process related areas than the feedstock unloading area. For office/inside, although the similar trend can also be seen, however, higher concentrations were found for both LMW-PAHs and MMW-PAHs than those occurring at the office/outside and the boundary, which again might be mainly due to the consumption of cigarette in the office

Table 2

Averaged particle-bound PAHs concentrations for samples collected from the eight studied areas of the carbon black manufacturing plant^a

Compound	Feedstock unloading	Furnace	Filtering/micro-pulverization	Pelletizing	Packaging	Office/outside	Office/inside	Boundary
Total particle-bound PAHs	19.96	11.50	18.62	68.87	612.00	4.24	5.36	4.95
Nap	1.86	1.82	4.31	34.72	283.42	1.52	1.46	1.83
2-Ring	1.86	1.82	4.31	34.72	283.42	1.52	1.46	1.83
AcPy	0.30	0.27	0.63	12.91	38.95	0.10	0.18	0.15
Acp	0.27	0.26	0.45	0.45	145.02	0.18	0.20	0.25
Flu	0.21	0.18	0.32	0.06	45.08	0.08	0.09	0.11
Ant	0.49	1.53	1.47	12.74	58.66	0.27	0.24	0.28
PA	1.52	0.22	0.92	0.51	5.89	0.04	0.01	0.01
3-Ring	2.79	2.46	3.78	26.68	293.61	0.67	0.71	0.79
FL	2.91	1.83	0.44	1.13	10.64	0.20	0.01	0.11
Pyr	6.40	1.96	4.80	0.77	16.64	0.20	0.25	0.22
BaA	0.81	0.30	0.36	0.55	0.56	0.19	0.20	0.01
CHR	0.79	0.03	0.06	0.11	0.11	0.01	0.05	0.00
4-Ring	10.91	4.12	5.66	2.56	27.96	0.60	0.51	0.36
CYC	0.39	0.14	0.33	0.89	1.63	0.06	0.13	0.09
BbF	0.40	0.24	0.34	0.40	0.64	0.12	0.21	0.21
BkF	0.00	0.13	0.02	0.03	0.16	0.00	0.09	0.06
BeP	0.48	0.36	0.53	0.27	0.97	0.12	0.28	0.27
BaP	0.22	0.28	0.16	0.50	0.17	0.12	0.04	0.09
PER	0.12	0.17	0.74	0.13	0.52	0.05	0.21	0.13
5-Ring	1.61	1.33	2.12	2.22	4.09	0.48	0.96	0.85
IND	0.31	0.30	0.53	1.01	0.64	0.28	0.35	0.04
DBA	0.16	0.17	0.31	0.17	0.19	0.22	0.36	0.09
BbC	0.31	0.44	0.77	0.84	0.77	0.24	0.53	0.40
BghiP	0.11	0.45	0.29	0.14	0.16	0.09	0.18	0.35
6-Ring	0.90	1.35	1.91	2.17	1.76	0.82	1.42	0.99
COR	1.89	0.42	0.85	0.51	1.16	0.14	0.30	0.24
7-Ring	1.89	0.42	0.85	0.51	1.16	0.14	0.30	0.24

^a Unit: ng/m³.

building. But at this stage, whether cigarette smoking would result in higher concentrations of both LMW-PAHs and MMW-PAHs required further investigations.

3.3. The concentrations of total particle-bound PAHs and total gaseous-phase PAHs and their contributions to the total PAH content

Tables 2 and 3 show the concentrations of total particle-bound PAHs and total gaseous-phase PAHs, respectively. For total particle-bound PAHs, the packaging area had the highest

Table 3
Averaged gaseous-phase PAHs concentrations for samples collected from the eight studied areas of the carbon black manufacturing plant^a

Compounds	Feedstock unloading	Furnace	filtering/micro-pulverization	Pelletizing	Packaging	Office/ outside	Office/ inside	Boundary
Total gaseous-phase PAHs	7858.92	3205.34	1627.87	1787.18	1378.02	366.52	1444.99	329.46
Nap	2818.72	2799.34	1398.11	1520.81	1239.28	262.72	1175.48	277.08
2-Ring	2818.72	2799.34	1398.11	1520.81	1239.28	262.72	1175.48	277.08
AcPy	122.56	48.39	101.51	29.89	43.15	40.71	93.98	6.05
Acp	1315.89	95.99	22.14	53.07	37.02	31.90	87.42	7.62
Flu	883.32	57.63	16.93	26.19	16.59	27.39	45.10	8.60
Ant	1975.85	144.49	41.24	125.07	27.79	4.46	0.99	18.23
PA	1.07	11.35	3.68	9.12	3.02	35.38	24.83	1.49
3-Ring	4298.69	357.84	185.50	243.33	127.56	139.84	252.33	42.00
FL	429.66	26.70	12.18	7.61	3.23	11.36	8.24	4.68
Pyr	308.01	18.41	28.25	13.56	4.22	8.43	7.05	3.81
BaA	0.64	0.27	0.19	0.10	0.12	0.41	0.12	0.02
CHR	1.83	0.61	0.19	0.18	0.19	0.09	0.26	0.04
4-Ring	740.14	46.00	40.81	21.44	7.75	21.09	15.68	8.54
CYC	0.04	0.07	0.05	0.58	0.10	0.03	0.14	0.07
BbF	0.13	0.19	0.18	0.12	0.27	0.20	0.09	0.05
BkF	0.04	0.05	0.07	0.01	0.05	0.10	0.07	0.08
BeP	0.05	0.16	0.19	0.04	0.14	0.19	0.04	0.11
BaP	0.10	0.02	0.13	0.01	0.16	0.31	0.00	0.09
PER	0.13	0.25	0.25	0.12	0.33	0.18	0.03	0.33
5-Ring	0.48	0.73	0.87	0.88	1.06	1.00	0.37	0.73
IND	0.22	0.38	0.37	0.15	0.66	0.41	0.28	0.06
DBA	0.13	0.36	0.30	0.06	0.42	0.37	0.28	0.21
BbC	0.26	0.40	0.98	0.24	0.33	0.79	0.43	0.48
BghiP	0.23	0.05	0.67	0.17	0.54	0.18	0.09	0.28
6-Ring	0.85	1.19	2.31	0.62	1.95	1.75	1.08	0.83
COR	0.04	0.24	0.27	0.10	0.42	0.12	0.06	0.08
7-Ring	0.04	0.24	0.27	0.10	0.42	0.12	0.06	0.08

^a Unit: ng/m³.

concentration of $0.61 \mu\text{g}/\text{m}^3$, the pelletizing area had the second highest concentration of $0.07 \mu\text{g}/\text{m}^3$, and the others had significant lower concentrations with values $<0.02 \mu\text{g}/\text{m}^3$. Above findings were obviously relevant to the corresponding dust concentrations obtained in this study (see Table 1), since PAHs were expected absorbed in the carbon black dusts. For total gaseous-phase PAHs, the feedstock unloading area had a significant higher concentration of $7.85 \mu\text{g}/\text{m}^3$ than those occurred at the process area (ranging from 1.38 to $3.20 \mu\text{g}/\text{m}^3$), which again could be due to the thermal decomposition of PAHs. In addition, experimental data also reveal that the concentration of total gaseous-phase PAHs occurring at the furnace area ($3.20 \mu\text{g}/\text{m}^3$) was significantly higher than those occurring at the filter/micro-pulverization area ($1.63 \mu\text{g}/\text{m}^3$), the pelletizing area ($1.79 \mu\text{g}/\text{m}^3$), and the packaging area ($1.38 \mu\text{g}/\text{m}^3$). Above findings further confirms that PAHs could have been decomposed during furnace thermal combustion process. In this study, the concentrations of total gaseous-phase PAHs were quite similar at the office/outside and plant boundary (0.36 and $0.33 \mu\text{g}/\text{m}^3$, respectively), which again confirms that gaseous-phase PAHs generated by the manufacturing process might have a limiting effect on both areas. Regarding the higher gaseous-phase PAHs concentration ($1.44 \mu\text{g}/\text{m}^3$) occurred at the office/inside area was again considered due to the contribution of cigarette smoking.

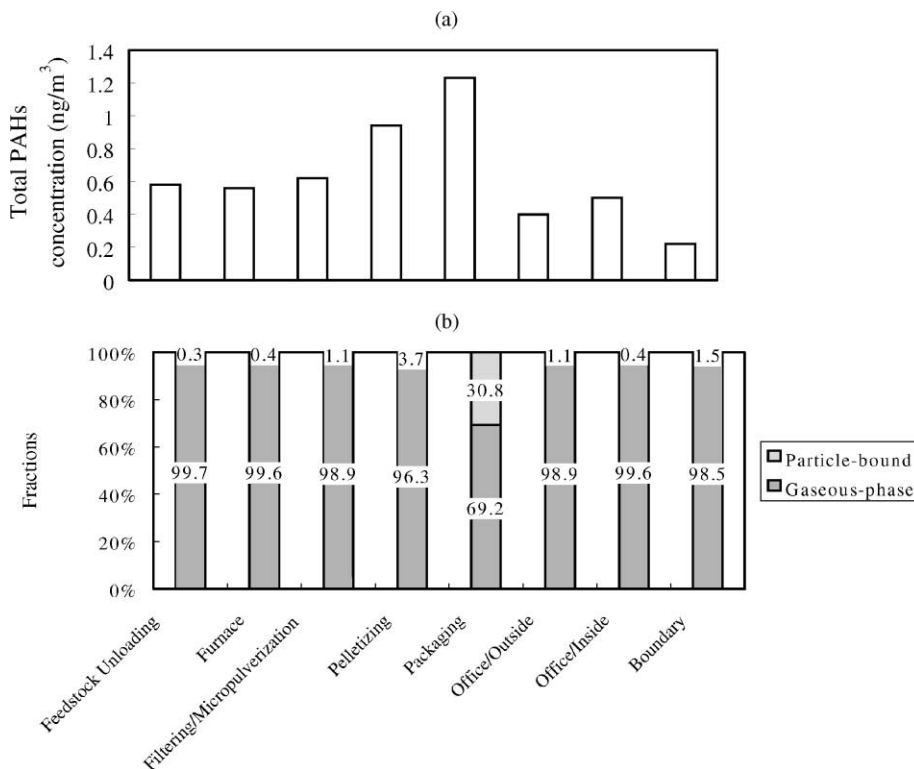


Fig. 2. Sampling results for the eight studied areas: (a) total PAH content, and (b) distributions of particle-bound and gaseous-phase PAH contents.

Fig. 2(a) and (b) show the total PAH content, and the contributions of both total particle-bound and total gaseous-phase PAHs to the total PAH content, respectively. Results show the contributions of total particle-bound PAHs differ greatly (ranging from 0.3 to 30.8%), which were found relevant to the dust concentrations occurred at the studied areas. Therefore, it can be seen that samples collected from the packaging area had the highest contribution (30.8%). Nevertheless, it should be noted that even for samples collected from the packaging area, about 70% of the total PAH content was contributed by the total gaseous-phase PAHs. This suggests the exposure of gaseous-phase PAHs was not negligible. Moreover, as we examine the contributions of total gaseous-phase PAHs for samples collected from other areas, it can be seen that most of the total PAH content (>90%) were contributed by the gaseous-phase PAHs. Considering that almost all known standards for assessing workers' carbon black exposures are based on total dust determinations [8–10], however, from the total PAH content view of point, both particle-bound and gaseous-phase PAHs should be measured for carbon black manufacturing industries.

3.4. The contributions of particle-bound PAHs and gaseous-phase PAHs to the total BaP equivalent content

In this study, the concentration of each PAH species was converted to the BaP equivalent (BaP_{eq}) concentration based on the TEF suggested by Nisbet and LaGoy (Table 4) from the

Table 4
PAHs and their toxic equivalent factors (TEFs) based on Nisbet and LaGoy [15]

PAH	TEF
Naphthalene (Nap)	0.001
Acenaphthylene (AcPy)	0.001
Acenaphthene (Acp)	0.001
Fluorene (Flu)	0.001
Phenanthrene (PA)	0.001
Anthracene (Ant)	0.01
Fluoranthene (FL)	0.001
Pyrene (Pyr)	0.001
Cyclopenta[<i>c,d</i>]pyrene (CYC)	– ^a
Benzo[<i>a</i>]anthracene (BaA)	0.1
Chrysene (CHR)	0.01
Benzo[<i>b</i>]fluoranthene (BbF)	0.1
Benzo[<i>k</i>]fluoranthene (BkF)	0.1
Benzo[<i>e</i>]pyrene (BeP)	– ^a
Benzo[<i>a</i>]pyrene (BaP)	1
Perylene (PER)	– ^a
Indeno[1,2,3- <i>c,d</i>]pyrene (IND)	0.1
Dibenzo[<i>a,h</i>]anthracene (DBA)	1
Benzo[<i>b</i>]chrysene (BbC)	– ^a
Benzo[<i>g,h,i</i>]perylene (BghiP)	0.01
Coronene (COR)	– ^a

^a No TEF has been suggested by Nisbet and LaGoy [15].

Table 5

BaP equivalent concentrations converted from the concentrations of particle-bound PAHs for samples collected from the eight studied areas of the carbon black manufacturing plant based on the list of toxic equivalent factors (TEFs) suggested by Nisbet and LaGoy [15]^a

Compounds	Feedstock unloading	Furnace	Filtering/micro-pulverization	Pelletizing	Packaging	Office/ outside	Office/ inside	Boundary
Total particle-bound PAHs	0.58	0.56	0.62	0.94	1.23	0.40	0.50	0.22
Nap	0.00186	0.00182	0.00431	0.03472	0.28342	0.00152	0.00146	0.00183
2-Ring	0.00186	0.00182	0.00431	0.03472	0.28342	0.00152	0.00146	0.00183
AcPy	0.0003	0.00027	0.00063	0.01291	0.03895	0.0001	0.00018	0.00015
Acp	0.00027	0.00026	0.00045	0.00045	0.14502	0.00018	0.0002	0.00025
Flu	0.00021	0.00018	0.00032	0.00006	0.04508	0.00008	0.00009	0.00011
Ant	0.00049	0.00153	0.00147	0.01274	0.05866	0.00027	0.00024	0.00028
PA	0.0152	0.0022	0.0092	0.0051	0.0589	0.0004	0.0001	0.0001
3-Ring	0.01647	0.00444	0.01207	0.03126	0.34661	0.00103	0.00081	0.00089
FL	0.00291	0.00183	0.00044	0.00113	0.01064	0.0002	0.00001	0.00011
Pyr	0.0064	0.00196	0.0048	0.00077	0.01664	0.0002	0.00025	0.00022
BaA	–	–	–	–	–	–	–	–
CHR	0.079	0.003	0.006	0.011	0.011	0.001	0.005	0
4-Ring	0.08831	0.00679	0.01124	0.0129	0.03828	0.0014	0.00526	0.00033
CYC	0.0039	0.0014	0.0033	0.0089	0.0163	0.0006	0.0013	0.0009
BbF	0.04	0.024	0.034	0.04	0.064	0.012	0.021	0.021
BkF	0	0.013	0.002	0.003	0.016	0	0.009	0.006
BeP	–	–	–	–	–	–	–	–
BaP	0.22	0.28	0.16	0.5	0.17	0.12	0.04	0.09
PER	–	–	–	–	–	–	–	–
5-Ring	0.2639	0.3184	0.1993	0.5519	0.2663	0.1326	0.0713	0.1179
IND	0.031	0.03	0.053	0.101	0.064	0.028	0.035	0.004
DBA	0.16	0.17	0.31	0.17	0.19	0.22	0.36	0.09
BbC	–	–	–	–	–	–	–	–
BghiP	0.0011	0.0045	0.0029	0.0014	0.0016	0.0009	0.0018	0.0035
6-Ring	0.1921	0.2045	0.3659	0.2724	0.2556	0.2489	0.3968	0.0975
COR	–	–	–	–	–	–	–	–
7-Ring	–	–	–	–	–	–	–	–

^a Unit: ng/m³.

health-risk assessment view of point [15]. Tables 5 and 6 show the total BaP_{eq} concentrations for the eight studied areas converted from total particle-bound and gaseous-phase PAH content, respectively. Results show the sequence of the BaP_{eq} concentrations that shown in Tables 5 and 6 were quite comparable to the sequence of PAH concentrations that shown in Tables 2 and 3, respectively. However, it should be noted the differences among the eight studied areas that shown in Tables 5 and 6 were not as significant as that shown in Tables 2 and 3. This was because the differences shown in both Tables 2 and 3 were mainly

Table 6

BaP equivalent concentrations converted from the concentrations of gaseous-phase PAHs for samples collected from the eight studied areas of the carbon black manufacturing plant based on the list of toxic equivalent factors (TEFs) suggested by Nisbet and LaGoy [15]^a

Compound	Feedstock Unloading	Furnace	Filtering/micro-pulverization	Pelletizing	Packaging	Office/ outside	Office/ inside	Boundary
Total gaseous-phase PAHs	8.22	3.78	2.17	1.98	2.10	1.54	2.01	0.66
Nap	2.81872	2.79934	1.39811	1.52081	1.23928	0.26272	1.17548	0.27708
2-Ring	2.81872	2.79934	1.39811	1.52081	1.23928	0.26272	1.17548	0.27708
AcPy	0.12256	0.04839	0.10151	0.02989	0.04315	0.04071	0.09398	0.00605
Acp	1.31589	0.09599	0.02214	0.05307	0.03702	0.0319	0.08742	0.00762
Flu	0.88332	0.05763	0.01693	0.02619	0.01659	0.02739	0.0451	0.0086
Ant	1.97585	0.14449	0.04124	0.12507	0.02779	0.00446	0.00099	0.01823
PA	0.0107	0.1135	0.0368	0.0912	0.0302	0.3538	0.2483	0.0149
3-Ring	4.30832	0.46	0.21862	0.32542	0.15475	0.45826	0.47579	0.0554
FL	0.42966	0.0267	0.01218	0.00761	0.00323	0.01136	0.00824	0.00468
Pyr	0.30801	0.01841	0.02825	0.01356	0.00422	0.00843	0.00705	0.00381
BaA	–	–	–	–	–	–	–	–
CHR	0.183	0.061	0.019	0.018	0.019	0.009	0.026	0.004
4-Ring	0.92067	0.10611	0.05943	0.03917	0.02645	0.02879	0.04129	0.01249
CYC	0.0004	0.0007	0.0005	0.0058	0.001	0.0003	0.0014	0.0007
BbF	0.013	0.019	0.018	0.012	0.027	0.02	0.009	0.005
BkF	0.004	0.005	0.007	0.001	0.005	0.01	0.007	0.008
BeP	–	–	–	–	–	–	–	–
BaP	0.1	0.02	0.13	0.01	0.16	0.31	0	0.09
PER	–	–	–	–	–	–	–	–
5-Ring	0.1174	0.0447	0.1555	0.0288	0.193	0.3403	0.0174	0.1037
IND	0.022	0.038	0.037	0.015	0.066	0.041	0.028	0.006
DBA	0.13	0.36	0.3	0.06	0.42	0.37	0.28	0.21
BbC	–	–	–	–	–	–	–	–
BghiP	0.0023	0.0005	0.0067	0.0017	0.0054	0.0018	0.0009	0.0028
6-Ring	0.1543	0.3985	0.3437	0.0767	0.4914	0.4128	0.3089	0.2188
COR	–	–	–	–	–	–	–	–
7-Ring	–	–	–	–	–	–	–	–

^a Unit: ng/m³.

resulting from the differences of LMW-PAH concentrations. Since the LMW-PAH species are known to be less carcinogenic (i.e. with small TEFs), thus, lead to the differences, in terms of total BaP_{eq} concentrations, among the eight studied areas became less significant (as seen in Tables 5 and 6).

Fig. 3(a) and (b) show the total BaP_{eq} concentrations and the contributions of both particle-bound and gaseous-phase PAHs to the total BaP_{eq} concentrations for the eight studied areas, respectively. For total particle-bound PAHs, the contributions differ greatly

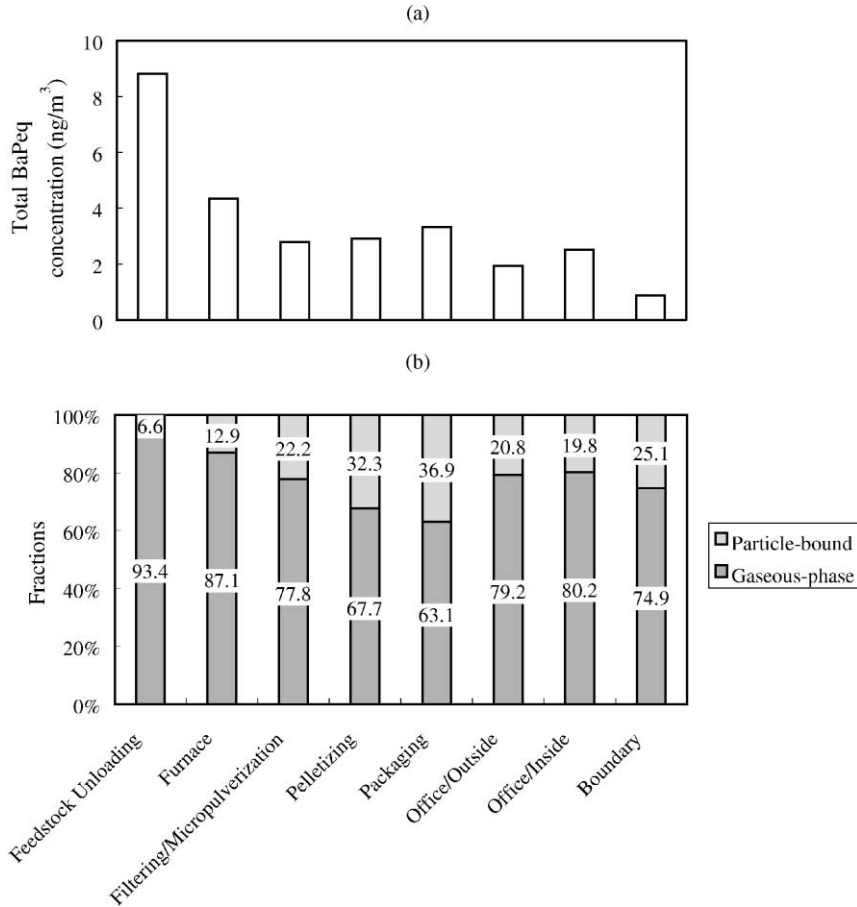


Fig. 3. Sampling results for the eight studied areas: (a) total BaP equivalent concentration, and (b) distributions of both particle-bound and gaseous-phase BaP equivalent concentrations.

among the eight studied areas, ranging from 6.56 to 36.87%. However, it should be noted the contributions of particle-bound PAHs to the total BaP_{eq} concentration for each individual area was consistently higher than the corresponding contribution to the total PAH content (as shown in Fig. 2). This was obviously due to the amount of LMW-PAHs containing in particle-bound PAHs was less significant than that containing in the gaseous-phase PAHs for each studied area. Above result suggests that particle-bound PAHs did play important roles on total BaP_{eq} concentrations from the health-risk assessment view of point. However, it should be noted that more than 60% of total BaP_{eq} concentrations were resulting from the contributions of gaseous-phase PAHs for all studied areas. The result further supports the argument that gaseous-phase PAHs should be measured when we conducting a PAHs exposure assessment program for carbon black manufacturing workers in the future.

4. Conclusion and remarks

In this study, we find samples collected from the feedstock unloading area had the highest total PAH content than those collected from the process area. The results suggest the specified combustion temperatures might be high enough to decompose PAHs that originally containing in the feedstock oil. However, whether the thermal decomposition process would result in the conversion of 3-ringed PAHs that originally contained in the feedstock oil to the 2-ringed PAH that occurred in the atmosphere of the process area required further investigations. As we examine the contributions of gaseous-phase PAHs to the total PAH content, results show it contributed to >70% for all studied areas, which indicated the importance on measuring gaseous-phase PAHs when conducting exposure assessment program for carbon black manufacturing workers. The argument was further confirmed by converting PAHs concentrations that obtained in this study to BaP_{eq} concentrations from health-risk assessment view of point. The results show that gaseous-phase PAHs contributed to >60% of total BaP_{eq} concentrations for all studied areas. In this study, although only static samples were collected, however, it has clearly characterized the PAH content that occurred at atmosphere of different workplaces, and therefore is believed will be helpful for initiating an effective exposure assessment program for workers in carbon black plants in the future.

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