Characterization of PAHs exposure in workplace atmospheres of a sinter plant and health-risk assessment for sintering workers

Yuan-Chung Lin [a,b], Wen-Jhy Lee [c,d], Shui-Jen Chen [d,e], Guo-Ping Chang-Chien [a,b], Perng-Jy Tsai [d,f,*]

[a] *Department of Chemical and Materials Engineering, Cheng Shiu University, 840 Chengching Road, Kaohsiung County 833, Taiwan*
[b] *Super Micro Mass Research & Technology Center, Cheng Shiu University, 840 Chengching Road, Kaohsiung County 833, Taiwan*
[c] *Department of Environmental Engineering, National Cheng Kung University, 1 University Road, Tainan 70101, Taiwan*
[d] *Sustainable Environment Research Center, National Cheng Kung University, 1 University Road, Tainan 70101, Taiwan*
[e] *Department of Environmental Science and Engineering, National Pingtung University of Science and Technology, 1 Shieh-Fu Rd, Nei Pu, Pingtung 91201, Taiwan*
[f] *Department of Environmental and Occupational Health, Medical College, National Cheng Kung University, 138 Sheng-Li Road, Tainan 70428, Taiwan*

Abstract

This study first measured concentrations of polycyclic aromatic hydrocarbons (PAHs) in four selected workplace atmospheres, including the raw materials inlet, sintering grate, rough roll shredder and control room, and the outdoor environment of a sinter plant. Then, PAHs exposures and their resultant health-risks were assessed for sintering workers. We found that total PAH concentrations of the three selected sintering process areas were higher than that of the control room. The above results could be explained by the filtration effect of the air conditioning device installed inside the control room. PAH homologue distributions of the three selected sintering process areas were significantly different from that of the outdoor environment suggesting that PAHs found in the sintering workplace atmospheres were mainly contributed by process fugitives. Total PAH exposure levels were lower than the current permissible exposure limits, thus revealing that sintering workers are not a high risk group for long-term effects attributable to PAHs. Moreover, the lung cancer risks associated with the above PAH exposures were lower than the significant risk level defined by US Supreme Court further confirming that their exposures could be acceptable at this stage.
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1. Introduction

It is known that several polycyclic aromatic hydrocarbons (PAHs) are mutagenic and/or carcinogenic in rodents, and some of them are human potential carcinogens [1]. PAHs can be generated from many human activities, such as industrial production, transportation, and waste incineration. In principle, the mechanisms associated with the generation and/or depletion of PAHs in the high-temperature combustion process followed three major pathways, including pyrosynthesis [2], direct emission of unburned fuel [3], and thermal destruction of fuel components [4]. For iron and steel industries, PAHs are released from coke manufacturing, sintering, iron making, casting, molding, cooling, and steel making processes [5]. PAHs emitted from iron and steel industries have been recognized as the second major source in Norway (accounting for 12% of the yearly total PAH emission) [6]. Intensive studies have been conducted to investigate PAH emissions from the stacks of various manufacturing pro-

cesses in iron and steel industries [7]. However, measurements of process fugitive PAH concentrations in workplace atmospheres have been focused mainly on coke ovens [8–11]. To the best of our knowledge, PAHs concentrations in sinter plant workplaces and their resultant health-risk impact on sintering workers have never been reported.

To assess health-risks associated with PAH exposures, it is important to know the total carcinogenic potency arising from the exposures of various PAH compounds. In principle, the carcinogenic potency of a given PAH compound can be assessed according to its benzo[a]pyrene equivalent concentration (BaP$_{eq}$). Calculating the BaP$_{eq}$ concentration for a given PAH compound requires the use of its toxic equivalent factor (TEF; using benzo[a]pyrene as a reference compound) to adjust its original concentration [12–14]. Among the available TEFs lists, the one established by Nisbet and LaGoy has been demonstrated to best reflect the actual state of knowledge of the toxic potency of each individual PAH species [14]. By using the TEF list the carcinogenic potency of total PAHs (total BaP$_{eq}$) can be determined as the sum of BaP$_{eq}$ concentrations of the 21 selected PAH compounds.

For estimating the lung cancer risk associated with inhalatory PAH exposures, the World Health Organization (WHO) has suggested a unit risk of 8.7×10^{-2} (μg m^{-3})$^{-1}$ for the lifetime (70 years) PAH exposure, assuming one was exposed to BaP concentration of 1 μg m^{-3} [15]. It is worth noting that the above unit risk was proposed for lifetime exposure, therefore, it has been adopted for assessing the exposure of general adults to the ambient atmospheric PAHs [16]. For occupational exposure, Pott established a relationship between BaP exposure and lung cancer risk [17], based on a data bank provided by an epidemiological study conducted by Redmond et al. [18]. He suggested the unit risk of 7.0×10^{-2} (μg m^{-3})$^{-1}$ for a 25-year occupational PAHs exposure with the averaged BaP concentration of 1 μg m^{-3}. By using the same data bank, the US Environmental Protection Administration [19], however, suggested a different unit risk of 6.4×10^{-4} (μg m^{-3})$^{-1}$ for PAHs exposure based on its total PAH content (expressed as the benzene soluble fractions). Since a recent study has indicated BaP could be a better indicator than total PAH content on characterizing the carcinogenic potency of PAHs [20], the unit risk suggested by Pott 1985 has been used in our previous study [21].

In this study, static air samplings were conducted in the above mentioned four workplaces to characterize PAH fugitive emissions from the sintering process. Time/activity patterns for workers of different job titles were recorded according to our field observation. By combining the above two types of information workers' PAH exposure levels were assessed and their resultant health-risks were estimated.

2. Materials and methods

2.1. The selected sintering process

One sinter plant located in southern Taiwan, with a selective catalytic reduction (SCR) air pollution control device, was selected in this study. For the selected sintering process, it first involves the mixing of iron ore fines, iron-bearing recovery materials (such as iron-bearing dusts and slag), and fluxes (lime or dolomite) with a ~5% finely divided fuel, such as coke breeze or anthracite. The mixture is then placed on a traveling grate to form a sintering bed. The traveling grate resembles an endless loop of a conveyor belt, forming a shallow trough with small holes in the bottom. The bed is ignited by passing under an ignition burner which is fired with natural gas and air. During the ignition process, the air is pulled down through the bed as the grate moves slowly toward the discharge end. As the coke fines burn in the bed, the generated heat sinters/or fuses the fine particles. The temperature of the bed is around 1300–1500 °C. Mean production rates are 20–40 metric tons m^{-2} d^{-1} depending upon the characteristics of the ore materials and the sintering conditions [22]. Typical operation conditions for the sintering process have been described in more details elsewhere [23,24]. For sinter plant workers, they are required to perform their work tasks at the nearby of the raw materials inlet, sintering grate, rough roll shredder, and control room.

2.2. Sampling strategy and worker's time/activity pattern

Three sampling sites located approximately 2 m away from the raw materials inlet (Site #1), sintering grate (Site #2), and rough roll shredder (Site #3) were selected to characterize PAH concentrations in the sintering workplaces of the selected sinter plant. For the selected sinter plant, the air introduced to the control room (located at the end of the sintering grate) was directly drawn from the workplace atmosphere of the sinter plant but was filtered by an air conditioner. Static air samplings were also conducted in the control room (Site #4) in order to characterize fugitives transferring from the sintering zone to the control room. The locations of the above sampling sites in the selected sintering plant are shown in Fig. 1. Field samplings were also conducted on the outdoor environment located at the upwind side of the selected sinter plant (Site #5) for comparisons. All air samples were colleted by using a high-volume PS-1 sampler (Greaseby Anderson, GA). This sampler was equipped with a quartz–fibre filter to collect PAHs of the particle-phase, and followed by a XAD-16 cartridge for collecting PAHs of the gas-phase. To avoid effluent stream from PS-1 dilute the total suspended particle (TSP) and PAH concentration in control room, the effluent gas from PS-1 sampler was discharged to the outside of the control room. The sampling flow rate was specified at ~0.18 m^3 min^{-1}. Each sample was collected continuously for ~24 h (i.e., sampling volume = ~250 m^3).

The time/activity patterns of the four selected groups sintering workers were recorded based on our field observation (Table 1). Group A (i.e., raw material charging workers) on average stayed at Site #1 (raw materials inlet) and Site #4 (control room) for 1.67 h and 6.33 h, accounting for 20.8% and 79.2% of their total work time (8 h), respectively. Group B (i.e., sintering grate workers) on average stayed at Site #2 (sintering grate) and Site #4 for 2.5 h and 5.5 h, accounting for 31.2% and 68.8% of their total work time, respectively. Group C (i.e., shredding workers) on average stayed in Site #3 (rough roll shredder) and
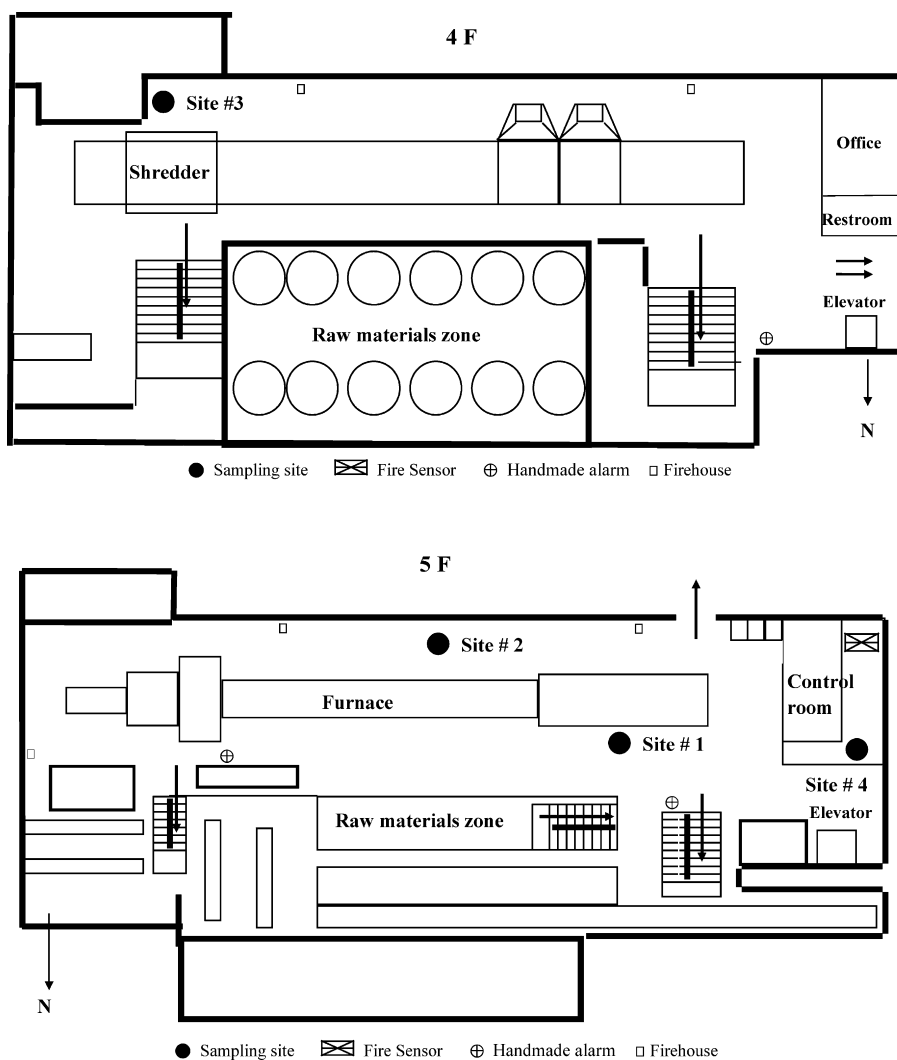
Fig. 1. Sampling sites in the selected sintering plant.

Table 1
Time/activity patterns for the four selected groups of workers of the Group A: raw material charging workers, Group B: sintering grate workers, Group C: shredding workers, and Group D: sintering process engineers and supervisors at the four selected workplaces inside the sinter plant of the Site #1: raw materials inlet, Site #2: sintering grate, Site #3: rough roll shredder, and Site #4: control room

Group of workers	Retention time (h)			
	Site #1	Site #2	Site #3	Site #4
A ($n = 9$)	1.67 (20.8%)	0	0	6.33 (79.2%)
B ($n = 6$)	0	2.5 (31.2%)	0	5.5 (68.8%)
C ($n = 3$)	0	0	3.0 (37.5%)	5.0 (62.5%)
D ($n = 6$)	1.33 (16.67%)	1.33 (16.7%)	1.33 (16.7%)	4.0 (50.0%)

Site #4 for 3.0 h and 5.0 h, accounting for 37.5% and 62.5% of their total work time, respectively. Group D (i.e., sintering process engineers and supervisors) on average stayed in Site #1, Site # 2, Site #3 and Site #4 for 1.33 h, 1.33 h, 1.33 h and 4.0 h, accounting for 16.7%, 16.7%, 16.7% and 50.0% of their total work time, respectively.

2.3. PAH analysis

For PAH analysis, each collected sample (including particulate and gaseous PAH samples) was extracted in a Soxhlet extractor with a mixed solvent (*n*-hexane and dichloromethane; vol/vol, 1:1; 500 mL each) for 24 h. The extract was then concentrated by nitrogen (N_2), cleaned up by sodium sulfate and re-concentrated to exactly 1.0 mL by N_2. PAH contents were determined using a Hewlett-Packard (HP) gas chromatograph (GC) (HP 6890N; Hewlett-Packard, Wilmington, DE, USA) with a mass selective detector (MSD) (HP 5973) and a computer workstation (Aspire C500; Acer, Taipei, Taiwan). This GC/MSD was equipped with a capillary column (HP Ultra 2, 50 m × 0.32 mm × 0.17 μm) and an auto sampler (HP-7683). It was operated under the following conditions; injection volume of 1 μL, splitless injection at 310 °C, an ion source temperature of 310 °C, an oven from 50 °C to 100 °C at 20 °C min^{-1}; from 100 °C to 290 °C at 3 °C min^{-1}; and held at 290 °C for 40 min. The masses of primary and secondary ions of PAHs were determined in scan mode using pure PAH standards.

PAHs were qualified in the selected ion monitoring (SIM) mode [25–29].

The PAH homologues grouped by the number of rings are naphthalene (Nap) for two-ring, acenaphthylene (AcPy), acenaphthene (Acp), fluorine (Flu), phenanthrene (PA), and anthracene (Ant) for three-ring, fluoranthene (FL), pyrene (Pyr), benzo[a]anthracene (BaA), and chrysene (CHR) for four-ring, cyclopenta[c,d]pyrene (CYC), benzo[b]fluoranthene (BbF), benzo[k]fluoranthene (BkF), benzo[e]pyrene (BeP), benzo(a)pyrene (BaP), perylene (PER), dibenzo[a,h]anthracene (DBA), benzo[b]chrycene (BbC) for five-ring, indeno[1,2,3,-cd]pyrene (IND), benzo[ghi]perylene (Bghip) for six-ring, and coronene (COR) for seven-ring. The GC/MSD was calibrated with a diluted standard solution of 16 PAH compounds (PAH mixture-610M; Supelco, Bellefonte, PA, USA) plus five additional individual PAHs obtained from Merck (Darmstadt, Germany). Ten consecutive injections of a PAH 610-M standard yielded an average relative standard deviation of the integrated GC/MSD area of 8.02% (range = 5.45–10.33%).

In this study, two internal standards (phenanthrene-d10 and perylene-d12) were used to check their response factors, the recovery efficiencies for PAHs analysis and to determine final concentrations. The recovery efficiencies of 21 individual PAHs and these two internal standards were determined by processing a solution containing known PAH concentrations through the same experimental procedure used for the samples. Recovery efficiency was measured via analyzed mass of PAH divided by input mass of known PAH. This study showed the recovery efficiencies for the 21 PAH compounds range from 0.795 to 0.972, with an average value of 0.881. The recovery efficiencies of two internal standards (phenanthrene-d10 and perylene-d12) were between 85.7% and 93.5% and were fairly constant. The recovery efficiencies of these two internal standards (phenanthrene-d10 and perylene-d12) were averaged and used for the quantification. This action will control the analysis error to be less than 15%, which guarantees the reported data of this study being at an excellent level. Analyses of field blanks, including aluminum foil, glass fiber filter and a PUF/XAD-16 cartridge, revealed no significant contamination (GC/MSD integrated area < detection limit).

2.4. Data analysis

In this study, the total PAH concentration represents the sum of the concentrations of 21 PAH compounds for each collected sample. PAHs were grouped into three categories based on their molecular weights, including low molecular weight PAHs (LMW-PAHs, containing two- and three-ringed PAHs), middle molecular weight PAHs (MMW-PAHs, containing four-ringed PAHs), and high molecular weight PAHs (HMW-PAHs, containing five- to seven-ringed PAHs).

In this study, the carcinogenic potencies associated with PAH emissions to each workplace atmosphere were also determined. Here, the carcinogenic potency of a given PAH compound was assessed according to its benzo[a]pyrene equivalent concentration (i.e., BaP_{eq}) by using the TEFs list established by Nisbet and LaGoy [14]. The carcinogenic potency of total PAHs (i.e., total

BaP_{eq}) was determined as the sum of BaP_{eq} concentrations of the 21 selected PAH compounds. To assess workers' excessive lung cancer risks associated with a 25-year occupational exposure, the unit risk suggested by Pott (7×10^{-5} (BaP_{eq} ng m^{-3})$^{-1}$) was used in the present study [17]. This is mainly because BaP is a better indicator than total PAH content on characterizing the carcinogenic potency of PAHs [20].

All measured and estimated concentrations were presented in their means ± standard deviation (±S.D.). Statistical significance was examined by using the *t*-test.

3. Results and discussion

3.1. TSP concentrations in sintering workplaces and the outdoor environment

Table 2 shows the mean total suspended particle concentrations of the four selected workplaces and the outdoor environment of the selected sinter plant. For the four selected workplaces, the highest TSP was found at Site #1 (2690 µg Nm^{-3}), which was considered due to dust emissions from the raw material charging process. The second and third highest TSP was found at Site #2 and Site #3 (2130 µg Nm^{-3} and 1600 µg Nm^{-3}, respectively), bur their concentrations were much lower than that of Site #1 ($p < 0.05$). This might be because the strong airflow was pulled down through the sintering bed resulting in less fugitive TSP emitted into the sintering zone. TSP concentrations in Site #1, Site #2 and Site #3 were 18.4, 14.6 and 10.9 times in magnitude higher than that in Site #4 (146 µg Nm^{-3}) ($p < 0.05$). This might be explained either by the location of the control room being far away from the sintering process, or by the filtration efficiency (TSP reduction fraction >95%) of the air conditioning device used in the control room. The permissible TSP concentration in workplace environment in Taiwan is 10,000 µg Nm^{-3}, which was significantly higher than that of Site #1–Site #4 ($p < 0.05$). Nevertheless, it should be noted that the concentrations found in Site #1–Site #3 were still higher than that of the outdoor environment (i.e., Site #5 = 143 µg Nm^{-3}) ($p < 0.05$). The above result suggests that TSP concentrations found in the sintering process areas were mainly contributed by the process fugitives, rather than those transported from the outdoor environment.

3.2. Characterization of PAH concentrations in sintering workplaces and the outdoor environment

Table 3 shows the mean PAH concentrations (gas- + particle-phase) of the four selected workplaces and the outdoor environment of the sinter plant. For the mean total PAH concentrations, we found that Site #2 (30.4 µg Nm^{-3}) was significantly higher than that of Site #1 (17.9 µg Nm^{-3}) and Site #3 (16.3 µg Nm^{-3}) ($p < 0.05$), which was considered due to molten process in the furnace. The concentrations found in the above three selected sintering zone workplaces were significantly higher than that of the Site #4 (8.37 µg Nm^{-3}) ($p < 0.05$). The relatively low total PAH concentrations found in the Site #4 (i.e., control room) could be explained again

Table 2
Mean TSP concentrations (±S.D.) of the four selected workplaces inside the sinter plant of the Site #1: raw materials inlet, Site #2: sintering grate, Site #3: rough roll shredder, and Site #4: control room, and its outdoor environment (Site #5)

Concentration	Selected workplace atmosphere				Site #5 ($n = 6$)
	Site #1 ($n = 6$)	Site #2 ($n = 6$)	Site #3 ($n = 6$)	Site #4 ($n = 6$)	
TSP ($\mu g\,Nm^{-3}$)	2690 ± 557	2130 ± 653	1600 ± 342	146 ± 23.5	143 ± 54.9

Table 3
Mean PAH concentrations (±S.D.) of the four selected workplace atmospheres of the sinter plant of the Site #1: raw materials inlet, Site #2: sintering grate, Site #3: rough roll shredder, and Site #4: control room, and its outdoor environment (Site #5)

PAH compound	Selected workplace atmosphere ($\mu g\,Nm^{-3}$)				Site #5 ($n = 6$) ($\mu g\,Nm^{-3}$)	TEF[a]
	Site #1 ($n = 6$)	Site #2 ($n = 6$)	Site #3 ($n = 6$)	Site #4 ($n = 6$)		
Nap	10.3 ± 3.74	17.3 ± 1.80	7.94 ± 1.22	4.73 ± 0.667	2.93 ± 0.999	0.001
AcPy	0.804 ± 0.210	1.35 ± 0.236	1.55 ± 0.431	0.508 ± 0.121	0.396 ± 0.098	0.001
Acp	1.46 ± 0.692	3.01 ± 1.83	1.07 ± 0.690	0.512 ± 0.170	0.201 ± 0.117	0.001
Flu	0.940 ± 0.284	1.90 ± 0.298	1.69 ± 0.657	0.660 ± 0.233	0.931 ± 0.430	0.001
PA	1.98 ± 0.568	2.69 ± 1.22	1.73 ± 0.806	1.21 ± 0.461	1.39 ± 0.296	0.001
Ant	0.093 ± 0.053	0.120 ± 0.032	0.080 ± 0.027	0.018 ± 0.004	0.036 ± 0.016	0.01
FL	0.704 ± 0.344	0.920 ± 0.443	0.701 ± 0.282	0.251 ± 0.095	0.361 ± 0.193	0.001
Pyr	0.921 ± 0.699	1.61 ± 0.757	0.398 ± 0.266	0.225 ± 0.137	0.746 ± 0.375	0.001
CYC	0.039 ± 0.021	0.162 ± 0.094	0.061 ± 0.028	0.011 ± 0.004	0.032 ± 0.016	–[b]
BaA	0.031 ± 0.015	0.171 ± 0.088	0.172 ± 0.099	0.023 ± 0.013	0.068 ± 0.037	0.1
CHR	0.050 ± 0.019	0.220 ± 0.148	0.115 ± 0.075	0.011 ± 0.004	0.043 ± 0.026	0.01
BbF	0.299 ± 0.164	0.278 ± 0.179	0.190 ± 0.127	0.055 ± 0.032	0.061 ± 0.039	0.1
BkF	0.061 ± 0.031	0.081 ± 0.037	0.061 ± 0.032	0.031 ± 0.021	0.024 ± 0.011	0.1
BeP	0.097 ± 0.054	0.139 ± 0.090	0.119 ± 0.090	0.026 ± 0.020	0.043 ± 0.027	–[b]
BaP	0.043 ± 0.021	0.061 ± 0.031	0.052 ± 0.025	0.009 ± 0.007	0.009 ± 0.007	1.0
PER	0.031 ± 0.018	0.030 ± 0.018	0.028 ± 0.018	0.010 ± 0.007	0.011 ± 0.006	–[b]
IND	0.028 ± 0.014	0.021 ± 0.012	0.050 ± 0.024	0.009 ± 0.007	0.008 ± 0.006	0.1
DBA	0.021 ± 0.011	0.012 ± 0.005	0.011 ± 0.005	0.011 ± 0.005	0.007 ± 0.006	1.0
BbC	0.018 ± 0.013	0.225 ± 0.156	0.098 ± 0.055	0.021 ± 0.012	0.065 ± 0.045	–[b]
BghiP	0.041 ± 0.026	0.031 ± 0.019	0.041 ± 0.027	0.019 ± 0.013	0.012 ± 0.007	0.01
COR	0.021 ± 0.014	0.091 ± 0.047	0.120 ± 0.078	0.011 ± 0.006	0.038 ± 0.027	–[b]
LMW-PAH	15.5 ± 5.55	26.4 ± 6.42	14.1 ± 3.83	7.64 ± 1.66	5.89 ± 1.96	–
MMW-PAH	1.72 ± 1.08	2.92 ± 1.44	1.39 ± 0.722	0.510 ± 0.249	1.22 ± 0.631	–
HMW-PAH	0.698 ± 0.387	1.13 ± 0.689	0.830 ± 0.510	0.220 ± 0.134	0.310 ± 0.198	–
Total PAHs	17.9 ± 7.02	30.4 ± 8.54	16.3 ± 5.07	8.37 ± 2.04	7.42 ± 2.78	–
Total BaP$_{eq}$	0.120 ± 0.066	0.160 ± 0.081	0.130 ± 0.068	0.040 ± 0.020	0.044 ± 0.024	–

[a] [14].
[b] No TEF has been suggested.

Table 4
Mean PAH concentrations (±S.D.) of the four selected workplace atmospheres of the sinter plant of the Site #1: raw materials inlet, Site #2: sintering grate, Site #3: rough roll shredder, and Site #4: control room, and its outdoor environment (Site #5)

PAH compound	Selected workplace atmosphere ($\mu g\,Nm^{-3}$)				Site #5 ($n = 6$) ($\mu g\,Nm^{-3}$)
	Site #1 ($n = 6$)	Site #2 ($n = 6$)	Site #3 ($n = 6$)	Site #4 ($n = 6$)	
Total PAHs	17.9 ± 7.02	30.4 ± 8.54	16.3 ± 5.07	8.37 ± 2.04	7.42 ± 2.78
Gas-phase	17.7 ± 7.95	30.1 ± 9.80	16.0 ± 5.68	8.33 ± 2.56	7.36 ± 2.90
Particle-phase	0.251 ± 0.148	0.365 ± 0.203	0.277 ± 0.158	0.042 ± 0.023	0.059 ± 0.035
Total BaP$_{eq}$	0.120 ± 0.066	0.160 ± 0.081	0.130 ± 0.068	0.040 ± 0.020	0.044 ± 0.024
Gas-phase	0.099 ± 0.048	0.121 ± 0.043	0.104 ± 0.040	0.037 ± 0.013	0.038 ± 0.016
Particle-phase	0.021 ± 0.013	0.039 ± 0.022	0.026 ± 0.015	0.003 ± 0.002	0.006 ± 0.003

either by its location being far away from the sintering zone, or the filtration effect of the air conditioning device used in the control room. Moreover, we also found that the PAH concentrations obtained from the sintering zones (Site #1–Site #3 = 16.3–30.4 $\mu g\,Nm^{-3}$) were much higher than that of outdoor environment (Site #5 = 7.42 $\mu g\,Nm^{-3}$) ($p < 0.05$). The above results further confirmed that PAHs found in the workplace atmospheres could be mainly contributed by sintering process fugitives, rather than that transported from the outdoor environment.

Table 5
Time-weighted average exposure levels (±S.D.) of total PAHs$_{ave}$ and total BaP$_{eq_{ave}}$ and their corresponding particle-phase and gas-phase exposure levels (±S.D.), and the resultant lung cancer risks (±S.D.) for the four selected exposure groups of the Group A: raw material charging workers, Group B: sintering grate workers, Group C: shredding workers, and Group D: sintering process engineers and supervisors

Time-weighted average exposure level and estimated lung cancer risk	Groups of workers			
	A ($n = 9$)	B ($n = 6$)	C ($n = 3$)	D ($n = 6$)
Total PAHs$_{ave}$ (ng m^{-3})	83.0 ± 22.8	122 ± 31.1	90.8 ± 24.4	120 ± 34.3
Gas-phase	82.3 ± 27.7	121 ± 37.9	89.8 ± 29.2	96.7 ± 33.1
Particle-phase	0.685 ± 0.385	1.14 ± 0.633	1.04 ± 0.584	23.3 ± 13.1
Total BaP$_{ave}$ (ng m^{-3})	0.454 ± 0.232	0.620 ± 0.313	0.590 ± 0.302	0.705 ± 0.363
Gas-phase	0.450 ± 0.254	0.614 ± 0.344	0.583 ± 0.330	0.568 ± 0.322
Particle-phase	0.004 ± 0.001	0.006 ± 0.002	0.007 ± 0.002	0.137 ± 0.051
Cancer risk	$3.18 \times 10^{-5} \pm 1.63 \times 10^{--5}$	$4.34 \times 10^{-5} \pm 2.19 \times 10^{-5}$	$4.13 \times 10^{-5} \pm 2.11 \times 10^{-5}$	$4.98 \times 10^{-5} \pm 2.57 \times 10^{-5}$
Gas-phase	$3.15 \times 10^{-5} \pm 1.78 \times 10^{-5}$	$4.30 \times 10^{-5} \pm 2.41 \times 10^{-5}$	$4.08 \times 10^{-5} \pm 2.31 \times 10^{-5}$	$4.01 \times 10^{-5} \pm 2.27 \times 10^{-5}$
Particle-phase	$2.62 \times 10^{-7} \pm 9.69 \times 10^{-8}$	$4.06 \times 10^{-7} \pm 1.40 \times 10^{-7}$	$4.73 \times 10^{-7} \pm 1.69 \times 10^{-7}$	$9.66 \times 10^{-6} \pm 2.47 \times 10^{-6}$

Regarding the measured total BaP$_{eq}$ concentrations (i.e., gas- + particle-phase), the concentration found in the Site #2 (0.16 μg Nm^{-3}) was higher than those found in Site #1 and Site #3 (0.12 μg Nm^{-3} and 0.13 μg Nm^{-3}, respectively) ($p < 0.05$). The pattern was similar to that found in the corresponding total PAH concentrations, since the above three selected sampling sites shared with similar PAH homologue distributions. Finally, total BaP$_{eq}$ concentrations found in sintering zone workplaces (i.e., Site #1, Site #2, and Site #3) were much higher than that of the Site #4 (0.040 μg Nm^{-3}) ($p < 0.05$). The above results suggest that the isolation of the control room and the ventilation measures had a useful impact on PAHs exposure profile, especially by lowering the concentrations of carcinogenic species.

Table 3 also shows the PAH homologue distributions of the five selected sampling sites. We found the fractions of LMW-, MMW-, and HMW-PAHs in total PAHs were quite similar among Site #1 (86.5%, 9.52%, and 4.01%, respectively), Site #2 (86.7%, 9.60%, and 3.71%, respectively), and Site #3 (86.3%, 8.53%, and 5.16%, respectively). The above results again suggest PAHs found in the sintering zone were of the same nature (i.e., emitted from the sintering process with a similar coagulation effect due to their low concentrations). On the other hand, a very different pattern was found in Site #4 (91.4%, 6.09%, and 2.51%, respectively). Less fractions in both MMW- and HMW-PAHs found in Site #4 could be because less particle-phase PAHs were found in the control room, considering both MMW- and HMW-PAHs were mainly presented in particle-phase due to their low volatile characteristics. Finally, a very different pattern was found in the outdoor environment (79.5%, 16.4%, and 4.18%, respectively) further confirmed our previous inference: PAHs found in the workplace atmospheres were mainly contributed by process fugitives, rather than those transported from the outdoor environment.

3.3. Gas- and particle-phase PAHs containing in total PAH and total BaP$_{eq}$ concentrations in the workplace atmospheres

Table 4 shows gas- and particle-phase PAHs containing in total PAH and total BaP$_{eq}$ concentrations for samples

collected from the workplace atmosphere of the selected sinter plant. For total PAH, concentrations of the gas-phase PAHs (8.33–30.1 μg Nm^{-3}, accounting for 98.3–99.5% total PAHs) were consistently higher than that of particle-phase (0.042–0.365 μg Nm^{-3}, accounting for 0.5–1.7% total PAHs) for any given studied workplaces ($p < 0.05$). The above results can be explained by total PAHs were dominated by LMW-PAHs (Table 3). For total BaP$_{eq}$, concentrations of the gas-phase (0.037–0.121 μg Nm^{-3}) were also higher than that of particle-phase (0.003–0.039 μg Nm^{-3}) for any given studied workplaces ($p < 0.05$). However, particle-phase PAHs had more contribution to total BaP$_{eq}$ (8.1–24.1%) than to total PAHs (0.5–1.7%). The above results can be explained by total PAHs were dominated by LMW-PAHs which are known with low TEFs (Table 3).

Finally, it should be noted that the concentrations of both gas- and particle-phase PAHs found in the outdoor environment (Site #5) were consistently lower than that of the sintering zone (i.e., Site #1–Site #3) ($p < 0.05$) (Table 4). Particularly, the contributions of gas- and particle-phase PAHs to both total PAHs and total BaP$_{eq}$ for samples collected from the outdoor environment were quite different from that of sintering zone ($p < 0.05$) (Table 4). The above results further confirm that PAHs found in the workplace environments were mainly contributed by the process fugitives rather than the outdoor environment.

3.4. Health-risk assessment for sintering workers exposed to PAHs

In this study, worker's time-weighted average exposure was estimated based on the following equation:

$$C_{ave} = \frac{C_i \times T_i}{\Sigma T_i}$$

where, C_{ave} was the worker's time-weighted average exposure to total PAHs (denoted as total PAHs$_{ave}$) and total BaP$_{eq}$ (denoted as total BaP$_{eq_{ave}}$); C_i was the worker's exposure concentration to total PAHs at the ith site (i.e., total PAHs$_i$, see Table 3) and to total BaP$_{eq}$ at the ith site (i.e., total BaP$_{eq_i}$, see Table 2); T_i was the time of the given worker spent at the ith site (see Table 1);

and ΣT_i was the time for the given worker spent at all involved work sites.

Table 5 shows total PAHs$_{ave}$ and total BaP$_{eq_{ave}}$, and their corresponding gas-phase and particle-phase concentrations. In addition, the estimated lung cancer risks for the four selected exposure groups based on their total BaP$_{eq_{ave}}$ and the corresponding gas-phase and particle-phase concentrations were also presented in Table 5. For total PAHs$_{ave}$, its corresponding gas-phase concentration (82.3–121 ng m^{-3}) was consistently higher than that of particle-phase (0.685–23.3 ng m^{-3}) ($p < 0.05$). Particularly, all selected exposure groups were found with total PAHs$_{ave}$ (83.0–122 ng m^{-3}) significantly lower than the current permissible exposure limit regulated in Taiwan for PAHs (200,000 ng/m^3) ($p < 0.05$). The above results suggest that PAH exposures to sintering workers might not be particularly significant. In this study, the unit risk suggested by Pott (7×10^{-5} (BaP$_{eq}$ ng m^{-3})$^{-1}$) was used to assess workers' any excess of risk for lung cancer associated with a 25-year occupational exposure [17]. We found that the total BaP$_{ave}$ fell to the range of 0.454–0.705 ng m^{-3}. The corresponding gas-phase concentration (0.450–0.614 ng m^{-3}) was significantly higher than that of particle-phase (0.004–0.137 ng m^{-3}) ($p < 0.05$) suggesting that the former had a more contribution on worker's lung cancer risk. However, by taking both gas- and particle-phase together (i.e., total BaP$_{ave}$), the resultant lung cancer risks (3.18×10^{-5}–4.98×10^{-5}) were consistently lower than the significant risk level (10^{-3}) which was defined by the US Supreme Court [30]. The above results further confirm that PAH exposures to sintering workers might be acceptable at this stage.

4. Conclusions

The present paper shows that both TSP and total PAH concentrations of the three selected sintering process areas were higher than that of the control room. The above results could be explained by the filtration efficiency of the air conditioning device installed inside the control room. PAH homologue distributions of the three selected sintering process areas were significantly different from that of the outdoor environment suggesting that PAHs found in the sintering workplace atmospheres were mainly contributed by process fugitives. Total PAH exposure levels in the selected areas of the sintering plant were lower than the current permissible exposure limits, thus suggesting that sintering workers are usually exposed to quite low PAH concentrations. Consistently, our risk estimate for the lung cancer risks associated with the above PAH exposures gave lower values as compared to the significant risk level defined by US Supreme Court.

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