

Risk assessment of gaseous/particulate phase PAH exposure in foundry industry

Hung-Hsin Liu^b, Hsi-Hsien Yang^c, Choa-Da Chou^a, Ming-Hsiu Lin^d, Hsiu-Ling Chen^{a,*}

^a Department of Safety, Health and Environmental Engineering, Hung Kuang University, 34 Chung Chie Rd., Sha Lu, Taichung 433, Taiwan

^b School of Occupational Safety and Health, Chung Shan Medical University, Taichung, Taiwan

^c Department of Environmental Engineering and Management, Chaoyang University of Technology, Taichung, Taiwan

^d Institute of Occupational Safety and Health, Council of Labor Affairs, Taipei, Taiwan

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ABSTRACT

Thirty-seven air samplings in different working areas of two foundry industries were collected to assess polycyclic aromatic hydrocarbon (PAH) levels. The average PAH level inside Foundry A was $19.56 \mu\text{g}/\text{m}^3$, which was higher than that in Foundry B ($8.26 \mu\text{g}/\text{m}^3$), whereas for the benzo[a]pyrene toxic equivalent (BaPeq) level ($38.81 \text{ ng}/\text{m}^3$ vs. $46.52 \text{ ng}/\text{m}^3$). A higher PAH level was found for big moulding process than for the small one, and the chemical binder in the different size moulds was hypothesized to be the main cause. The higher PAH levels were found in the painting area ($95.51 \mu\text{g}/\text{m}^3$), pouring area ($18.42 \mu\text{g}/\text{m}^3$), and inside the office ($16.48 \mu\text{g}/\text{m}^3$); as well as the higher BaPeq level was in the painting area ($152.3 \text{ ng}/\text{m}^3$), and the furnace for melting iron ($96.9 \text{ ng}/\text{m}^3$). The gas phase (over 90%) was the major contributor of total PAHs in the manufacturing areas. Moreover, health risk assessment of PAHs exposure showed that lung cancer risks were 9.06×10^{-4} and 1.09×10^{-3} in Foundries A and B, respectively. This study suggests that the workers shall use appropriate respiratory masks in painting, melting, and pouring areas to prevent their occupational exposure to PAHs.

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1. Introduction

Several studies have reported that foundry workers may be exposed to high levels of polycyclic aromatic hydrocarbons (PAHs) [1–3]. Special PAHs, such as anthracene (Ant), fluorene (Flu), naphthalene (Nap) and phenanthrene (PA), are generated in many foundry sands and have been detected in over 79% of foundry sand waste [4]. In previous studies, PAH exposure was demonstrated to induce DNA strand breaks in workers exposed to fireproof materials and bitumen [5,6]. Higher risks for DNA damage or oxidative damage lesions have also been found in coke-oven workers with occupational PAH exposure [6,7]. Meanwhile, the increased risks of lung, bladder and urinary cancers were also associated with PAH-related occupations [8,9], as well as the increased risk of cardiovascular disease in foundry workers has also been documented [10]. Therefore, PAH exposure is definitely a cause of many adverse health effects in workers with this kind of exposure.

More than 600 PAHs have been identified; the simplest and most volatile compound is Nap, which has two aromatic rings and is present specifically in the gaseous phase. Meanwhile, Nap has been considered as a potential surrogate for workers with occupational PAH exposure [3]. The PAHs with the most aromatic rings (five- and six-ring) are predominantly in the particulate phase, and the three- and four-ring PAHs exist both in the gaseous and particulate phases, depending on the specific compound and the environmental conditions [11]. The carcinogenic PAHs are five- and six-ring ones, however, a “previous study” reports that the total PAH load of the individual fractions increases steadily with increasing particle size. The inhalable fine particle comprises 31.4% of the total dust and contains 49.9% of the total adsorbed PAH. The percentage of the gaseous phase PAH amounts to 77% of the total PAH load in an iron foundry. Meanwhile, the gas phase contains on average threefold more carcinogenic four- and five-ring PAHs than the particulate phase [12]. A study from Omland et al. [13] in iron foundry workers shows that the average concentration of 16 PAHs is $10.40 \mu\text{g}/\text{m}^3$ in the breathing zone, and the average dust-adsorbed PAH concentration is only $0.15 \mu\text{g}/\text{m}^3$, which demonstrates that the most predominant PAHs are in the gaseous phase. Shimmo et al. [14] indicate that the proportion of gaseous PAHs range from 0% to 100% for each PAH. It is well known that inhalation and skin uptake are both important routes for PAH exposure. Tsapakis and Stephanou [15] suggest that a shift in the gaseous/particulate distribution of PAHs may be caused by a change in the ambient temperature. Meanwhile, high temperatures are found in all manufacturing

Abbreviations: PAHs, polycyclic aromatic hydrocarbons; BaPeq, benzo[a]pyrene toxic equivalent; Nap, naphthalene; AcPy, acenaphthylene; Acp, acenaphthene; Flu, fluorene; PA, phenanthrene; Ant, anthracene; FL, fluoranthene; Pyr, pyrene; BaA, benzo[a]anthracene; CHR, chrysene; BbF, benzo[b]fluoranthene; BkF, benzo[k]fluoranthene; BaP, benzo[a]pyrene; IND, indeno[1,2,3-c,d]pyrene; DBA, dibenz[a,h]anthracene; BghiP, benzo[g,h,i]perylene.

* Corresponding author. Tel.: +886 4 26318652x4010; fax: +886 4 26319175.

E-mail address: hsiulin@sunrise.hk.edu.tw (H.-L. Chen).

processes, especially for metal melting and metal liquid pouring processes. The toxicity of each PAH is related to its ring number, which can affect whether the homologues are in a particulate or gaseous phase. Additionally, because of the high temperature in the foundry environment, it is difficult for the foundry workers to wear masks during their workday. Thus, the distribution of PAH levels in gaseous/particulate phase is important for evaluating the prevention strategy of occupational PAH exposure.

To date, previous studies have used various strategies to present the amount of PAH exposure: 20 PAHs in the Knecht et al. report [12], 16 PAHs in Omland et al. report [13], and 32 PAHs in the spent sand study [16]. In the leaching study of the spent foundry sand, the spent sand is shown to have higher PAH concentration in the green sand than the chemical binder sands, despite the fact that phenolic/ester sands have higher levels of PAHs than furan/acid and silicate sands [16]. These data indicate that PAH concentrations also vary due to the types of foundry sands.

Therefore, this study aims to investigate the gaseous/particulate phase PAHs in two kinds of iron foundry industries in different casting processes. Meanwhile, air samples for PAH analysis in the workplace are also utilized to assess the health risk of PAH exposure for foundry workers.

2. Materials and methods

2.1. Sampling selection in foundry plants

The study was conducted in two typical foundry plants in central Taiwan. Foundry A typically uses an induction furnace for melting metal, and Foundry B uses a cupola. A pre-sampling walk-through was conducted to determine the layout of each work site and its borders. In principle, the zones in the foundry plant are based on various operational functions. Several areas inside the foundries, including core making, melting furnace, moulding, sand shakeout, grinding, sand recovery, and office areas, as well as areas outside of the foundries were selected for this study. Totally, 37 air samples were taken inside the foundry industries and 6 air samples were taken in office and in outdoor of the 2 industries.

2.2. Ambient samples

Airborne samples were collected using a glass cartridge linked to personal air pump samplers (Gillian) with a flow rate of approximately 3 L/min, which was modified by Li et al. report [25]. A glass cartridge containing a glass fibre filter to collect particulate PAHs and total suspended particles in the upper layer and a 5-cm polyurethane foam (PUF) was plugged into the cartridge as the second layer after the filter. XAD-16 resin (1.5 g) and 3-cm PUF were also plugged into the cartridge as the second and bottom layer, respectively, to collect gaseous PAHs. The glass fibre filters were conditioned in the same temperature and humidity. In addition, the filters were weighed 48 h post-conditioning. The post-sampling weights were subtracted from the pre-sampling weights to provide the particle mass in the ambient sampling. Before sampling, the stuffed glass cartridges were cleaned with Soxhlet extracted with a 1:1 solution (Merck) of *n*-hexane and dichloromethane (v/v) for 24 h, and the cartridges were then dried in an oven at 60 °C to remove residual solvent. During sample transportation, sampling and storage, the glass cartridges were covered with aluminium foil to avoid photolysis degradation.

2.3. PAH analysis

The glass fibre filters and cartridges were extracted with Soxhlet with a mixed solvent for 24 h after the ambient sampling was completed. The extracts were then concentrated on a rotary

evaporator to 3–5 mL, which was modified by Fang et al. [17]. The subsequent proceeding was the removal of any pollutants to avoid contaminating the gas chromatograph (GC) column. Following the re-concentration procedure, 1.5 mL of extract was obtained after ultra-pure nitrogen treatment. All sampling solvents were analysed using a GC (Agilent 6890)/mass selective (MS) detector (Agilent 5973) equipped with a GC capillary column (Agilent Ultra 2–50 m × 0.32 mm × 0.17 mm) and an automatic sample (Agilent 7683r). The injection volume was 1 µL. A computer workstation was used for the PAH analysis. The temperatures for the injector, transfer line, ion source and Quadrupole were 310 °C, 290 °C, 230 °C and 230 °C, respectively. The oven temperature gradient began at 50 °C and rose to 100 °C at a rate of 20 °C/min and then rose from 100 °C to 290 °C at a rate of 3 °C/min; the final temperature of 290 °C was held for 40 min.

In this study, a total of 16 PAH species were analysed, including naphthalene (Nap), acenaphthylene (AcPy), acenaphthene (Acp), fluorene (Flu), phenanthrene (PA), anthracene (Ant), fluoranthene (FL), pyrene (Pyr), benzo[a]anthracene (BaA), chrysene (CHR), benzo[b]fluoranthene (BbF), benzo[k]fluoranthene (BkF), benzo[a]pyrene (BaP), indeno[1,2,3,-c,d]pyrene (IND), dibenz[a,h]anthracene (DBA) and benzo[g,h,i]perylene (BghiP).

2.4. Quality control

After consecutive sampling for 8 h, the filters and glass cartridges were stored at –20 °C. The masses of the molecular and fragment ions of PAHs were determined by using the scan mode for pure 16 PAH standards (2000 µg/mL; SUPELCO 48905-U). Qualification of the PAHs was performed by using the selected ion monitoring (SIM) mode. The instruments were calculated using at least five standard concentrations. The correlation coefficient of the calibration curve was >0.995 for a linear least-squares fit of the data. The detection limit was determined from a selected concentration that was slightly lower than the lowest concentration of the calibration curve. Measurements at this concentration were repeated seven times to estimate the standard deviation. The detection limit was determined to be three times of the standard deviation. The detection limit of the GC/MS for the 16 PAHs was between 0.024 ng and 0.740 ng. In this study, recovery efficiency tests for PAHs were accomplished by performing the same sample analysis procedure by adding the standard solution before extraction. The recovery efficiency of particulate PAHs ranged from 79.5% to 99.6% (average 89.1%), and gaseous PAHs ranged from 80.2% to 99.5% (average 89.6%) [18].

2.5. Data analysis

The JMP 5.0 (SAS Institute, Cary, NC, USA) and SigmaPlot software (version 8.0, SPSS Inc.) packages were used for data management and statistical analysis. The Wilcoxon rank sum test was carried out to evaluate differences in particle levels between Foundries A and B. Many researchers have calculated the cancer risk of PAH exposure based on the toxic equivalency factors (TEFs), which is considered to be BaPeq [17,19,20], because of BaPeq is a better indicator than total PAH level on characterizing the carcinogenic potency of PAHs. The cancer risks herein were calculated as described by Nisbet and LaGoy [19]. To assess workers' excessive lung cancer risks associated with a 25-year occupational exposure, the unit risk of 7×10^{-5} (BaPeq ng m⁻³)⁻¹.

3. Results

3.1. PAH levels in two foundries

The average particle levels in Foundries A and B were 1.64 mg/m³ (standard deviation, 1.57) and 1.87 mg/m³ (standard

deviation, 2.20), respectively (data not shown). The levels were almost equal in the two foundries. The particle measurements in different areas showed that the highest level was found in shakeout area (5.64 mg/m^3), the second highest level was in grinding area (3.77 mg/m^3), and the third highest level in moulding area (2.93 mg/m^3), whereas the lowest one was in outdoor (0.08 mg/m^3), and in the office (0.11 mg/m^3), respectively. Overall, the particle level inside the foundry plants was significantly higher than those outside of the plants and those of the indoor or outdoor offices (Fig. 1).

The average PAH level inside Foundry A was $19.56 \mu\text{g/m}^3$, which was higher than in Foundry B ($8.26 \mu\text{g/m}^3$). When we looked at the gaseous/particulate phase PAHs, the gaseous PAH level was $19.3 \mu\text{g/m}^3$ in Foundry A and $7.98 \mu\text{g/m}^3$ in Foundry B; however, no statistical difference was found (p value = 0.446). Additionally, the average particulate phase of PAH levels was not significantly different between the two foundries. Meanwhile, the gaseous/particulate phase PAHs was 98.67% and 96.38% in Foundries A and B, respectively. The difference may be due to two- and three-ring PAHs, including AcPy, Acp, Flu, PA, Ant, and Fl (Table 1). The BaPeq level inside Foundry A was 38.81 ng/m^3 , that was smaller than that in Foundry B (46.52 ng/m^3) (Table 2); the reverse trend was found for

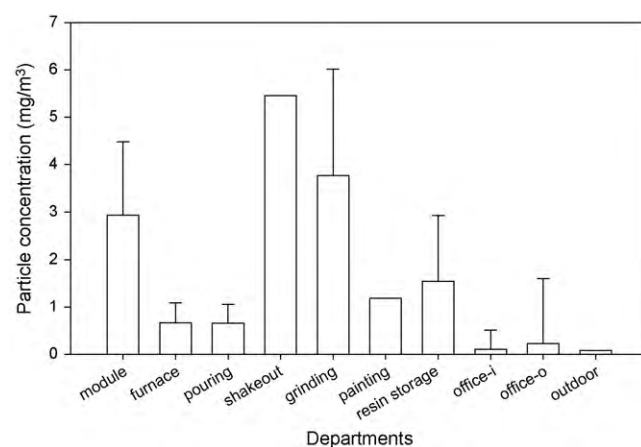


Fig. 1. Average particulate concentrations in different working areas of two foundry industries.

Table 1
Average concentrations of 16 gaseous and particulate PAHs in two foundry industries.

PAHs ($\mu\text{g/m}^3$)	Industry A (n = 20)				Industry B (n = 17)			
	Particle	Gas	Total	Gas%	Particle	Gas	Total	Gas%
Nap	0.11 (0.28)	17.87 (35.06)	17.98 (35.08)	99.39	0.16 (0.32)	6.15 (5.94)	6.31 (5.51)	97.46
AcPy	N.D.	0.47 (0.74)	0.47 (0.74)	100.00	0.02 (0.04)	0.39 (0.51)	0.42 (0.50)	92.86
Acp	N.D.	0.09 (0.10)	0.09 (0.10)	100.00	N.D.	0.05 (0.08)	0.05 (0.08)	100.00
Flu	N.D.	0.21 (0.39)	0.21 (0.39)	100.00	0.01 (0.03)	0.28 (0.40)	0.29 (0.40)	96.55
PA	0.04 (0.04)	0.37 (0.55)	0.41 (0.57)	90.24	0.03 (0.07)	0.75 (1.74)	0.78 (1.75)	96.15
Ant	0.01 (0.02)	0.12 (0.25)	0.13 (0.25)	92.31	0.02 (0.02)	0.07 (0.11)	0.09 (0.10)	77.78
FL	0.01 (0.02)	0.11 (0.13)	0.12 (0.13)	91.67	0.00 (0.01)	0.20 (0.39)	0.21 (0.40)	95.24
Pyr	0.01 (0.01)	0.06 (0.10)	0.07 (0.10)	85.71	N.D.	0.02 (0.02)	0.02 (0.02)	100.00
BaA	0.01 (0.01)	N.D.	0.01 (0.01)	–	0.01 (0.02)	0.01 (0.04)	0.03 (0.04)	33.33
CHR	0.01 (0.01)	N.D.	0.01 (0.02)	–	N.D.	N.D.	N.D.	–
BbF	0.01 (0.01)	N.D.	0.01 (0.01)	–	N.D.	N.D.	0.01 (0.01)	–
BkF	0.01 (0.01)	N.D.	0.01 (0.01)	–	N.D.	N.D.	N.D.	–
BaP	N.D.	N.D.	N.D.	–	0.02 (0.05)	0.01 (0.03)	0.03 (0.06)	33.33
IND	0.01 (0.01)	N.D.	0.01 (0.01)	–	N.D.	0.03 (0.05)	0.03 (0.05)	100.00
DBA	0.01 (0.01)	N.D.	0.01 (0.02)	–	N.D.	N.D.	N.D.	–
Bghip	0.02 (0.02)	N.D.	0.02 (0.02)	–	N.D.	0.01 (0.01)	0.01 (0.01)	100.00
Total	0.26 (0.26)	19.30 (35.62)	19.56 (35.64)	98.67	0.30 (0.41)	7.98 (7.60)	8.28 (7.67)	96.38

Note: The standard deviation are shown inside parenthesis; N.D.: non-detected; –: it cannot be calculated.

Table 2
Average BaPeq concentrations of 16 gaseous and particulate PAHs in two foundry industries.

BaPeq (ng/m^3)	Industry A (n = 20)				Industry B (n = 17)			
	Particle	Gas	Total	Gas%	Particle	Gas	Total	Gas%
Nap	0.11 (0.28)	17.87 (35.06)	17.98 (35.8)	99.39	0.16 (0.32)	6.15 (5.49)	6.31 (5.51)	97.46
AcPy	N.D.	0.47 (0.74)	0.47 (0.74)	100.00	0.02 (0.04)	0.39 (0.51)	0.42 (0.50)	92.86
Acp	N.D.	0.09 (0.10)	0.09 (0.10)	100.00	0.00 (0.01)	0.05 (0.08)	0.05 (0.08)	100.00
Flu	N.D.	0.21 (0.39)	0.21 (0.39)	100.00	0.01 (0.03)	0.28 (0.40)	0.29 (0.40)	96.55
PA	0.04 (0.04)	0.37 (0.55)	0.41 (0.57)	90.24	0.03 (0.07)	0.75 (1.74)	0.78 (1.75)	96.15
Ant	0.07 (0.18)	1.20 (2.50)	1.26 (2.49)	95.24	0.23 (0.23)	0.67 (1.09)	0.90 (1.01)	74.44
FL	0.01 (0.02)	0.11 (0.13)	0.12 (0.13)	91.67	0.00 (0.01)	0.20 (0.39)	0.21 (0.40)	95.24
Pyr	0.01 (0.01)	0.06 (0.10)	0.07 (0.10)	85.71	0.00 (0.00)	0.02 (0.02)	0.02 (0.02)	100.00
BaA	0.52 (0.65)	0.24 (0.64)	0.76 (1.15)	31.58	1.20 (1.60)	1.44 (3.67)	2.64 (4.27)	54.55
CHR	0.09 (0.08)	0.04 (0.09)	0.14 (0.16)	28.57	0.00 (0.01)	0.03 (0.04)	0.03 (0.04)	100.00
BbF	1.26 (1.47)	0.08 (0.11)	1.34 (1.42)	5.97	0.11 (0.11)	0.39 (0.94)	0.50 (1.00)	78.00
BkF	0.62 (0.69)	0.06 (0.26)	0.68 (0.83)	8.82	0.15 (0.17)	0.07 (0.11)	0.22 (0.25)	31.82
BaP	3.73 (4.94)	0.02 (0.01)	3.76 (4.94)	0.53	17.84 (54.99)	10.70 (28.23)	28.55 (59.11)	37.48
IND	1.24 (1.40)	0.01 (0.02)	1.25 (1.40)	0.80	0.14 (0.23)	2.97 (5.29)	3.11 (5.26)	95.50
DBA	9.86 (17.77)	0.24 (0.55)	10.10 (17.74)	2.38	1.25 (4.65)	1.13 (2.40)	2.39 (6.87)	47.28
Bghip	0.17 (0.24)	0.01 (0.02)	0.18 (0.23)	5.56	0.04 (0.05)	0.06 (0.07)	0.10 (0.10)	60.00
Total	17.74 (23.15)	21.07 (36.9)	38.81 (43.78)	54.29	21.22 (55.17)	25.31 (41.88)	46.52 (67.57)	54.41

Note: The standard deviation is shown inside parenthesis; N.D.: non-detected.

Table 3
Mean concentrations ($\mu\text{g}/\text{m}^3$) and BaP_{eq} levels (ng/m^3) of 16 gaseous and particulate PAHs by large or small moulds in two foundry industries.

Departments	N	PAHs		TEQ-PAHs						
		Particle	Gas	Total	Gas%	Particle	Gas	Total	Gas%	
A	Big	Moulding	0.17 (0.05–0.18)	7.19 (4.09–12.37)	7.36 (4.27–12.53)	97.69	20.44 (16.84–27.23)	7.74 (4.30–13.34)	28.18 (21.56–32.80)	27.47
		Pouring	0.68 (0.19–1.17)	36.88 (9.18–64.57)	37.56 (9.37–65.74)	98.19	25.94 (17.58–34.31)	44.13 (10.41–77.86)	70.08 (44.71–95.44)	62.97
	Small	Moulding	0.07 (0.02–0.11)	4.35 (0.13–8.57)	4.42 (0.24–8.60)	98.42	10.36 (5.31–15.40)	4.81 (0.54–9.08)	15.16 (14.39–15.94)	31.73
		Pouring	0.08 (0.05–0.12)	17.74 (14.21–21.27)	17.82 (14.26–21.39)	99.55	2.70 (2.60–2.81)	18.39 (14.74–22.05)	21.09 (17.33–24.85)	87.20
B	Big	Moulding	0.06 (0.04–0.08)	3.94 (1.68–5.88)	4.00 (1.72–5.94)	98.50	1.14 (0.78–1.70)	7.13 (2.51–11.73)	8.28 (3.29–12.95)	86.11
		Pouring	0.47 (0.17–0.98)	10.53 (6.93–14.03)	11.00 (7.44–15.01)	95.73	13.48 (1.25–44.71)	16.74 (11.90–23.16)	30.22 (18.48–56.61)	55.39

Note: Big indicates the big mould and small indicates the small mould; minimum–maximum are shown inside parenthesis.

total PAH levels. Although the total BaP_{eq} levels of particulate phase and gaseous phase were almost equal between the two industries, the five- and six-ring PAHs contributed the most toxicity to BaP_{eq} levels in Foundry A than those of Foundry B, including BaP, IND, DBA, and BghiP.

Foundry A produces big and small moulds, while only big moulds are produced in Foundry B. The differences in air PAH levels in moulding and pouring areas were therefore further evaluated between the two foundries in Table 3. In Foundry A, a new environmental control system was installed in the manufacturing areas over a year ago. The air sampling showed that in Foundry B, even though there were only big moulding processes were performed, which use more chemical binders–furan resin, the higher PAH levels were found in Foundry A than in Foundry B ($7.36 \mu\text{g}/\text{m}^3$ and $4.00 \mu\text{g}/\text{m}^3$ in the moulding areas, and $36.56 \mu\text{g}/\text{m}^3$ and $11.0 \mu\text{g}/\text{m}^3$ in the pouring areas, respectively). When comparing the PAH emission between the big moulds and small moulds in Foundry A, a higher level was found in the big mould production process than the small mould. Furthermore, a high variation of the BaP_{eq} level in the two foundries was also found between big moulds and small moulds, as well as those in different foundry industries.

3.2. PAH emission in different working departments

The 16 PAH levels in different working departments are shown in Table 4. The higher concentrations of 16 PAH were found in the painting area ($95.51 \mu\text{g}/\text{m}^3$), pouring area ($18.42 \mu\text{g}/\text{m}^3$), and inside office ($16.48 \mu\text{g}/\text{m}^3$); the lower levels were found in the grinding area ($2.90 \mu\text{g}/\text{m}^3$) and outdoors ($2.78 \mu\text{g}/\text{m}^3$). Meanwhile, of the 16 PAHs measured in the foundry plants, over 90% were in the gaseous phase in inside and outside offices. Table 5 presents the BaP_{eq} levels of the 16 PAHs in different manufacturing areas of the two foundries. The higher levels of BaP_{eq} were found in the painting area ($152.3 \text{ ng}/\text{m}^3$), the furnace for melting iron ($96.9 \text{ ng}/\text{m}^3$), and the pouring area ($37.05 \text{ ng}/\text{m}^3$); the lower levels were found outdoors ($5.74 \text{ ng}/\text{m}^3$) and in the grinding area ($7.91 \text{ ng}/\text{m}^3$). The gaseous/particulate ratio varied more for BaP_{eq} levels than for 16 PAH levels.

3.3. Health risk assessment of PAHs in foundry workers

The cancer risk calculations based on time-weighted average exposure levels of BaP_{eq} of foundries' workers are presented in Table 6. The unit risk of BaP_{eq} was adopted from Nisbet and LaGoy [19], and Lin et al. [23]. The cancer risks of PAH exposure in Foundries A and B were 9.06×10^{-4} and 1.09×10^{-3} , respectively. The risk of gaseous phase and particulate phase PAHs were almost equal in both foundries.

4. Discussion

4.1. PAH levels in the foundry industries

A previous study that focused on evaluating sources of PAHs in urban soil suggested that foundries were potentially important sources of PAH in the vicinity of urban soil and sediment [21].

When comparing environmental samplings, the air PAHs ranged from $0.022 \mu\text{g}/\text{m}^3$ to $156.7 \mu\text{g}/\text{m}^3$ in this occupational study, which was obviously higher than those ranged from $44.3 \text{ ng}/\text{m}^3$ to $129.2 \text{ ng}/\text{m}^3$ in an urban region of Greece [15], as well as those also higher than PAH levels in the gaseous phase ranged between 6.89 and $124 \text{ ng}/\text{m}^3$, while in the particulate phase between 0.44 and $13.2 \text{ ng}/\text{m}^3$ in suburban area of Athens greater area [22].

When comparing the occupational groups, the higher levels were found in the painting department ($95.41 \mu\text{g}/\text{m}^3$) and the pouring department ($18.48 \mu\text{g}/\text{m}^3$), and which were also higher

Table 4
Average concentrations ($\mu\text{g}/\text{m}^3$) of 16 gaseous and particulate PAHs by the working process.

Department	Moulding	Furnace	Pouring	Shakeout	Grinding	Painting	Resin storage	Office-i	Office-o	Outdoor
N=	9	7	9	2	5	2	3	2	2	2
Nap	3.93	9.53	16.05	5.00	2.52	89.61	6.15	15.87	7.18	2.50
AcPy	0.44	0.45	0.70	0.06	0.06	0.73	0.41	0.18	0.14	0.05
Acp	0.02	0.11	0.10	0.04	0.07	0.09	0.05	0.07	0.06	0.02
Flu	0.21	0.20	0.44	0.03	0.02	0.49	0.23	0.08	0.12	0.03
PA	0.31	0.66	0.59	0.12	0.09	3.66	0.27	0.17	0.25	0.09
Ant	0.04	0.12	0.25	0.04	0.05	0.08	0.04	0.07	0.08	0.01
FL	0.15	0.15	0.11	0.04	0.03	0.74	0.26	0.01	0.06	0.04
Pyr	0.03	0.08	0.08	0.02	0.01	N.D.	0.02	0.01	0.03	0.01
BaA	N.D.	0.04	0.02	N.D.	0.01	0.04	N.D.	N.D.	0.01	0.01
CHR	0.01	0.02	0.01	N.D.	N.D.	N.D.	0.01	N.D.	N.D.	N.D.
BbF	0.02	0.02	N.D.	N.D.	N.D.	N.D.	0.01	0.01	0.01	N.D.
BkF	N.D.	0.01	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
BaP	N.D.	0.05	0.01	N.D.	N.D.	0.05	N.D.	N.D.	N.D.	N.D.
IND	0.01	0.04	0.01	0.03	0.03	0.01	N.D.	0.01	0.01	0.02
DBA	N.D.	0.02	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
Bghip	0.03	0.02	0.01	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
Particulate PAHs	0.10 (0.06)	0.42 (0.51)	0.43 (0.40)	0.30 (0.32)	0.30 (0.54)	0.08 (0.08)	0.14 (0.08)	0.11 (0.01)	0.41 (0.43)	0.04 (0.03)
Gas-PAHs	5.11 (3.65)	11.11 (10.81)	17.99 (17.96)	5.10 (5.27)	2.59 (1.98)	95.43 (86.62)	7.32 (8.70)	16.37 (20.70)	7.55 (2.18)	2.74 (2.12)
Total PAHs	5.21 (3.66)	11.53 (10.79)	18.42 (18.22)	5.40 (5.59)	2.90 (1.90)	95.51 (86.54)	7.45 (8.74)	16.48 (20.68)	7.96 (1.75)	2.78 (2.14)
Gas%	98.12	96.36	97.67	94.49	89.47	99.92	98.17	99.32	94.85	98.69

Note: Office-i means inside the office and Office-o means outside the office; N.D.: non-detected; the standard deviation is shown inside parenthesis.

Table 5
Mean BaPeq levels (ng/m^3) of 16 gaseous and particulate PAHs by the working process.

Department	Moulding	Furnace	Pouring	Shakeout	Grinding	Painting	Resin storage	Office-i	Office-o	Outdoor
N=	9	7	9	2	5	2	3	2	2	2
Nap	3.93	9.53	16.05	5.00	2.52	89.61	6.15	15.87	7.18	2.50
AcPy	0.44	0.45	0.70	0.06	0.06	0.73	0.41	0.18	0.14	0.05
Acp	0.02	0.11	0.10	0.04	0.07	0.09	0.05	0.07	0.06	0.02
Flu	0.21	0.20	0.44	0.03	0.02	0.49	0.23	0.08	0.12	0.03
PA	0.31	0.66	0.59	0.12	0.09	3.66	0.27	0.17	0.25	0.09
Ant	0.37	1.25	2.47	0.43	0.54	0.75	0.39	0.72	0.80	0.15
FL	0.15	0.15	0.11	0.04	0.03	0.74	0.26	0.01	0.06	0.04
Pyr	0.03	0.08	0.08	0.02	0.01	N.D.	0.02	0.01	0.03	0.01
BaA	0.38	3.73	2.15	0.26	0.59	3.54	0.21	0.23	0.89	0.69
CHR	0.07	0.17	0.13	0.01	0.01	0.03	0.05	N.D.	0.04	N.D.
BbF	1.52	1.82	0.48	0.20	0.19	0.28	0.89	0.82	0.69	0.03
BkF	0.38	1.29	0.36	0.09	0.06	0.04	0.37	0.01	0.01	0.04
BaP	3.54	51.24	6.96	0.95	0.83	50.09	0.34	0.04	0.04	0.05
IND	1.45	4.41	1.45	2.51	2.55	0.98	0.39	1.31	1.20	1.67
DBA	3.38	21.60	4.82	0.96	0.30	1.24	3.86	0.21	0.30	0.35
Bghip	0.26	0.20	0.14	0.02	0.03	0.03	0.03	0.01	0.01	0.02
Particulate PAHs	9.62 (9.75)	65.57 (78.66)	13.85 (15.71)	3.52 (3.24)	3.33 (2.61)	2.03 (0.14)	5.84 (5.91)	2.54 (0.81)	2.89 (1.74)	0.94 (0.59)
Gas-PAHs	6.82 (4.21)	31.33 (44.22)	23.19 (20.92)	7.23 (3.05)	4.58 (3.59)	150.27 (10.60)	8.09 (8.88)	17.21 (20.33)	8.93 (1.50)	4.80 (0.68)
Total PAHs	16.44 (10.04)	96.90 (83.78)	37.05 (25.43)	10.75 (6.29)	7.91 (1.74)	152.30 (10.47)	13.93 (7.09)	19.75 (19.52)	11.83 (0.24)	5.74 (0.09)
Gas%	41.46	32.33	62.61	67.26	57.91	98.67	58.06	87.15	75.54	83.63

Note: Office-i means inside the office and Office-o means outside the office; N.D.: non-detected; the standard deviation is shown inside parenthesis.

Table 6
Time-weighted average exposure levels of total BaPeq and the cancer risk of workers exposed to gaseous/particle phase PAHs between Foundries A and B.

	Foundry A	Foundry B
Unit risk (ng/m ³) ^{-1a}	7.00 × 10 ⁻⁵	7.00 × 10 ⁻⁵
BaPeq (ng/m ³)		
Gas phase	7.02	8.44
Particle phase	5.91	7.07
Cancer risk ^b		
Gas phase	4.92 × 10 ⁻⁴	5.91 × 10 ⁻⁴
Particle phase	4.14 × 10 ⁻⁴	4.95 × 10 ⁻⁴
Total cancer	9.06 × 10 ⁻⁴	1.09 × 10 ⁻³

^a The unit risk was adopted from Lin et al. [23].

^b Risk of cancer = air levels (μg/m³) × unit risk (μg/m³)⁻¹.

than the PAH concentration (461.8–935.6 ng/m³) near the continuous casting area of an electric steel foundry [1]. Additionally, these levels were higher than the airborne PAH concentrations (sum of 15 selected PAH compounds: 9.6–11.2 μg/m³) in the casting, machine moulding, and shakeout departments [2]. As compared to the samplings in the sinter plant, the concentrations in these working zones were obviously higher than the concentrations in the raw material inlet, sintering grate, rough roll shredder and control room (8.37–30.4 μg/m³) [23].

Meanwhile, a previous study conducted in iron foundries found that workers engaged in different stages of the production of iron casts were exposed to carcinogenic PAHs, especially in casting of moulds [24]. The BaPeq levels were high in resin storage and moulding areas in the current study, which was not totally consistent with other studies [2,24]. The reasons for the difference may be interpreted as follows: (1) many chemicals, such as chemical binding-furan resin, present in the resin storage areas. (2) The melting and pouring processes may be the major sources of PAHs due to the high temperature used during these processes. However, the cover on top of the furnace is usually closed and is only opened when the melting process is completed. (3) The pouring process is a short-term process, and the moulding areas are where the moulds cool down after the pouring is completed. Therefore, the pouring and moulding processes cannot be separated completely. The occupational hazards of PAHs cannot be neglected if the worker's job integrates the moulding, pouring, and melting processes.

4.2. The PAH levels in the two foundries

This study was conducted in two typical foundry plants in central Taiwan. Foundry A typically uses an induction furnace for melting metal, and Foundry B uses a cupola for melting metal. The production of Foundry A includes big and small moulds, but only big moulds are produced in Foundry B. Another difference between the two foundries is that furan resin and silicate sands are used in Foundry A, and only furan resin is used in Foundry B. No significant difference in particle concentration was found between the two foundries, whereas a difference was found for the total levels of 16 PAHs. When expressed in BaPeq, the gaseous/particulate phases were almost equal in BaPeq levels. Therefore, these data suggest that the gaseous phase may have a major effect on the distribution of BaPeq in foundries. Meanwhile, a previous study indicated that variations of PAH levels can be attributed to chemical binders of iron casting moulds [25], and a leaching study also indicated that PAH concentrations varied between green sand and chemical binder spent sands in addition to the variation according to whether the bindings were made of phenolic/ester or furan/acid [16]. From Table 3, we can see that the operating process and products may

influence the use of foundry sand and binding chemicals, which are important factors to affect the PAH components in foundries.

4.3. Gas/particle phase of PAHs in foundries

The gaseous phase contributed 98.67% and 96.38% of the total 16 PAH levels in Foundries A and B, respectively. These values were equal to 98.4% and 98.8% contributions that were found in the workplace atmospheres of iron foundries and sinter plants, respectively [13,23]. When comparing the gas proportion indoors and outdoors, 98.65% of PAHs were found in the gaseous phase in outdoor samples, which was comparable to data that suggested that gas phase contributed to almost 90% of PAHs in suburban areas [22], but was higher than the gaseous phase contributions in an urban atmosphere [15]. Over 90% of 16 PAHs in some working areas was gaseous phase, including those in manufacturing areas and inside and outside offices. The amount of PAHs in the gaseous phase in the present study was higher than the levels inside an iron foundry (77%) [12]. Meanwhile, Knecht et al. found that the gaseous phase contained on average threefold more carcinogenic four- and five-ring PAHs than the particle phase. However, this distribution was only found in some workplaces, such as the shakeout, grinding, painting, resin storage and outdoor areas in this study. In addition, Shimmo et al. indicated that the proportion of the gaseous concentration of each PAH varied. For example, 100% of Ay was found in the gaseous phase, and 100% of DBA was found in the particulate phase [14]. Shimmo et al. also indicated that total particulate PAH concentrations were higher in particles smaller than 440 nm and 2.5 μm. Meanwhile, it has been suggested that shifts in gaseous/particulate distribution are due to differences in ambient temperature, which accounts for the seasonal variation of the concentration of PAHs in particles. Because high temperatures are used in foundry plants, possible influencing factors may include particle size and high temperatures in working areas, such as those happened in the moulding, melting, and pouring areas.

4.4. Risk assessment of PAHs

Although the average total BaPeq exposure levels were lower than the permissible exposure limit set by the Occupational Safety and Health Administration (OSHA, 8-h time-weighted average: 0.2 mg/m³), the lung cancer risks associated with the above PAH exposures ranged from 9.06 × 10⁻⁴ to 1.09 × 10⁻³, which were higher than those in sinter plant workers (3.18 × 10⁻⁵ to 4.98 × 10⁻⁵) and temple workers (10⁻⁶ to 10⁻⁴) who had occupational PAH exposure [23,26]. The lung cancer risk due to gaseous phase PAH exposure was much higher than that of particulate phase PAH exposure in the workers of oil mists in a fastener manufacturing industry, which showed an almost equal contribution of risk for exposure to the gaseous phase or particulate phase PAHs [27]. Meanwhile, the lung cancer risk does reflect a previous study that reported relative risk of lung and respiratory cancer in the workers with PAH exposure in iron and steel foundries (1.40, 95% CI 1.31–1.49) [8]. Additionally, this correlates with our previous study that demonstrated high oxidative damage in foundry workers [28,29].

Therefore, future studies should follow up to efficiently develop biological markers to show the effect of PAHs on the lung and respiratory tract [8], including bronchus and lung impairment in foundry workers.

5. Conclusion

The present study shows that total PAH levels in the selected areas of the manufacturing process are higher than outside the foundry industry. The higher PAH levels are also found inside

offices, which indicate that large quantities of PAHs are leached from the manufacturing areas to administrative areas. This can be explained by the incorrect layout of exhaust equipment in the manufacturing areas because the exhaust outlet is near the upper the office. Therefore, it cannot be overlooked that administrative workers in foundries are also exposed to PAHs emitted from the foundry operating processes. Gaseous phase PAHs comprise the majority of total PAHs, and the cotton masks that the workers use cannot effectively prevent gaseous PAHs exposure of the workers in the painting, melting, and pouring districts. Moreover, the workers at foundry plants have a significantly higher cancer risk based on the ambient BaP_{eq} levels. Together with our previous report, these data indicate that elevated oxidative damages are found in foundry workers. How to utilize biological effect markers to detect the precursor of lung cancer will be important in further studies.

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