Removal efficiency of vapour/particulate phase PAHs by using alternative protective respirators in PAHs exposure workers

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ARTICLE INFO

ABSTRACT

Due to the high heat environment in foundry industries, it is difficult for foundry workers to wear masks during their workday. Thus, how to prevent inhaling vapour or the particulate phase of polycyclic aromatic hydrocarbons (PAHs) is important for occupational hazard management. The present study assesses the characteristics of PAHs emission in foundry and plastic industries to evaluate the removal efficiencies of PAHs while workers use alternative personal protective equipment.

The highest 1-hydroxypyrene (1-OHP) level was found for workers who used a cotton-fabric face mask (1.19 µg/g creatinine) and activated-carbon face mask (1.16 µg/g creatinine), compared to a lower level in workers who wore a surgical face mask (0.27 µg/g creatinine) and a N95 respirator (0.51 µg/g creatinine). The urinary 1-OHP in end-of-shift samples correlated to the airborne vapour phase Bapeq, but not for the particulate phase Bapeq in the foundry industry. This is probably because workers wore personal protective equipment that only removed the particulate phase PAH. The current study suggests that future work focus on developing an appropriate and comfortable respirator with high removal efficiency for ultrafine particulates and vapour phase PAHs simultaneously in PAH work environments.

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1. Introduction

Several studies have reported that foundry workers expose to high levels of polycyclic aromatic hydrocarbons (PAHs) [1–3]. More than 1897 PAHs compounds, semi-volatile organic compounds at room temperature, have been identified, and the volatility of PAHs decreases as its molecular weight increases [4]. Therefore, the most volatile compound has two aromatic rings, specifically present in the vapour phase.

In many occupational studies, PAH exposure was demonstrated to induce DNA strand breaks in workers exposed to fireproof materials and bitumen [5,6], in coke-oven workers [5,7], and in foundry workers. The percentage of vapour PAH was about 77% of total PAH load in an iron foundry [8], and our previous study has shown that the vapour phase contributed over 90% of total PAHs

in the manufacturing areas of foundries [9]. The vapour phase contained on average three-fold more carcinogenic four- and five-ring PAHs than the particulate phase [8]. Three- and four-ring PAHs exist both in the vapour and particulate phases according to environmental conditions, and PAHs with the most aromatic rings (five-and six-ring), typically with carcinogenic potential, are predominantly in the particulate phase [10]. Thus, how to prevent inhaling the vapour or particulate phase of PAH is important for occupational risk management. Because of the high temperature in the foundry environment, it is difficult for foundry workers to wear masks during their workday. Therefore, to verify the percentage of vapour/particulate phase PAHs is important when discussing the prevention efficiency of PAHs exposure.

Many studies have used urinary 1-hydroxypyrene (1-OHP), a metabolite of PAHs for indicating PAH exposure, whether for tobacco smoke exposure or other occupational exposure [11–14]. The highest contribution of 1-OHP originated from environmental tobacco smoke, and that varied according to different cooking cultures [12] and body mass index (BMI) [11]. In 1916, the American Foundrymen's Association (AFA) published safety codes for respiratory protection in foundries. The code stated that, "Sandblasting by a hand-operating apparatus shall be carried on in suitable sand-blast rooms. Sand or shot blast operatives shall be provided with suitable helmets or masks, respirators, approved safety goggles, gloves, and leggings." [15,16]. Previous reports have shown that electrode paste workers wore respirator masks persistently, and

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their urinary 1-OHP showed a significant reduction in end-of-shift samples [17]. However, a contradictory result showed that the use of facial protection seemed to lead to an elevated increase of 1-hydroxypyrene over the workweek in workers of an aluminum smelter [18]. The other study has suggested that its need to fully evaluate whether air-purifying respirators reduce exposure to aggregate vapour present in overhaul activities of firefighters [19]. As the reported has shown that the half-mask respirators or facial-seal leaks might affect the protective efficiency of face mask. For example, the qualitative fit factor needs an overall protection factor of 20 or 50 for a wide range of aerosol size distributions, and 15 or more for an unknown aerosol size distribution [20]. Therefore, how to choose a suitable respirator is important in an occupational workplace with vapour and particulate exposure.

The present study therefore comprehensively assesses the characteristics of PAH exposure, and the removal efficiencies of PAHs using alternative personal protective equipment of workers used in foundry and plastic industries. Foundry industry typically uses styrofoam to manufacture giant molds, and the plastic industries use plastic material to manufacture raincoats by melting plastic pieces. The manufacturing processes those use high heat and chlorine-contained materials, which are suspected to produce PAHs emission. Therefore, the foundry and plastic industry were selected to assess the removal efficiency of PAHs in the present study.

2. Material and methods

2.1. Subject selection

The study was conducted in one typical foundry industry and one plastic industry in Taiwan. Twenty-nine and 15 workers were recruited from the foundry industry and the plastic industry, respectively. In the foundry, 83% of workers (24/29) used personal respiratory protection and none plastic worker used personal respiratory protection. Each employee was asked to complete a questionnaire interview requesting information about personal characteristics, lifestyle (e.g., tobacco use and alcohol intake) and occupational history (e.g., work history at current place of employment, work environment, job titles, periods of employment, and use of protective equipment). The study was approved by the Ethics Committee of Pingtung Christian Hospital (Pingtung, Taiwan).

2.2. Face masks

Four types of face masks were used in the foundry industry, including a activated-carbon mask (Serial: SA-45S 4 layer, Blue Egale Inc.), cotton-fabric mask, and N95 face mask (Lot#8262, 3M 8210), and R95 face mask (Lot#1044, 3M 8247, filtration rate of particulates >95% and contained activated-carbon inside the two layers). Twenty-four worker (24/44) participants used masks, and among them, 15 workers used a cotton-fabric mask. None of the workers in the plastic industry wore any face mask (Table 1).

2.3. Ambient samples

A pre-sampling walk-through was conducted to determine the layout of each work site. The present study selected working departments inside the foundry as the objects of concern, including the melting furnace, moulding, sand shake, and office areas, as well as the melting areas inside the plastic industry suspected with PAH emission. Twenty-two personal air samples were taken in the selected foundry ($N = 16$) and plastic industries ($N = 6$).

In this study, the British Institute of Occupational Medicine (Institute of Occupational Medicine) developed an IOM sampler, with an inner 25 mm glass fiber filter (GF-653-25 mm, Whatman

Table 1
Types of face masks the workers used.

Plants	Face masks			
	R95	Activated-carbon face mask	Cotton-fabric face mask	N95
Foundry ($N = 29$)				
Module	0	2	7	4
Shakeout	1	0	2	0
Furnace	0	1	3	0
Administration	0	0	3	1
Security	0	0	0	0
Plastic ($N = 15$)				
Melting	0	0	0	0

International Ltd., DI 2.5 cm, 0.8 μm), and a serial of XAD-2 sorbent tubes (100 mg/50 mg, USA, SKC, Catalog No. 226-30-04) was set for sampling the solid and vapour phase PAHs, modified by Tsai et al. [21]. The serial of IOM and XAD-2 sorbent tube linked to personal air pump samplers (Gillian) with a flow rate of approximately 2 l/min, and the later flow rate was adjusted to 0.9 l/min by a triple connected valve. Before sampling, the stuffed glass cartridges were cleaned with soxhlet extracted with a 1:1 solution (Merck, No. 1.06044.4000) of n-hexane and dichloromethane (v/v) for 24 h, and the cartridges were 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.

2.4. PAH analysis

The glass fiber filters and cartridges were extracted by soxhlet with a mixed solvent for 24 h after ambient sampling. The extracts were then concentrated on a rotary evaporator to 3–5 ml, modified by Fang et al. [22]. The subsequent process removed 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 analyzed 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). A computer workstation was used for the PAH analysis. The temperatures for the injector, transfer line, ion source, and quadruple 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.

This study analyzed a total of 16 PAH species, 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[l,2,3,-c,d]pyrene(IND), dibenz[a,h]anthracene (DBA), and benzo[g,h,i]perylene (BghiP).

2.5. 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 using the scan mode for pure 16 PAH standards (2000 μg/ml; SUPELCO 48905-U). Qualification of PAHs was performed 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

Table 2
The distribution of urine 1-OHP concentrations by the workers using different face masks.

Face masks	Number	Working hour (h)	Working years (year)	1-OHP (μg/g creatinine)
Activated-carbon face mask	3	9	7	1.16 ± 0.25
Cotton-fabric face mask	14[a]	7	9	1.19 ± 1.64
R95	1	10	5	0.27
N95	5	7	10	0.51 ± 0.38
No face mask	21	8	15	1.39 ± 1.03

[a] An analysis of 1-OHP was unavailable.

curve. Measurements at this concentration were repeated seven times to estimate the standard deviation, and the detection limit was determined to be three times that of the standard deviation [23]. The detection limit of the GC/MS for the 16 PAHs was between 0.049 ng and 0.428 ng. The recovery efficiency tests for PAHs in this study were accomplished by performing the same sample ($N = 8$) analysis procedure by adding the standard solution before extraction. The recovery efficiency of particulate PAHs ranged from 85.5% to 94.6% (average 90.1%), and vapour PAHs ranged from 84.4% to 96.9% (average 90.4%).

2.6. Urine collection

The sampling day was Friday, the last workday of the week. Friday as the sampling day would present hazards accumulating within a week. Each participant provided urine samples in a polyethylene bottle, which were washed with 0.2% HNO_3. Two urine samplings were taken in the beginning from the first urination in the morning and before the workers leaving the work in Friday of the plastic industry, but only one sampling was taken in the beginning in the foundry industry. The samples were kept at $-85\,^\circ$C for 1-OHP analysis.

2.7. 1-OHP analysis

All urine samples were analyzed for 1-OHP by high-performance liquid chromatography (HPLC) [24–26]. A 10 ml urine specimen was diluted with 1 N hydrochloric acid and 0.1 M acetate buffer (pH 5.0) to a total volume of 20 ml and adjusted to pH 5.0 with 4 M HCl. This mixture was incubated for 20 h with 25 μl of β-glucoronidase (116, 300 units/ml, SIGMA) at $37 \pm 0.5\,^\circ$C in an electronically controlled rotary shaking bath. A sample purification and enrichment cartridge (Sep-Pak ENVI-18 cartridges, 500 mg/3 ml, Supelco) was used to extract the metabolites. The cartridge was washed with 10 ml of distilled water and 5 ml of methanol, and then directly washed with 4 ml of distilled water. The final elution of 1-OHP fractions was performed in 4 ml of methanol. The eluted fractions were evaporated until dry at 50 $^\circ$C and passed through a syringe filter (PVDF, 0.22 μm, 13 mm, Millipore) reconstituted with 2 ml of methanol. An HPLC system (Waters 2695) containing a fluorescence detector (Water 474) was used for quantification. Aliquots (20 μl) of each prepared sample were injected into a 150 mm × 4.6 mm column (Varian C18-A, USA) and analyzed by HPLC with fluorescence detection. The fluorescence conditions were fixed at an excitation wavelength of 281 nm and an emission wavelength of 388 nm. Urinary 1-OHP concentrations were adjusted according to creatinine levels and expressed as μg/g creatinine.

2.8. Data analysis

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 conducted to evaluate differences in 1-OHP levels between the workers using different face masks. Because BaPeq is a better indicator than total

PAH level for characterizing the carcinogenic potency of PAHs [20,21,26,27], BaPeq was used in the present study. BaPeq are calculated base on the PAH levels multiply toxic equivalent factor for each PAH congeners. The Spearmen correlation and multivariate regression models were utilized to analyze the correlation between 1-OHP levels and particulate/vapour phase PAHs after adjusting for age, and for workers wearing different types of face masks.

3. Results

3.1. Urine 1-OHP concentration and face mask

The highest 1-OHP level was found in workers who used a cotton-fabric face mask (1.19 μg/g creatinine) and an activated-carbon face mask (1.16 μg/g creatinine) (Table 2), compared to lower levels in workers wore a R95 face mask (0.27 μg/g creatinine) and a N95 respirator (0.51 μg/g creatinine). This work further categorized all workers into two groups: Workers who wore a cotton-fabric and activated-carbon face mask, with low filtration rate (activated-carbon face mask < 46.8%) [28]; and workers who wore a R95 face mask and a N95, with higher 95% filtration rate based on Chein et al. [29]. Table 3 shows 1-OHP levels of 1.29 μg/g creatinine in workers who wore face masks with low filtration rate, and 0.47 μg/g creatinine in those who wore face masks with above 95% filtration rate. We further compared 1-OHP levels between workers who wore two types of face masks in their work departments. For moulding and sand shake workers, the obvious lower 1-OHP levels were found in workers who wore face masks with above 95% filtration rate (Fig. 1).

3.2. Concentrations of air vapour/particulate phase PAHs

The average PAH level inside foundry was 77.59 μg/m^3. When we looked at the vapour/particulate phase PAHs, the vapour PAH level was 57.64 μg/m^3. Meanwhile, the vapour phase PAHs was 74.29% of total PAH levels (Table 4). For BaPeq levels, the average BaPeq level was 23.63 ng/m^3. When we looked at the vapour/particulate phase BaPeq levels, the vapour BaPeq level was 16.52 ng/m^3. Although the total BaPeq levels of particulate phase and gaseous phase were almost equal between the two industries, the five ring PAHs contributed the most toxicity to BaPeq levels, including BaP and DBA.

Table 3
The distribution of urine 1-OHP concentrations dependent on their filtrated efficiency.

Removal rate (%)	Sample size	1-OHP (μg/g creatinine)	P value
Low: <46.8%[a]	15	1.29 ± 1.55	0.043[*]
High: 95%[b]	6	0.47 ± 0.36	

Note: Tested by Wilcoxon rank sum test.

[a] Consist of activated-carbon face mask and cotton-fabric face mask [28].
[b] Consist of face mask R95 and N95 respirator [29].
[*] $P < 0.05$.

Table 4
Average air concentrations of 16 gaseous and particulate PAHs and BaPeq.

PAHs	PAHs concentrations ($\mu g/m^3$) $N = 22$				PAH BaPeq concentrations (ng/m^3) $N = 22$			
	Particle	Gas	Total	Gas%	Particle	Gas	Total	Gas%
Nap	0.36 (0.32)	10.17 (12.86)	10.53 (12.81)	96.62	<0.001	0.01 (0.01)	0.01 (0.01)	96.62
AcPy	0.57 (0.59)	1.38 (0.59)	1.96 (0.86)	70.70	<0.001	<0.001	<0.001	70.70
Acp	0.03 (0.10)	0.27 (0.45)	0.30 (0.46)	90.70	<0.001	<0.001	<0.001	90.70
Flu	0.17 (0.28)	0.66 (0. 93)	0.83 (0. 93)	79.39	<0.001	<0.001	<0.001	79.39
PA	0.34 (0.43)	1.54 (1.66)	1.88 (1.66)	81.72	<0.001	<0.001	<0.001	81.72
Ant	0.33 (0.30)	2.48 (2.71)	2.81 (2.60)	88.32	<0.001	0.02 (0.03)	0.03 (0.03)	88.32
FL	1.29 (0.80)	3.75 (3.52)	5.05 (3.55)	74.36	<0.001	<0.001	0.01	74.36
Pyr	0.28 (0.46)	1.06 (1.37)	1.33 (1.42)	79.23	<0.001	<0.001	<0.001	79.23
BaA	0.29 (0.46)	0.75 (0.88)	1.04 (0.96)	71.79	0.03 (0.05)	0.07 (0.09)	0.10 (0.10)	71.79
CHR	0.31 (0.47)	0.39 (0.75)	0.70 (0.78)	55.34	<0.001	<0.001	0.01 (0.01)	55.34
BbF	2.64 (3.40)	5.33 (3.01)	8.17 (4.90)	67.71	0.26 (0.34)	0.55 (0.30)	0.82 (0.49)	67.71
BkF	3.37 (5.85)	6.09 (3.26)	9.45 (6.96)	64.38	0.34 (0.59)	0.61 (0.33)	0.95 (0.70)	64.38
BaP	4.32 (7.59)	7.09 (4.28)	11.41 (9.14)	62.15	4.32 (7.59)	7.09 (4.28)	11.41 (9.14)	62.15
IND	1.79 (1.27)	3.96 (2.19)	5.76 (2.33)	68.83	0.18 (0.13)	0.40 (0.22)	0.58 (0.23)	68.83
DBA	1.96 (1.35)	7.70 (6.29)	9.66 (6.48)	79.67	1.96 (1.35)	7.70 (6.29)	9.66 (6.48)	79.67
Bghip	1.89 (1.74)	4.82 (4.33)	0.71 (4.74)	71.80	0.02 (0.02)	0.05 (0.04)	0.07 (0.05)	71.80
Total	19.95 (20.03)	57.64 (33.79)	77.59 (44.80)	74.29	7.12 (9.27)	16.52 (9.65)	23.63 (15.27)	69.90

Note: The standard deviation is shown inside parenthesis.

Table 5
Occupational matrix.

Air concentrations	Working years	Protective equipments usage

According to the personal air sampling of PAHs[a,b]
Module: 79.8 ± 42.6
Shakeout: 50.4 ± 28.7
Furnace: 101.8 ± 22.7
Melting: 113.3 ± 89.0
Administration: 55.1 ± 22.6
Air PAH concentrations of BaPeq (ng/m^3)[a,c]
Module: 22.3 ± 11.3
Shakeout: 17.3 ± 12.7
Furnace: 26.3 ± 10.1
Melting: 38.9 ± 33.0
Administration: 18.8 ± 19.0
	According to a Questionnaire of Working year per workers
	a. Mean (Standard deviation): 12.07 ± 9.36
	b. Range: 2–40 year
		a. Dust masks (R95), APF[d] = 9.09, score: 1;
		b. N95, APF = 6.67, score: 2;
		c. Actived-carbon mask, APF = 4, score: 3;
		d. Fabric-cotton mask, APF = 2.5, score: 4;
		e. Without wearing protective masks, score: 5

Note: Occupational matrix = air concentration × working years × protective equipments usage.

[a] Mean ± standard deviation.
[b] Air PAH concentrations ($\mu g/m^3$).
[c] Air PAH concentrations of BaPeq (ng/m^3).
[d] Assigned Protection Factor, APF = [1/(face polyhedral leak rate + filter leak rate)]; scores were 1–5 based on APF (CNS 14755 Z2125 in Taiwan).

3.3. Vapour/particulate phase PAHs and face masks

To further evaluate whether the association between urine 1-OHP levels and vapour or particulate phase PAHs was affected by workers who wore face masks, the influence factors were integrated into an occupational matrix, including air concentrations of PAHs, working years and protective equipments used (Table 5). The higher PAH levels were found in the melting area (113.3 $\mu g/m^3$), furnace area (101.8 $\mu g/m^3$), and in module area (79.8 $\mu g/m^3$); as well as the higher BaPeq level were in the melting area (38.9 ng/m^3), and the furnace for melting iron (26.3 ng/m^3). Tables 6 and 7 show that the significant correlation for 1-OHP levels and the occupational matrix multiply by vapour PAH ($P < 0.05$), and a correlation was also found for vapour Bapeq level. The positive association between 1-OHP levels and vapour Bapeq levels was confirmed by multivariate regression analysis, after adjusting for age, face masks used, and particulate phase Bapeq levels. In contrast, no significant difference was found between 1-OHP levels and particulate phase Bapeq levels.

4. Discussion

4.1. Face mask for removing PAHs

To evaluate the removal efficiency of respirators used by foundry workers, the concentration data inside the face piece showed that dust-fume-mist class half-face piece respirators used conscientiously by foundry workers and in conjunction with other environmental control devices inside the foundries provide

Table 6
The association between exposure matrix and 1-OHP levels of the PAH exposure workers (sample size = 22).

	PAHs			BaPeq		
	Particulate,[a] r	Vapour,[a] r	Total,[a] r	Particulate,[a] r	Vapour,[a] r	Total,[a] r
1-OHP	−0.08	0.46*	0.33	−0.12	0.44	0.32
P value	0.740	0.041*	0.158	0.600	0.050*	0.167

[a] Particulate phase PAHs levels to multiply working years and protective equipment usage.
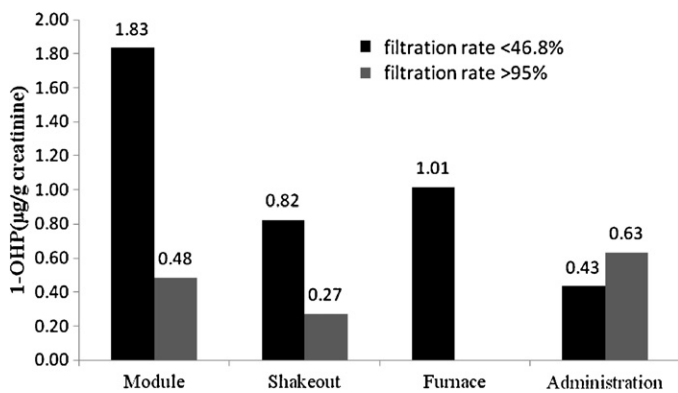* $P < 0.05$, Tested by spearman correlation.

Fig. 1. The distribution of urine 1-OHP concentration of the workers using alternative face masks in different working departments.

effective protection for zinc, lead, and silicon exposure [30]. However, no study has conducted system evaluation for personal respirators used by foundry worker to avoid PAHs exposure.

Previous studies have shown that the increasing excretion of 1-OHP is associated with environmental exposure to PAHs and air particles [31], and 1-OHP levels seem to have a good correlation ($r^2 = 0.77$) with airborne Bapeq levels from samples of workers not using respiratory protection [32]. However, a poor correlation ($r^2 \leq 0.1$) was found between levels of airborne Bapeq and urinary 1-OHP in end-of-shift samples without considering personal protective equipment and occupational hygiene practice [32]. The present study has shown a good correlation between vapour phase PAHs and urinary 1-OHP levels, but not for particulate PAHs while adjusted for wearing protective respirators. The differences of the relationship between 1-OHP levels and vapour phase, particulate PAHs are probably due to workers using protective respirators and those only remove part of particulate phase PAHs. However, for vapour phase PAH, the limited removal of PAHs will be expected for the personal protective equipments they used because of 74% (15/21) workers who using activated-carbon face mask and cotton-fabric face mask. According to mask performance testing, the two masks were recognized as low removing efficiency <46.8%, which implied that about 50% of the ambient particles would penetrate through the face-seal leakage of the masks [28]. Only 25% of particulate phase PAHs to total PAHs in this kind of work, and the removal of vapour phase PAHs haven't been evaluated. Therefore, the percentage of vapour/particulate phase PAHs is important in discussing a PAH prevention strategy.

4.2. Particulate/vapour phase PAHs

A study from Omland et al. of iron foundry workers showed that the average concentration of 16 PAHs is 10.40 μg/m^3 in the breathing zone, and the average dust-adsorbed PAH concentration is only 0.15 μg/m^3, which demonstrated that the most predominant PAHs are in the vapour phase [33]. Though in the current study, there was only 25% of particulate phase PAHs to total PAHs in this kind of work, in our previous finding in foundry working environments, the vapour PAHs contributed over 90% to total PAHs in manufacturing areas [9], and Knecht et al. [8] showed that vapour PAHs contributed 77% to total PAH load at the workplace in an iron foundry, which was identical to the present study showed the vapour phase contributed to 85.6% and 77.7% of total PAHs in melting and moduling areas (data not shown). Tsapakis and Stephanou [34] suggested that the change in ambient temperature may cause a shift in the vapour/particulate distribution of PAHs, especially in melting areas. Meanwhile, the pouring process is a short-term process in moulding areas, and then the moulds cool down after the pouring is completed. Therefore, the vapour phase PAH in furnace and moulding processes was abundant in the current study. Due to high temperature in the foundry environment, especially for metal melting and liquid metal pouring processes, it is difficult for foundry workers to wear uncomfortable face masks during their workday. The vapour PAHs in Styrofoam used for manufacturing giant moulds in the foundry industry would be more abundant compared to other foundry industries using silica sand [9]. Thus, the distribution of PAH levels in the vapour/particulate phase is important for evaluating the prevention strategy of occupational PAH exposure in this context.

Shimmo et al. [35] indicated that the proportion of vapour PAHs varied for each PAH, and PAHs with fewer rings were exclusively abundant in the vapour phase. In particles less than 2.5 μm in diameter (PM$_{2.5}$), the PAHs with aromatic rings (five- and six-ring) were predominantly in the particulate phase, and three- and four-ring PAHs existed both in the vapour and particulate phases due to vaporization losses, depending on the specific compound and environmental conditions [10]. The highest total PAH level was found in particulates with 0.5 μm aerodynamic diameter or less, and Py, CH, BbF, BaP, and BghiP contributed 76% of total PAH content in <0.25 μm fraction in steelworks [36]. The presences of extrinsic-particulates are within the ultrafine particulate range and it seems difficulty for removing the particulate and vapour phase PAHs simultaneously by wearing the personal protective equipments.

Caux et al. [37] found that firefighters exposed to higher PAH exposure than the environmental background, even if they used protective equipment. A face mask with a high protective level still cannot block all PAH penetration; therefore, how to choose an appropriate face mask to filtrate the particulate phase PAH or to absorb the vapour PAHs is important for PAH exposure prevention. Respiratory protection is a complex field involving several factors, including respirator filter material, face piece fitting and maintenance, storage, and reuse of respirator [38]. In the present study, most workers near the furnace and pouring areas wore a cotton-fabric face mask, N95 and active-carbon face mask, in addition to the restricted removal efficiency of particulates PAHs for these face masks, the major problem for each face mask might be how to remove vapour phase PAHs because the large proportion of vapour phase in this study areas (Tables 4, 6 and 7). Future studies need to consider developing an appropriate and comfortable face masks with high removal efficiency for both ultrafine particulates and vapour phase PAHs.

5. Conclusion

The present study found significantly lower 1-OHP levels in workers who wore face masks with above 95% filtration rate, compared to others with low filtration rate. The urinary 1-OHP in end-of-shift samples correlated to the airborne vapour Bapeq, but not to the particulate phase Bapeq in the foundry and in plastic

Table 7
The associations between vapour/particulate phase PAH exposure, face masks and age ($R^2 = 0.657$, P value = 0.006).

Dependent variables	Independent variables	β	P value
1-OHP	Intercept	0.901	0.002[*]
	Age	−9.740	0.002[*]
	Removal efficiency[a] [A]	−0.395	0.578
	Removal efficiency[a] [B]	−0.023	0.960
	Particulate Bapeq	−0.554	0.100
	Vapour Bapeq	0.505	0.021[*]

[a] Removal efficiency (A: >95% vs. non-face mask; B: <46.8% vs. non-face mask).
[*] $P < 0.05$.

industries. This might be due to workers who wore personal protective equipments and those who only removed particulate phase PAHs. Together with our previous report, these data indicate a high proportion of vapour PAHs components presents in the foundry and plastic environment. How to use an appropriate face masks to remove vapour phase PAHs and particulates simultaneously will be important to further studies.

Acknowledgement

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