

1 (Revised MS: HAZMAT-D-07-02616)

2  
3 **Characterization of PAHs exposure in workplace atmospheres of a sinter plant and**  
4 **health-risk assessment for sintering workers**

5  
6 **Yuan-Chung Lin<sup>1,2,3</sup>, Wen-Jhy Lee<sup>3,4</sup>, Shui-Jen Chen<sup>4,5</sup>,**

7 **Guo-Ping Chang-Chien<sup>1,2</sup>, Perng-Jy Tsai<sup>4,6\*</sup>**

8  
9 <sup>1</sup> Department of Chemical and Materials Engineering, Cheng Shiu University,  
10 Kaohsiung County 833, Taiwan.

11 <sup>2</sup> Super Micro Mass Research & Technology Center, Cheng Shiu University,  
12 Kaohsiung County 833, Taiwan.

13 <sup>3</sup> Department of Environmental Engineering, National Cheng Kung University.  
14 1, University Road, Tainan 70101, Taiwan

15 <sup>4</sup> Sustainable Environment Research Center, National Cheng Kung University. 1,  
16 University Road, Tainan 70101, Taiwan.

17 <sup>5</sup> Department of Environmental Science and Engineering, National Pingtung University of  
18 Science and Technology. 1, Shieh-Fu Rd, Nei Pu, Pingtung 91201, Taiwan,

19 <sup>6</sup> Department of Environmental and Occupational Health, Medical College, National Cheng  
20 Kung University. 138, Sheng-Li Road, Tainan 70428, Taiwan.

21  
22  
23  
24 **\*Correspondence author:** Perng-Jy Tsai. Department of Environmental and Occupational  
25 Health, Medical College, National Cheng Kung University. 138, Sheng-Li Road, Tainan  
26 704, Taiwan. Tel.: +886-6-2088390; Fax: +886-6-2752484; E-mail address:  
27 [pjtsai@mail.ncku.edu.tw](mailto:pjtsai@mail.ncku.edu.tw) (P.-J., Tsai)

28 **Abstract**

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

44 **Keywords:** Polycyclic aromatic hydrocarbons, Sinter plant, Process fugitives, Exposure  
45                   assessment, Health risk assessment

46 **1. Introduction**

47 It is known that several polycyclic aromatic hydrocarbons (PAHs) are mutagenic  
48 and/or carcinogenic in rodents, and some of them are human potential carcinogens [1].  
49 PAHs can be generated from many human activities, such as industrial production,  
50 transportation, and waste incineration. In principle, the mechanisms associated with the  
51 generation and/or depletion of PAHs in the high-temperature combustion process followed  
52 three major pathways, including pyrosynthesis [2], direct emission of unburned fuel [3],  
53 and thermal destruction of fuel components [4]. For iron and steel industries, PAHs are  
54 released from coke manufacturing, sintering, iron making, casting, molding, cooling, and  
55 steel making processes [5]. PAHs emitted from iron and steel industries has been  
56 recognized as the second major source in Norway (accounting for 12% of the yearly total  
57 PAH emission) [6]. Intensive studies have been conducted to investigate PAH emissions  
58 from the stacks of various manufacturing processes in iron and steel industries [7].  
59 However, measurements of process fugitive PAH concentrations in workplace atmospheres  
60 have been focused mainly on coke ovens [8–11]. To the best of our knowledge, PAHs  
61 concentrations in sinter plant workplaces and their resultant health-risk impact on sintering  
62 workers have never been reported.

63 To assess health risks associated with PAH exposures, it is important to know the total  
64 carcinogenic potency arising from the exposures of various PAH compounds. In principle,  
65 the carcinogenic potency of a given PAH compound can be assessed according to its  
66 benzo[a]pyrene equivalent concentration ( $BaP_{eq}$ ). Calculating the  $BaP_{eq}$  concentration for a  
67 given PAH compound requires the use of its toxic equivalent factor (TEF; using  
68 benzo[a]pyrene as a reference compound) to adjust its original concentration [12-14].  
69 Among the available TEFs lists, the one established by Nisbet and LaGoy in 1992 has been  
70 demonstrated to best reflect the actual state of knowledge of the toxic potency of each

71 individual PAH species [14]. By using the TEF list the carcinogenic potency of total PAHs  
72 (total BaP<sub>eq</sub>) can be determined as the sum of BaP<sub>eq</sub> concentrations of the 21 selected PAH  
73 compounds.

74 For estimating the lung cancer risk associated with inhalatory PAH exposures, the  
75 World Health Organization (WHO) has suggested a unit risk of  $8.7 \times 10^{-2} (\mu\text{g m}^{-3})^{-1}$  for the  
76 lifetime (=70 years) PAH exposure, assuming one was exposed to BaP concentration of 1  
77  $\mu\text{g m}^{-3}$  [15]. It is worth noting that the above unit risk was proposed for lifetime exposure,  
78 therefore, it has been adopted for assessing the exposure of general adults to the ambient  
79 atmospheric PAHs [16]. For occupational exposure, Pott established a relationship between  
80 BaP exposure and lung cancer risk [17], based on a data bank provided by an  
81 epidemiological study conducted by Redmond et al. [18]. He suggested the unit risk of  $7.0$   
82  $\times 10^{-2} (\mu\text{g m}^{-3})^{-1}$  for a 25-year occupational PAHs exposure with the averaged BaP  
83 concentration of  $1 \mu\text{g m}^{-3}$ . By using the same data bank, the US Environmental Protection  
84 Administration [19], however, suggested a different unit risk of  $6.4 \times 10^{-4} (\mu\text{g m}^{-3})^{-1}$  for  
85 PAHs exposure based on its total PAH content (expressed as the benzene soluble fractions).  
86 Since a recent study has indicated BaP could be a better indicator than total PAH content  
87 on characterizing the carcinogenic potency of PAHs [20], the unit risk suggested by Pott in  
88 1985 has been used in our previous study [21].

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

## 94 **2. Materials and Methods**

### 95 ***2.1. The selected sintering process***

96 One sinter plant located in southern Taiwan, with a selective catalytic reduction (SCR)  
97 air pollution control device, was selected in this study. For the selected sintering process, it  
98 first involves the mixing of iron ore fines, iron-bearing recovery materials (such as  
99 iron-bearing dusts and slag), and fluxes (lime or dolomite) with a ~5 % finely divided fuel,  
100 such as coke breeze or anthracite. The mixture is then placed on a traveling grate to form a  
101 sintering bed. The traveling grate resembles an endless loop of a conveyor belt, forming a  
102 shallow trough with small holes in the bottom. The bed is ignited by passing under an  
103 ignition burner which is fired with natural gas and air. During the ignition process, the air is  
104 pulled down through the bed as the grate moves slowly toward the discharge end. As the  
105 coke fines burn in the bed, the generated heat sinters/or fuses the fine particles. The  
106 temperature of the bed is around 1,300 to 1,500 °C. Mean production rates are 20 to 40  
107 metric tons m<sup>-2</sup> d<sup>-1</sup> depending upon the characteristics of the ore materials and the sintering  
108 conditions [22]. Typical operation conditions for the sintering process have been described  
109 in more details elsewhere [23-24]. For sinter plant workers, they are required to perform  
110 their work tasks at the nearby of the raw materials inlet, sintering grate, rough roll shredder,  
111 and control room.

112

## 113 ***2.2. Sampling strategy and worker's time/activity pattern***

114 Three sampling sites located approximately 2 m away from the raw materials inlet (Site  
115 #1), sintering grate (Site #2), and rough roll shredder (Site #3) were selected to characterize  
116 PAH concentrations in the sintering workplaces of the selected sinter plant. For the selected  
117 sinter plant, the air introduced to the control room (located at the end of the sintering grate)  
118 was directly drawn from the workplace atmosphere of the sinter plant but was filtered by an  
119 air conditioner. Static air samplings were also conducted in the control room (Site #4) in  
120 order to characterize fugitives transferring from the sintering zone to the control room. The

121 location of the above sampling sites in the selected sintering plant are shown in Figure 1.  
122 Field samplings were also conducted on the outdoor environment located at the upwind side  
123 of the selected sinter plant (Site #5) for comparisons. All air samples were collected by using  
124 a high-volume PS-1 sampler (Greaseby Anderson, GA). This sampler was equipped with a  
125 quartz-fibre filter to collect PAHs of the particle phase, and followed by a XAD-16  
126 cartridge for collecting PAHs of the gas phase. To avoid effluent stream from PS-1 dilute  
127 the total suspended particle (TSP) and PAH concentration in control room, the effluent gas  
128 from PS-1 sampler was discharged to the outside of the control room. The sampling flow  
129 rate was specified at  $\sim 0.18 \text{ m}^3 \text{ min}^{-1}$ . Each sample was collected continuously for  $\sim 24$  hrs  
130 (i.e., sampling volume =  $\sim 250 \text{ m}^3$ ).

131 The time/activity patterns of the four selected groups sintering workers were recorded  
132 based on our field observation (Table 1). Group A (i.e., raw material charging workers) on  
133 average stayed at Site #1 (raw materials inlet) and Site #4 (control room) for 1.67 hr and  
134 6.33 hr, accounting for 20.8% and 79.2% of their total work time (8hr), respectively.  
135 Group B (i.e., sintering grate workers) on average stayed at Site #2 (sintering grate) and  
136 Site #4 for 2.5 hr and 5.5 hr, accounting for 31.2% and 68.8% of their total work time,  
137 respectively. Group C (i.e., shredding workers) on average stayed in Site #3 (rough roll  
138 shredder) and Site #4 for 3.0 hr and 5.0 hr, accounting for 37.5% and 62.5% of their total  
139 work time, respectively. Group D (i.e., sintering process engineers and supervisors) on  
140 average stayed in Site #1, Site # 2, Site #3 and Site #4 for 1.33, 1.33, 1.33 and 4.0 hr,  
141 accounting for 16.7%, 16.7%, 16.7% and 50.0% of their total work time, respectively.

142

### 143 **2.3. PAH analysis**

144 For PAH analysis, each collected sample (including particulate and gaseous PAH  
145 samples) was extracted in a Soxhlet extractor with a mixed solvent (n-hexane and

146 dichloromethane; vol/vol, 1:1; 500 mL each) for 24 hrs. The extract was then concentrated  
147 by nitrogen (N<sub>2</sub>), cleaned up by sodium sulfate and re-concentrated to exactly 1.0 mL by N<sub>2</sub>.  
148 PAH contents were determined using a Hewlett-Packard (HP) gas chromatograph (GC) (HP  
149 6890N; Hewlett-Packard, Wilmington, DE, USA) with a mass selective detector (MSD)  
150 (HP 5973) and a computer workstation (Aspire C500; Acer, Taipei, Taiwan). This GC/MSD  
151 was equipped with a capillary column (HP Ultra 2, 50 m x 0.32 mm x 0.17 μm) and an auto  
152 sampler (HP-7683). It was operated under the following conditions; injection volume of 1  
153 μL, splitless injection at 310°C, an ion source temperature of 310°C, an oven from 50  
154 to 100°C at 20°C min<sup>-1</sup>; from 100 to 290°C at 3°C min<sup>-1</sup>; and held at 290°C for 40 min. The  
155 masses of primary and secondary ions of PAHs were determined in scan mode using pure  
156 PAH standards. PAHs were qualified in the selected ion monitoring (SIM) mode [25-29].

157 The PAH homologues grouped by the number of rings are naphthalene (Nap) for  
158 2-ring, acenaphthylene (AcPy), acenaphthene (Acp), fluorine (Flu), phenanthrene (PA), and  
159 anthracene (Ant) for 3-ring, fluoranthene (FL), pyrene (Pyr), benzo[a]anthracene (BaA),  
160 and chrysene (CHR) for 4-ring, cyclopenta[c,d]pyrene (CYC), benzo[b]fluoranthene (BbF),  
161 benzo[k]fluoranthene (BkF), benzo[e]pyrene (BeP), benzo(a)pyrene (BaP), perylene (PER),  
162 dibenzo[a,h]anthracene (DBA), benzo[b]chrysene (BbC) for 5-ring,  
163 indeno[1,2,3,-cd]pyrene (IND), benzo[ghi]perylene (Bghip) for 6-ring, and coronene (COR)  
164 for 7-ring. The GC/MSD was calibrated with a diluted standard solution of 16 PAH  
165 compounds (PAH mixture-610M; Supelco, Bellefonte, PA, USA) plus five additional  
166 individual PAHs obtained from Merck (Darmstadt, Germany). Ten consecutive injections  
167 of a PAH 610-M standard yielded an average relative standard deviation of the integrated  
168 GC/MSD area of 8.02 % (range = 5.45 % to 10.33 %).

169 In this study, two internal standards (phenanthrene-d10 and perylene-d12) were used  
170 to check their response factors, the recovery efficiencies for PAHs analysis and to

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

184

#### 185 ***2.4. Data analysis***

186 In this study, the total-PAH concentration represents the sum of the concentrations of  
187 21 PAH compounds for each collected sample. PAHs were grouped into three categories  
188 based on their molecular weights, including low molecular weight PAHs (LMW-PAHs,  
189 containing two- and three-ringed PAHs), middle molecular weight PAHs (MMW-PAHs,  
190 containing four-ringed PAHs), and high molecular weight PAHs (HMW-PAHs, containing  
191 five- to seven-ringed PAHs).

192 In this study, the carcinogenic potencies associated with PAH emissions to each  
193 workplace atmosphere were also determined. Here, the carcinogenic potency of a given  
194 PAH compound was assessed according to its benzo[a]pyrene equivalent concentration (i.e.,  
195 BaP<sub>eq</sub>) by using the TEFs list established by Nisbet and LaGoy in 1992 [14]. The



196 carcinogenic potency of total PAHs (i.e., total BaP<sub>eq</sub>) was determined as the sum of BaP<sub>eq</sub>  
197 concentrations of the 21 selected PAH compounds. To assess workers' excessive lung  
198 cancer risks associated with a 25-yr occupational exposure, the unit risk suggested by Pott  
199 in 1985 ( $=7 \times 10^{-5}$  (BaP<sub>eq</sub> ng m<sup>-3</sup>)<sup>-1</sup>) was used in the present study [17]. This is mainly  
200 because BaP is a better indicator than total PAH content on characterizing the carcinogenic  
201 potency of PAHs [20].

202 All measured and estimated concentrations were presented in their means  $\pm$  standard  
203 deviation ( $\pm$ SD). Statistical significance was examined by using the *t*-test.

### 204 **3. Results and Discussion**

#### 205 ***3.1. TSP concentrations in sintering workplaces and the outdoor environment***

206 Table 2 shows the mean total suspended particle (TSP) concentrations of the four  
207 selected workplaces and the outdoor environment of the selected sinter plant. For the four  
208 selected workplaces, the highest TSP was found at Site #1 ( $=2690 \mu\text{g Nm}^{-3}$ ), which was  
209 considered due to dust emissions from the raw material charging process. The second and  
210 third highest TSP were found at Site #2 and Site #3 ( $=2130$  and  $1600 \mu\text{g Nm}^{-3}$ ,  
211 respectively), but their concentrations were much lower than that of Site #1 ( $p < 0.05$ ). This  
212 might be because the strong airflow was pulled down through the sintering bed resulting in  
213 less fugitive TSP emitted into the sintering zone. TSP concentrations in Site #1, Site #2 and  
214 Site #3 were 18.4, 14.6 and 10.9 times in magnitude higher than that in Site #4 ( $=146 \mu\text{g}$   
215  $\text{Nm}^{-3}$ ) ( $p < 0.05$ ). This might be explained either by the location of the control room being  
216 far away from the sintering process, or by the filtration efficiency (TSP reduction fraction  
217  $>95\%$ ) of the air conditioning device used in the control room. The permissible TSP  
218 concentration in workplace environment in Taiwan is  $10,000 \mu\text{g Nm}^{-3}$ , which was  
219 significantly higher than that of Site #1–Site #4 ( $p < 0.05$ ). Nevertheless, it should be noted  
220 that the concentrations found in Site #1–Site #3 were still higher than that of the outdoor

221 environment (i.e., Site #5 =143  $\mu\text{g Nm}^{-3}$ ) ( $p<0.05$ ). The above result suggests that TSP  
222 concentrations found in the sintering process areas were mainly contributed by the process  
223 fugitives, rather than those transported from the outdoor environment.

224

### 225 ***3.2. Characterization of PAH concentrations in sintering workplaces and the outdoor*** 226 ***environment***

227 Table 3 shows the mean PAH concentrations (gas- + particle-phase) of the four  
228 selected workplaces and the outdoor environment of the sinter plant. For the mean total  
229 PAH concentrations, we found that Site #2 (30.4  $\mu\text{g Nm}^{-3}$ ) was significantly higher than  
230 that of Site #1 (17.9  $\mu\text{g Nm}^{-3}$ ) and Site #3 (16.3  $\mu\text{g Nm}^{-3}$ ) ( $p<0.05$ ), which was considered  
231 due to molten process in the furnace. The concentrations found in the above three selected  
232 sintering zone workplaces were significantly higher than that of the Site #4 (8.37  $\mu\text{g Nm}^{-3}$ )  
233 ( $p<0.05$ ). The relatively low total PAH concentrations found in the Site #4 (i.e., control  
234 room) could be explained again either by its location being far away from the sintering  
235 zone, or the filtration effect of the air conditioning device used in the control room.  
236 Moreover, we also found that the PAH concentrations obtained from the sintering zones  
237 (Site #1–Site #3 =16.3– 30.4  $\mu\text{g Nm}^{-3}$ ) were much higher than that of outdoor environment  
238 (Site #5 = 7.42 $\mu\text{g Nm}^{-3}$ ) ( $p<0.05$ ). The above results further confirmed that PAHs found in  
239 the workplace atmospheres could be mainly contributed by sintering process fugitives,  
240 rather than that transported from the outdoor environment.

241 Regarding the measured total BaP<sub>eq</sub> concentrations (i.e., gas- + particle-phase), the  
242 concentration found in the Site #2 (0.16  $\mu\text{g Nm}^{-3}$ ) was higher than those found in Site #1  
243 and Site #3 (0.12 and 0.13  $\mu\text{g Nm}^{-3}$ , respectively) ( $p<0.05$ ). The pattern was similar to that  
244 found in the corresponding total PAH concentrations, since the above three selected  
245 sampling sites shared with similar PAH homologue distributions. Finally, total BaP<sub>eq</sub>

246 concentrations found in sintering zone workplaces (i.e., Site #1, Site #2, and Site #3) were  
247 much higher than that of the Site #4 ( $0.040 \mu\text{g Nm}^{-3}$ ) ( $p < 0.05$ ). The above results suggest  
248 that the isolation of the control room and the ventilation measures had a useful impact on  
249 PAHs exposure profile, especially by lowering the concentrations of carcinogenic species.

250 Table 3 also shows the PAH homologue distributions of the 5 selected sampling sites.  
251 We found the fractions of LMW-, MMW-, and HMW-PAHs in total-PAHs were quite  
252 similar among Site #1 (86.5%, 9.52%, and 4.01%, respectively), Site #2 (86.7%, 9.60%,  
253 and 3.71%, respectively), and Site #3 (86.3%, 8.53%, and 5.16%, respectively). The above  
254 results again suggests PAHs found in the sintering zone were of the same nature (i.e.,  
255 emitted from the sintering process with a similar coagulation effect due to their low  
256 concentrations). On the other hand, a very different pattern was found in Site #4 (91.4%,  
257 6.09%, and 2.51%, respectively). Less fractions in both MMW- and HMW-PAHs found in  
258 Site #4 could be because less particle-phase PAHs were found in the control room,  
259 considering both MMW- and HMW-PAHs were mainly presented in particle-phase due to  
260 their low volatile characteristics. Finally, a very different pattern was found in the outdoor  
261 environment (79.5%, 16.4%, and 4.18%, respectively) further confirmed our previous  
262 inference: PAHs found in the workplace atmospheres were mainly contributed by process  
263 fugitives, rather than those transported from the outdoor environment.

### 264 ***3.3 Gas- and particle-phase PAHs containing in total PAH and total BaP<sub>eq</sub>*** 265 ***concentrations in the workplace atmospheres***

266 Table 4 shows gas- and particle-phase PAHs containing in total PAH and total BaP<sub>eq</sub>  
267 concentrations for samples collected from the workplace atmosphere of the selected sinter  
268 plant. For total PAH, concentrations of the gas-phase PAHs ( $8.33\text{-}30.1 \mu\text{g Nm}^{-3}$ , accounting  
269 for 98.3%-99.5% total PAHs) were consistently higher than that of particle-phase  
270 ( $0.042\text{-}0.365 \mu\text{g Nm}^{-3}$ , accounting for 0.5%-1.7% total PAHs) for any given studied

271 workplaces ( $p < 0.05$ ). The above results can be explained by total PAHs were dominated by  
272 LMW-PAHs (Table 3). For total BaP<sub>eq</sub>, concentrations of the gas-phase (0.037-0.121  $\mu\text{g}$   
273  $\text{Nm}^{-3}$ ) were also higher than that of particle-phase (0.003-0.039  $\mu\text{g}$   $\text{Nm}^{-3}$ ) for any given  
274 studied workplaces ( $p < 0.05$ ). However, particle-phase PAHs had more contribution to total  
275 BaP<sub>eq</sub> (8.1-24.1%) than to total PAHs (0.5%-1.7%). The above results can be explained by  
276 total PAHs were dominated by LMW-PAHs which are known with low TEFs (Table 3).

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

#### 284 **3.4. Health-risk assessment for sintering workers exposed to PAHs**

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

$$287 C_{\text{ave}} = (C_i \times T_i) / \Sigma T_i$$

288 Where,  $C_{\text{ave}}$  was the worker's time-weighted average exposure to total PAHs (denoted as  
289 total PAHs<sub>ave</sub>) and total BaP<sub>eq</sub> (denoted as total BaP<sub>eq,ave</sub>);  $C_i$  was the worker's exposure  
290 concentration to total PAHs at the  $i^{\text{th}}$  site (i.e., total PAHs <sub>$i$</sub> , see Table 3) and to total BaP<sub>eq</sub>  
291 at the  $i^{\text{th}}$  site (i.e., total BaP<sub>eq, $i$</sub> , see Table 2);  $T_i$  was the time of the given worker spent at  
292 the  $i^{\text{th}}$  site (see Table 1); and  $\Sigma T_i$  was the time for the given worker spent at all involved  
293 work sites.

294 Table 5 shows total PAHs<sub>ave</sub> and total BaP<sub>eq,ave</sub>, and their corresponding gas-phase  
295 and particle-phase concentrations. In addition, the estimated lung cancer risks for the four

296 selected exposure groups based on their total BaP<sub>ave</sub> and the corresponding gas-phase and  
297 particle-phase concentrations were also presented in Table 5. For total PAH<sub>s<sub>ave</sub></sub>, its  
298 corresponding gas-phase concentration (=82.3–121 ng m<sup>-3</sup>) was consistently higher than  
299 that of particle phase (=0.685–23.3 ng m<sup>-3</sup>) (*p*<0.05). Particularly, all selected exposure  
300 groups were found with total PAH<sub>s<sub>ave</sub></sub> (=83.0–122 ng m<sup>-3</sup>) significantly lower than the  
301 current permissible exposure limit regulated in Taiwan for PAHs (=200,000 ng/m<sup>3</sup>)  
302 (*p*<0.05). The above results suggest that PAH exposures to sintering workers might not be  
303 particularly significant. In this study, the unit risk suggested by Pott in 1985 (=7×10<sup>-5</sup>  
304 (BaP<sub>eq</sub> ng m<sup>-3</sup>)<sup>-1</sup>) was used to assess workers' any excess of risk for lung cancer associated  
305 with a 25-yr occupational exposure [17]. We found that the total BaP<sub>ave</sub> fell to the range of  
306 0.454–0.705 ng m<sup>-3</sup>. The corresponding gas-phase concentration (=0.450–0.614 ng m<sup>-3</sup>)  
307 was significantly higher than that of particle-phase (=0.004–0.137 ng m<sup>-3</sup>) (*p*<0.05)  
308 suggesting that the former had a more contribution on worker's lung cancer risk. However,  
309 by taking both gas- and particle-phase together (i.e., total BaP<sub>ave</sub>), the resultant lung cancer  
310 risks (=3.18×10<sup>-5</sup>–4.98×10<sup>-5</sup>) were consistently lower than the significant risk level (=10<sup>-3</sup>)  
311 which was defined by the US Supreme Court [30]. The above results further confirm that  
312 PAH exposures to sintering workers might be acceptable at this stage.

313

#### 314 **4. Conclusions**

315 The present paper shows that both TSP and total PAH concentrations of the three  
316 selected sintering process areas were higher than that of the control room. The above results  
317 could be explained by the filtration efficiency of the air conditioning device installed inside  
318 the control room. PAH homologue distributions of the three selected sintering process areas  
319 were significantly different from that of the outdoor environment suggesting that PAHs  
320 found in the sintering workplace atmospheres were mainly contributed by process fugitives.

321 Total PAH exposure levels in the selected areas of the sintering plant were lower than the  
322 current permissible exposure limits, thus suggesting that sintering workers are usually  
323 exposed to quite low PAH concentrations. Consistently, our risk estimate for the lung  
324 cancer risks associated with the above PAH exposures gave lower values as compared to  
325 the significant risk level defined by US Supreme Court.

326

327 **Acknowledgments:** This research was supported in part by the Institute of Occupational  
328 Safety and Health (IOSH) of the Council of Labor Affairs in Taiwan. Mr. H.C. Hou and  
329 Miss UnSam Ha, Department of Environmental Engineering, National Cheng Kung  
330 University, are appreciated for assisting in the laboratory work.

331

### 332 **References**

- 333 [1] Internal Agency for Research on Cancer, IARC monographs on evaluation of  
334 carcinogenic risks to humans, overall evaluation of carcinogenicity: An updating of  
335 monographs. IARC Monogr. Eval. Carcinog. Risk Chem. Hum., Lyon, 1-42(1987)  
336 1-440. <http://monographs.iarc.fr>
- 337 [2] A. Bjørseth, Handbook of polycyclic aromatic hydrocarbons, vol. 1. Marcel Dekker,  
338 New York, 1983.
- 339 [3] P.T. Williams, M.K. Abbass, G.E. Andrews, Diesel particulate emission: the role of  
340 unburned fuel, *Combustion Flame* 75(1989) 1-24.
- 341 [4] P.J. Tancell, M.M. Rhead, R.D. Pemberton, J. Braven, Survival of polycyclic  
342 aromatic hydrocarbons during diesel combustion, *Environ. Sci. Technol.* 29(1995)  
343 2871-2876.
- 344 [5] D. Nelson, P.A. Scheff, C. Keil, Characterization of volatile organic compounds  
345 contained in coke plant emissions. In: The 84th Annual meeting & Exhibition of Air

- 346 & Waste Manage. Assoc., Vancouver, BC, vol. 6. pp. 79–91, 1991.
- 347 <http://www.awma.org> or Keil email: ckeil@bgnet.bgsu.edu
- 348 [6] A. Bjorseth, T. Ramdahl, Sources and emissions of PAH. In: Emission Sources and  
349 Recent Progress in Analytical Chemistry Handbook of Polycyclic Aromatic  
350 Hydrocarbons, vol. 2. Marcel Dekker, New York and Barcel, 1985.
- 351 [7] H.-H Yang, S.-O. Lai, L.-T. Hsieh, H.-J. Hsueh, T.-W. Chi, Profiles of PAH  
352 emission from steel and iron industries, Chemosphere 48(2002) 1061-1074.
- 353 [8] W.L. Lloyd, Long-term study of steelworkers-respiratory cancer in coke plant  
354 workers. J. Occup. Med. 13(1971) 53–68.
- 355 [9] E.S. Gibson, R.H. Martin, J.N. Lockington, Lung cancer mortality in a steel foundry.  
356 J. Occup. Med. 19(1977) 807–812.
- 357 [10] N.R. Khalili, P.A. Scheff, T.M. Holsen, PAH source fingerprints for coke ovens,  
358 diesel and gasoline engines, highway tunnels, and wood combustion emissions. Atm.  
359 Environ. 29(1995) 533-542.
- 360 [11] L. Pyy, M. Mäkelä, E. Hakala, K. Kakko, T. Lapinlampi, A. Lisko, E. Yrjänheikki,  
361 K. Vähäkangas, Ambient and biological monitoring of exposure to polycyclic  
362 aromatic hydrocarbons at a coking plant. Sci. Total Environ. 199(1997) 151-158.
- 363 [12] M.-M. Chu, C.-W. Chen, Evaluation and estimation of potential carcinogenic risks of  
364 polynuclear aromatic hydrocarbons; Conference Record of the 1984 Pacific Rim  
365 Risk Conference on polycyclic aromatic hydrocarbons in the workplace, Honolulu,  
366 HI, 1984.
- 367 [13] T. Thorslund, D. Farrer, Development of relative potency estimated for PAHs and  
368 hydrocarbon combustion product fractions compared to benzo(a)pyrene and their  
369 use in carcinogenic risk assessments; U.S. Environmental Protection Administration  
370 (EPA), Washington DC, 1991.

- 371 [14] C. Nisbet, P. LaGoy, Toxic equivalency factors (TEFs) for polycyclic aromatic  
372 hydrocarbons (PAHs), Reg. Tox. Pharmacol 16(1992) 290-300.
- 373 [15] WHO, Air quality guideline for Europe. WHO European Series, WHO Regional  
374 office for Europe, Copenhagen, 1987, 105-117. <http://www.euro.who.int/air>
- 375 [16] D. Zmirou, P. Masclat, C. Boudet, F. Dor, J. Dechenaux, Personal exposure to  
376 atmospheric polycyclic aromatic hydrocarbons in a general adult population and  
377 lung cancer risk assessment, J. Occup. Environ. Health 42(2000) 121-125.
- 378 [17] F. Pott, Pyrolyseagase, PAH und lungenkrebrisiko – daten und bewertung.  
379 Staub-Reinhaltung dedr Luft 45(1985) 368-379.
- 380 [18] C. Redmond, B. Strobino, R. Cypess, Cancer experience among coke by-product  
381 workers. Ann. NY Acad. Sci. 217(1976) 102-115.
- 382 [19] US EPA., Health effects assessments for polycyclic aromatic hydrocarbons (PAHs).  
383 US Environmental Protection Agency EPA, Environmental Criteria and Assessment  
384 Office, EPA 549/1-86-013, Cincinnati, OH, 1984.  
385 <http://cfpub.epa.gov/ncea/cfm/recordisplay.cfm?deid=38617>
- 386 [20] T. Petry, P. Schmid, C. Schlatter, The use of toxic equivalency factors in assessing  
387 occupational and environmental health risk associated with exposure to airborne  
388 mixtures of polycyclic aromatic hydrocarbons (PAHs), Chemosphere 32(1996)  
389 639-648.
- 390 [21] P.-J. Tsai, H.-Y. Shieh, W.-J. Lee, , S.-O. Lai, Health-risk assessment for workers  
391 exposed to polycyclic aromatic hydrocarbons (PAHs) in a carbon black  
392 manufacturing industry. Sci. Total Environ. 278(2001) 137–150.
- 393 [22] U.S. EPA, Database of sources of environmental releases of dioxin like compounds  
394 in the United States. EPA/600/C-01/012. Washington, DC: U. S. Environmental  
395 Protection Agency, 2001. <http://www.epa.gov/fedrgstr/2001-jan.htm>



- 396 [23] M.K. Cieplik, J.P. Carbonell, C. Muñoz, S. Baker, S. Krüger, P. Liljelind, S.  
397 Marklund, R. Louw, On dioxin formation in iron ore sintering,. *Environ Sci Technol*  
398 37(2003) 3323-3331.
- 399 [24] L.-C. Wang, W.-J. Lee, P.-J. Tsai, W.-S. Lee, G.-P.Chien-Chang, Emissions of  
400 polychlorinated dibenzo-p-dioxins and dibenzofurans from stack flue gases of sinter  
401 plants. *Chemosphere* 50(2003) 1123-1129.
- 402 [25] P.-J. Tsai, H.-Y. Shieh, W.-J. Lee, S.O. Lai, Characteristics of the exposure profiles  
403 for workers exposed to airborne dusts and polycyclic aromatic hydrocarbons (PAHs)  
404 in the carbon black manufacturing industry. *J Occup Health* 43(2001) 118-128.
- 405 [26] H.-H. Mi, W.-J. Lee, S.-J. Chen, T.-C. Lin, T.-L. Wu, J.-C. Hu, Effect of the Gasoline  
406 Additives on PAH Emission. *Chemosphere* 36(1998) 2031-2041.
- 407 [27] H.-H. Mi, W.-J. Lee, P.-J. Tsai, C.-B. Chen, A Comparison on the Emission of  
408 Polycyclic Aromatic Hydrocarbons and Their Corresponding Carcinogenic  
409 Potencies from a Vehicle Engine Using Leaded and Lead-Free Gasoline. *Environ*  
410 *Health Persp* 109(2001) 1285-1290.
- 411 [28] C.-T. Li, Y.-C. Lin, W.-J. Lee, P.-J. Tsai, 2003. Emission of polycyclic aromatic  
412 hydrocarbons and their carcinogenic potencies from cooking sources to the urban  
413 atmosphere. *Environ. Health Persp.* 111(2001) 483-487.
- 414 [29] Y.-C. Lin, W.-J. Lee, H.-W. Li, C.-B. Chen, G.-C. Fang, P.-J. Tsai, Impact of using  
415 fishing boat fuel with high poly-aromatic content on the emission of polycyclic  
416 aromatic hydrocarbons from the diesel engine. *Atm. Environ.* 40(2006) 1601-1609.
- 417 [30] J.V. Rodrics, S.M. Brett, G.C. Wrenn, Significant risk decisions in Federal regulatory  
418 agencies, *Regul. Toxicol. Pharmacol.* 7(1987) 307-320.

419 **Table Captions**

- 420 Table 1 Time/activity patterns for the four selected groups of workers of the Group A:  
421 raw material charging workers, Group B: sintering grate workers, Group C:  
422 shredding workers, and Group D: sintering process engineers and supervisors  
423 at the four selected workplaces inside the sinter plant of the Site #1: raw  
424 materials inlet, Site #2: sintering grate, Site #3: Rough roll shredder, and Site  
425 #4: control room
- 426 Table 2 Mean TSP concentrations ( $\pm$ SD) of the four selected workplaces inside the  
427 sinter plant of the Site #1: raw materials inlet, Site #2: sintering grate, Site  
428 #3: Rough roll shredder, and Site #4: control room, and its outdoor  
429 environment (Site #5)
- 430 Table 3 Mean PAH concentrations ( $\pm$ SD) of the four selected workplace atmospheres  
431 of the sinter plant of the Site #1: raw materials inlet, Site #2: sintering grate,  
432 Site #3: Rough roll shredder, and Site #4: control room, and its outdoor  
433 environment (Site #5)
- 434 Table 4 Mean PAH concentrations ( $\pm$ SD) of the four selected workplace atmospheres  
435 of the sinter plant of the Site #1: raw materials inlet, Site #2: sintering grate,  
436 Site #3: Rough roll shredder, and Site #4: control room, and its outdoor  
437 environment (Site #5)

438 Table 5 Time-weighted average exposure levels ( $\pm$ SD) of total PAHs<sub>ave</sub> and total  
439 BaP<sub>ave</sub> and their corresponding particle-phase and gas-phase exposure  
440 levels ( $\pm$ SD), and the resultant lung cancer risks ( $\pm$ SD) for the four selected  
441 exposure groups of the Group A: raw material charging workers, Group B:  
442 sintering grate workers, Group C: shredding workers, and Group D: sintering  
443 process engineers and supervisors

444

445 **Figure Caption**

446 Figure 1 Sampling sites in the selected sintering plant

447