



## Characterization of Endocrine Disruptors and Particulate Matter Emissions from Laser Cutting of Plastic Film in the TFT-LCD Industry

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### ABSTRACT

In the last five years laser cutting has been identified as one of the solutions for converting and shaping the plastic films used in the Thin Film Transistor Liquid Crystal Display (TFT-LCD) industry due to its positive effects on cost management. However, there has been quite limited information available with regard to the hazards of the air pollutants released during the laser cutting process, and in particular in relation to the real operations that occur in a factory. This is the first study that aims to assess the Endocrine Disruptors (EDs) and Particulate Matter (PM) emitted during the laser cutting process. Phthalate Esters (PAEs) and Polycyclic Aromatic Hydrocarbons (PAHs) are the representative EDs in this research. The results indicate that the power of the laser and type of plastic significantly affect the composition of air pollutants. Di(2-ethylhexyl) phthalate (DEHP) of PAEs was identified in the Laser Generated Air Contaminants (LGACs) from both Polycarbonate (PC) and Polyethylene Terephthalate (PET) films. DEHP was detected in the gas-phase LGACs of PC and PET at low, medium and high power (80 W, 160 W, 240 W), but not detected in the particle-phase LGACs of PC and PET, except when the laser was operated at a low power setting. With the laser power increased, the concentrations of PM and PAHs also increased. This research found that during laser cutting PC released more DEHP than PET, but PET released more PAHs than PC.

**Keywords:** Laser cutting; Phthalate esters; Polycyclic aromatic hydrocarbons; Particulate matter.

### INTRODUCTION

The Thin Film Transistor Liquid Crystal Display (TFT-LCD) industry is one of the most rapidly developing industries in the world. Between 2010 and 2015 the annual market output value of TFT-LCD products exceeded 240 millions square meters on average, and was expected to grow to a higher level in 2016. Laser cutting techniques have received considerable attention since the shape and size of TFT-LCD films evolve rapidly (Eguiazabal, 1989). Laser cutting has thus started to replace traditional die-cutting and mold-pressing to be the dominant technique for the production of optical and related plastic films (Charschan, 1972; Kuo *et al.*, 2014). Sublimation cutting involves the processes of melting, burning and evaporation of the film when high temperature laser radiation acts on its surface, resulting in disassociation. However, a large amount of Laser-generated Air Contaminants (LGACs) are produced during the film cutting process. PAEs are long-standing

plasticizers commonly used to enhance material flexibility and limpness in plastic manufacturing (Sims *et al.*, 1993; Roach *et al.*, 1995). Chemical exposure assessment of workers in plastic material related industry was studied for understanding solvent exposure as multiple organic solvent are commonly found in this industry (Chen *et al.*, 2013). Health effect of electronic plant employees have also been assessed for their occupational exposure to air contaminants by taking the samples of air-conditioner-filter dust (Chou *et al.*, 2016).

Endocrine disruptors are chemicals which people can be exposed to through inhalation, ingestion, and dermal contact. EDs may disturb the operation of endogenous hormones of organisms and thus affect their metabolism, development, and reproduction. Indoor exposure to EDs can cause negative impacts, including disruption of thyroid hormone secretion and induction of neurotoxic effects (Chao *et al.*, 2014). These compounds are fat-soluble, stable, and difficult to metabolize and they can accumulate in organisms and become developmental immunotoxicants (Fenaux, 2004). So far, there are more than 70 endocrine disruptors have been identified. They include insecticide, pesticide, industrial compounds (such as alkylphenols), plasticizer (such as phthalates esters, PAEs), PAHs, and dioxins. Previous studies have shown that some endocrine disruptors (such

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as PAEs and PAHs) are emitted during the manufacturing process in plastic-related factories and they may cause negative health effect on workers.

The PAEs are not bound to nor chemically bond to plastic products. Therefore, they are easily released to the environment by diffusion or heating (Fromme *et al.*, 2002). Because of their high stability, low volatility, and solubility in organic solvents, PAEs are widely used in industries to increase the plasticity of plastic products (Rahman *et al.*, 2004). The six common PAEs include di-n-Butyl phthalate (DBP), di-n-octyl phthalate (DNOP), di(2-ethylhexyl) phthalate (DEHP), diisononyl phthalate (DINP), diisodecyl phthalate (DIDP), and butyl benzyl phthalate (BBP) among these PAEs DEHP is the most popular (Lorz *et al.*, 2002). Major exposure routes of PAEs include ingestion and inhalation. Workers in PAEs manufacturing industries or plastic factories are mainly exposed to PAEs by air pollution (Unwin *et al.*, 2012). Animal experiments found the reproductive toxicity effects of PAEs on testis and sperm in male rats (Park *et al.*, 2002; Bao *et al.*, 2011). After long-term exposure to DEHP workers exhibited with lower quality in sperm and their sperm chromosome was affected (Huang *et al.*, 2011). In addition, effects of PAEs on kidney, liver, lung, and breast cancer were also reported (Kevy *et al.*, 1982; Rothenbacher *et al.*, 1998; Ward *et al.*, 1998; Magliozzi *et al.*, 2003; López-Carrillo *et al.*, 2010).

PAHs are mainly formed via incomplete combustion or pyrolysis of organic materials containing hydrocarbons (Grimmer *et al.*, 1983; Bjorseth *et al.*, 1985). There are 16 priority pollutant PAHs, including naphthalene, acenaphthylene, acenaphthene, fluorene, phenanthrene, anthracene, fluoranthene, pyrene, benzo[a]anthracene, benzo[b]fluoranthene, chrysene, benzo[k]fluoranthene, benzo[a]pyrene, indeno[1,2,3-cd]pyrene, dibenzo[a,h]anthracene, and benzo[g,h,i]perylene (ATSDR,

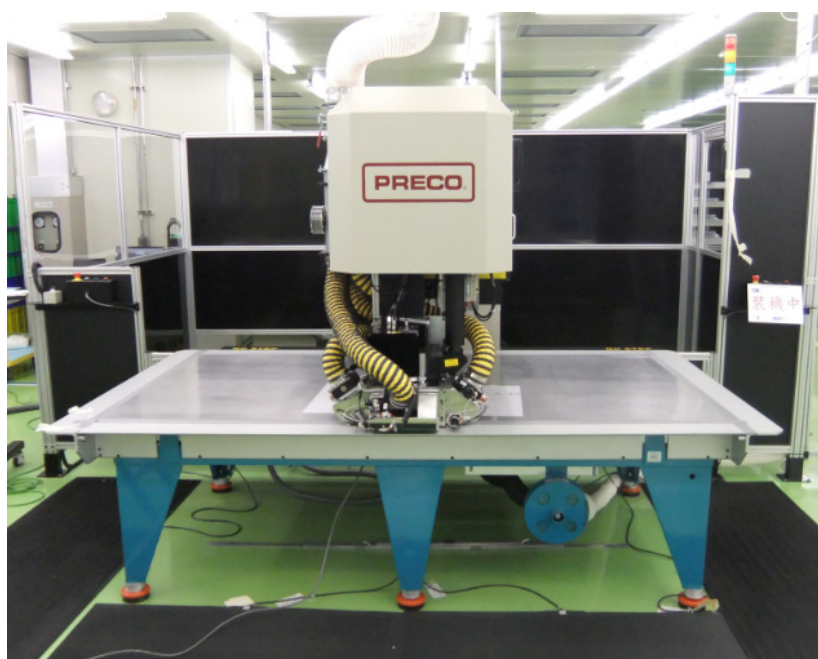
2005). Sources of PAHs include plastic factories, hospitals, automobile exhaust, and daily life (such as incense burning, cooking, or smoking) (Lee *et al.*, 1995; Slezakova *et al.*, 2009; Unwin *et al.*, 2012). Previous studies have confirmed that most PAHs are potential environmental endocrine disruptors and they are carcinogenic and/or mutagenic (Grimmer, 1983; Elovaara *et al.*, 2007; Smith *et al.*, 2007). Animal studies found that some PAHs affected the function of estrogen and were related to infertility (Kummer *et al.*, 2008; Smith *et al.*, 2007). In addition, studies have shown that the cancer incidences of general population were increased when they were exposed to PAHs (Nielsen *et al.*, 1985; Baek *et al.*, 1991). Some PAHs, such as benzo[a]anthracene, benzo[b]fluoranthene, benzo[k]fluoranthene, chrysene, dibenzo[a,h]anthracene, and indeno[1.2.3-cd]pyrene, have been classified as probable human carcinogens and benzo[a]pyrene has been classified as Group 1 (Carcinogenic to humans) (IARC, 2010).

This study is the first attempt to clarify the characteristics of endocrine disruptors (PAEs and PAHs) in the gas and particle phase emissions from laser cutting in an industrial plastic processing plant. More specifically, the scope of this particular study is to characterize the emissions of PAEs, PAHs, and PM as toxicants from various plastics at different laser power levels during the laser cutting process.

## METHODS

### *Characterization of Laser Cutter and Film Substrate*

The laser cutting process in the factory investigated in this work was carried out by a CO<sub>2</sub> type laser cutter (Fig. 1), with a maximum output power of 400 Watt (W) at a wavelength of 10.6 μm, and manufactured by PRECO (SL8600, PRECO, USA). To evaluate the characteristics of the pollutants emitted during manufacturing under various



**Fig. 1.** CO<sub>2</sub> type laser cutter.

conditions, power levels at 80 W, 160 W, and 240 W were used, and the cutting speed was 5 m min<sup>-1</sup>. The two types of plastic films chosen in this study were polycarbonate (PC) and polyethylene terephthalate (PET), which are the main materials used in the optical industry. The thickness of the films was 0.20 mm ± 10%.

### **Air Sampling**

This study assessed the exposure to PAEs and PAHs by the workers during laser cutting of plastics. Three source samples along with a field blank were collected at 10 cm above the laser cutting point at various power levels (80 W, 160 W, and 240 W) to investigate the concentrations and gas/particle-phase distributions of PAEs and PAHs during the laser cutting of PC and PET. The sampling period was 15 min for each sample as the laser cutting process is stable and consistent. For gas-phase collection, PAE and PAH were sampled at 1 L min<sup>-1</sup> flow rate by OVS-Tenax (Cat. NO. 226-56, SKC, USA) sampling tubes and XAD-2 (Cat. NO. 226-30-04, SKC, USA) sampling tubes, respectively. For particle-phase sampling, the pollutants were collected at 3 L min<sup>-1</sup> flow rate by pre-extracted glass microfiber filters (Cat. NO. 1820-037, Whatman International Ltd., UK) for PAEs and by polyfluortetraethylene (PTFE) filters (Cat. NO. 225-17-04, SKC, USA) for PAHs as the total suspended particles (TSP) sample.

### **Worker Exposure and Risk Assessment**

Three air samples along with a field blank were collected at locations from 1 m, 3 m, and 7 m away from the laser cutter to assess the exposure of neighboring workers to PAEs and PAHs emissions. Inside the clean room (class 10000) of the focal TFT-LCD factory, only one laser cutter was installed for operation and was the only source that generates air pollutants in this study. Except this laser cutter, other workstations in the building were designed for pressing, inspecting and packing process. The distance of 1 m is used to assess the risks faced by workers in charge of laser cutting of plastics, while the distances of 3 m and 7 m are used to assess them for material preparation workers and product inspection workers, respectively. The laser cutter was operated at a power of 240 W and a cutting speed of 15 m min<sup>-1</sup>. The sampling period for exposure assessment was 15 min as well.

This study conducted risk assessments of the PAEs and PAHs exposure of staff during the laser cutting of plastics. With regard to PAEs, daily intakes (DI) were first calculated, and the values were then used to evaluate the hazard index (HI). For PAHs, toxic equivalence factors were used to calculate BaP equivalents for individual PAHs, and used unit risk (UR) for BaP, as announced by the World Health Organization, to estimate lifetime cancer risks.

### **PAEs and PAHs Analysis**

With regard to the PAEs, fourteen of them were selected for investigation in the emissions of laser cutting process, including Dimethyl phthalate (DMP), Diethyl phthalate (DEP), Diisobutyl phthalate (DIBP), Di-n-butyl phthalate (DBP), Bis(2-methoxyethyl) phthalate (BMEP), Bis(4-

methyl-2-pentyl) phthalate (BMPP), Bis(2-ethoxyethyl) phthalate (DEoEP), Dipentyl phthalate (DPeP), Dihexyl phthalate (DHP), Butyl benzyl phthalate (BBP), Bis(2-n-butoxyethyl) phthalate (DBEP), Dicyclohexyl phthalate (DCHP), Bis(2-ethylhexyl) phthalate (DEHP), and Di-n-octyl phthalate (DOP). With regard to the PAHs, sixteen of them were selected for investigation in the emissions of laser cutting process, including Naphthalene (Nap), Acenaphthylene (Acpy), Acenaphthene (Acp), Fluorene (Flu), Phenanthrene (PA), Anthracene (Ant), Fluoranthene (FL), Pyrene (Pyr), Benzo[a]anthracene (BaA), Chrysene (CHR), Benzo[a]pyrene (BbF), Benzo[b]fluoranthene (BkF), Benzo[k]fluoranthene (BaP), Indeno[1,2,3-cd]pyrene (IND), Benzo[g,h,i]perylene (DBA), and DiBenzo[a,h]anthracene (BghiP).

To analyze PAEs in the particle phase, Test Method 5020 from the National Institute for Occupational Safety and Health (NIOSH) was used. A mixed solvent (1:1 acetone and dichloromethane) was used to extract the glass microfiber filters. Samples were subjected to 30 minutes ultrasonication, 20 minutes centrifugation, and concentration by nitrogen blowing. For analysis of the gaseous pollutants, four mL toluene was added to each OVS-Tenax tubes, which then underwent 30 minutes ultrasonication for extraction. Both particle-phase and gas-phase treated PAEs aliquots were then analyzed with a gas chromatography (HP GC-6890A, Agilent Technologies, USA) with mass selective detector (MSD-5973N, Agilent Technologies, USA) (GC/MSD). To analyze PAEs in the plastic films, NIEA T801.10B from the Taiwan Environmental Protection Agency (EPA) was used for dissolution test. The films were cut to 2 mm and 0.5 g of films were taken for extraction. Plastic film samples added with 5 mL tetrahydrofuran were subjected to 30 minutes ultrasonication for dissolution. Dissolved samples added with 10 mL hexane were subjected to 5 minutes ultrasonication then sent to GC/MSD for analysis. Operating conditions for analysis were as follows: 50 m 0.32 mm i.d. capillary column with film thickness of 0.17 μm (J&W Ultra 2); the flow rate of constant helium (He) carrier gas was 1.0 mL min<sup>-1</sup>; injector temperature 250°C; the GC temperature ramp employed was 100°C, 10°C min<sup>-1</sup> to 220°C, 15°C min<sup>-1</sup> to 280°C, hold 8 minutes. With regard to the PAHs analysis, Soxhlet extraction, concentrated nitrogen blowing, and silica-gel-column chromatography were conducted for the particle-phase PAHs on PTFE filters. Two mL dichloromethane was added to XAD-2 tubes which then underwent 30 minutes ultrasonication by following the NIOSH Test Method 5515. Both particle-phase and gas-phase treated PAEs aliquots were also analyzed with a GC/MSD. Operating conditions were as follows: 50 m 0.32 mm i.d. capillary column with film thickness of 0.17 μm (J&W Ultra 2); the flow rate of constant He carrier gas was 1.0 mL min<sup>-1</sup>; injector temperature 300°C; the GC temperature ramp employed was 50°C, 20°C min<sup>-1</sup> to 100°C, 3°C min<sup>-1</sup> to 290°C, hold 20 minutes.

Breakthrough experiments indicate that the breakthrough for all collected particle phase and gas phase samples were below 5%. The method detection limit (MDL) was also conducted for 14 PAEs and 16 PAHs. The MDLs were

between 0.0018 and 0.0067  $\mu\text{g mL}^{-1}$ , and between 0.0027 and 0.0070  $\mu\text{g mL}^{-1}$ , for PAEs and PAHs respectively. The mean recoveries of these PAEs and PAHs were respectively 91.8% and 92.1% for products in the particle phase, and 94.3% and 94.9% in the gas phase.

## RESULTS AND DISCUSSION

### PAEs Emissions

In this study, among the 14 PAEs, only DEHP was detected in the collected samples. This indicates that DEHP might be the prominent plasticizer added in the optical functioned plastic films. DEHP is a common and cheap additive with a high compatibility and stability to the products (Lorz *et al.*, 2002), and often be a trade secret addition disclosed in the Safety Data Sheet (SDS). Fig. 2 shows the DEHP concentrations in the gas and particle phases during the laser cutting process under different laser powers. The total concentrations of DEHP were not significantly different under various laser powers for both PC and PET. They were 115.2  $\mu\text{g m}^{-3}$ , 111.2  $\mu\text{g m}^{-3}$ , and 108.7  $\mu\text{g m}^{-3}$  of DEHP under 80 W, 160 W, and 240 W for PC, and were 84.2  $\mu\text{g m}^{-3}$ , 86.2  $\mu\text{g m}^{-3}$ , and 87.8  $\mu\text{g m}^{-3}$  of DEHP under 80 W, 160 W, and 240 W for PET. Similar concentrations of DEHP found in the airborne emissions under different laser powers can be attributed to the fixed amount of DEHP added into the plastic films based on producers' confidential manufacturing formula, which was completely released upon heating. This study then conducted a dissolution test for plastic films to investigate the original additive in the subjects. The dissolution test result also indicates the DEHP was the only identified plasticizers among the 14 PAEs. Significantly higher total DEHP concentrations emitted from PC than PET because the original DEHP concentration was higher in PC, based on the dissolution test result (PC: 9.48  $\mu\text{g g}^{-1}$ ; PET: 6.73  $\mu\text{g g}^{-1}$ ). In addition, DEHP was

only detected in the gas phase under different laser powers for PET. For PC, DEHP was detected in both gas and particle phases under 80 W of laser power (74.3  $\mu\text{g m}^{-3}$  and 40.9  $\mu\text{g m}^{-3}$ , respectively). At 160 W and 240 W DEHP was found only in the gas phase. This is because added plasticizer, DEHP, was vaporized by the heated high temperature of material surface and soon collected in the OVS-Tenax. PET, which has a lower specific heat and higher absorption efficiency of the laser energy, would thus result in a temperature higher than PC under the same power of laser.

### PAHs Emissions

Table 1 shows that the concentrations of total gas-phase PAHs detected from PC under laser powers of 80 W, 160 W, and 240 W were 125  $\mu\text{g m}^{-3}$ , 172  $\mu\text{g m}^{-3}$ , and 256  $\mu\text{g m}^{-3}$ , respectively. Notice that one 5-ring (BaP) and three 6-ring (IND, DBA, and BghiP) PAHs were not detected. As for the particle phase, the concentrations of total PAHs emitted from PC under laser powers of 80 W, 160 W, and 240 W were 43.81  $\mu\text{g m}^{-3}$ , 52.09  $\mu\text{g m}^{-3}$ , and 61.35  $\mu\text{g m}^{-3}$ , respectively. For PET under laser powers of 80 W, 160 W, and 240 W, the concentrations of gas-phase PAHs were 138  $\mu\text{g m}^{-3}$ , 201  $\mu\text{g m}^{-3}$ , and 285  $\mu\text{g m}^{-3}$ , respectively, and the concentrations of particle-phase PAHs were 63.03  $\mu\text{g m}^{-3}$ , 72.59  $\mu\text{g m}^{-3}$ , and 87.15  $\mu\text{g m}^{-3}$ , respectively (Table 1). For both PC and PET, all PAHs concentrations of gas-phase, particle-phase, and total PAHs increased along with the laser cutting power. In addition, more total PAHs were emitted from PET than those from PC under the same laser power, because laser cutting of PET generates higher temperatures. Previous studies have found that heating at higher temperatures is correlated with a greater concentration of PAHs emitted (Liu *et al.*, 2001; Singh *et al.*, 2007), which is a result of higher energy supply attributed to the incomplete burning at high temperatures (Durlak *et al.*, 1998).

The present study further classified the 16 PAHs by the

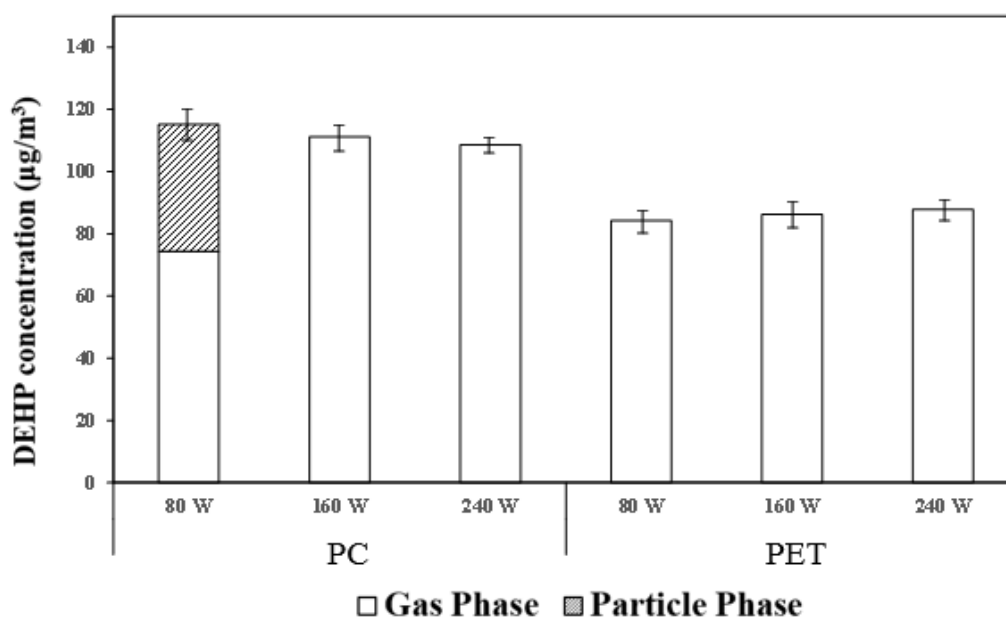


Fig. 2. DEHP emissions from plastic cutting with various laser powers.

**Table 1.** PAHs emissions from cutting PC and PET with various laser powers.

PAHs	Rings	PC						PET					
		80 W		160 W		240 W		80 W		160 W		240 W	
		g-phase	p-phase	g-phase	p-phase	g-phase	p-phase	g-phase	p-phase	g-phase	p-phase	g-phase	p-phase
Nap	2-ring	50.98	0.2	69.77	0.17	107.7	0.15	55.86	0.24	81.3	0.2	117.6	0.15
Acpy	3-ring	15.04	0.62	23.44	0.54	36.39	0.42	17.56	0.63	24.93	0.6	38.4	0.54
Acp		17.88	0.27	28.32	0.25	45.17	0.23	11	0.24	22.77	0.19	39.18	0.17
Flu	4-ring	10.37	0.19	14.3	0.17	23.94	0.15	12.73	0.59	21.64	0.51	30.92	0.47
PA		8.53	4.8	11.26	5.75	14.39	6.33	9.79	5.76	15.4	6.87	20.47	8.58
Ant		3.7	5.63	4.55	6.38	5.28	7.17	3.73	4.09	3.83	5.28	4.55	6.42
FL		7.26	5.01	7.85	5.52	9.07	6.43	8.86	3.57	10.29	4.3	11.18	5.03
Pyr	5-ring	4.82	9.83	5.24	12.53	5.82	14.3	8.81	11.85	10.94	13.43	11.14	16.29
BaA		3.68	8.52	4.31	10.17	4.96	12.34	5.85	11.56	5.94	12.93	6.41	15.59
CHR		2.25	5.27	2.7	6.27	3.05	8.11	2.53	17.34	2.93	20.09	3.65	22.63
BbF		0.32	1.54	0.34	1.98	0.36	2.78	0.31	3.55	0.37	3.94	0.4	4.39
BkF	6-ring	0.19	1.27	0.21	1.57	0.24	1.82	0.147	1.21	0.2	1.36	0.205	1.92
BaP		N.D.	0.67	N.D.	0.8	N.D.	1.11	0.186	1.38	0.24	1.83	0.308	2.5
IND		N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	0.075	0.43	0.081	0.68	0.086	1.17
DBA		N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	0.039	0.32	0.042	0.43	0.046	0.86
BghiP		N.D.	N.D.	N.D.	N.D.	N.D.	0.057	0.27	0.059	0.32	0.06	0.43	
ΣPAHs		125	43.81	172.3	52.09	256.4	61.35	137.6	63.03	201	72.95	284.6	87.15
tPAH		168.8		224.4		317.8		200.6		274		371.8	

Note: g-phase: gaseous phase PAHs; p-phase: particulate phase PAHs.

ring numbers, and found that the total concentrations of each ring number of PAHs increased with increase laser power when cutting either PC or PET (Table 1). Among the 16 PAHs, the increases in the concentrations of low-molecular-weight PAHs (2- and 3-ring) were significantly higher than those of medium- (4-ring) and high-molecular-weight PAHs (5- and 6-ringed). This trend is similar to those observed in previous studies (Grimmer, 1983; Lange *et al.*, 2007). For PC, the highest ratio of gas phase/total concentration (about 99.9%) was found in 2-ring PAHs (such as NaP) when the laser power was 240 W, and the highest ratio of particle phase/total concentration (about 90.5%) was found in 5-ring PAHs (such as BbF, BkF, and BaP) under 240 W laser power. For PET, the highest ratio of gas phase/total concentration (99.9%) was also found in 2-ring PAHs with a laser power of 240 W, and the highest ratio of particle phase/total concentration (92.8%) was found in 6-ring PAHs under 240 W laser power. In addition, the distributions of the gas and particle phases for each ring of PAHs were similar in both PC and PET when the same laser power was used. The gas phase was dominated by the 2- and 3-ring PAHs, while the particle phase was dominated by the 5- and 6-ring PAHs. This is due to the fact that low-molecular-weight PAHs (2- and 3- ringed), being more volatile, favors the partition in the gas phase, while the less volatile 4-ringed PAHs would partition in both the gas and particle phases (Grosjean, 1983).

Finally, being practically, non-volatile, the partition of high-molecular-weight PAHs (5- and 6-ring) were mainly in the particle phase, which can also be accounted by the high gravel settling effect of particle surface (Li *et al.*, 2000). In accordance, this study also found that high-molecular-weight PAHs were mainly found in the particle phase emitted under various laser powers (Table 1). In addition, both

proportions of the low-molecular-weight PAHs in the gas phase and the high-molecular-weight PAHs in particle phase increased with raised laser power. Previous studies also found similar outcome that both the proportion of gas/particle phase for low and high-molecular-weight PAHs are affected by temperature.

#### Worker PAEs Exposure Assessment

When the PC film was cut at 240 W, the concentrations of gas-phase DEHP at distances of 1 m, 3 m, and 7 m among from the laser cutter were  $70.6 \mu\text{g m}^{-3}$ ,  $40.2 \mu\text{g m}^{-3}$ , and  $6.1 \mu\text{g m}^{-3}$ , respectively, while for the particle-phase DEHP concentrations were respectively  $26.7 \mu\text{g m}^{-3}$ ,  $17.0 \mu\text{g m}^{-3}$ , and  $2.8 \mu\text{g m}^{-3}$ . For PET, DEHP concentration in the gas-phase were  $55.1 \mu\text{g m}^{-3}$ ,  $30.7 \mu\text{g m}^{-3}$ , and  $5.0 \mu\text{g m}^{-3}$  at the distances of 1 m, 3 m, and 7 m, respectively, while the results for particle-phase DEHP were  $20.6 \mu\text{g m}^{-3}$ ,  $12.4 \mu\text{g m}^{-3}$ , and  $2.2 \mu\text{g m}^{-3}$  (Fig. 3). These results show that all gas-phase, particle-phase, and total DEHP concentrations decreased with increased distance from the laser cutter, which was due to the effects of transmission, dilution, and diffusion (Adamczewska *et al.*, 2000). This study also found that, at the same distance the concentration of DEHP was higher from PC than that from PET. Again, this is because PC film contains more DEHP than PET.

The results of this study show that when cutting PC and PET films with laser, the worker (at a distance of 1 m) were exposed to total DEHP of  $97.3 \mu\text{g m}^{-3}$  and  $75.6 \mu\text{g m}^{-3}$ , respectively, while the neighboring workers at 3 m and 7 m were exposed to  $57.2 \mu\text{g m}^{-3}$  and  $43.1 \mu\text{g m}^{-3}$ , for PC, and  $8.9 \mu\text{g m}^{-3}$  and  $7.2 \mu\text{g m}^{-3}$  of total DEHP, respectively. Compared to the high-exposure group in this study, i.e., the laser operators, previous works reported either significantly higher or lower concentrations of DEHP exposure

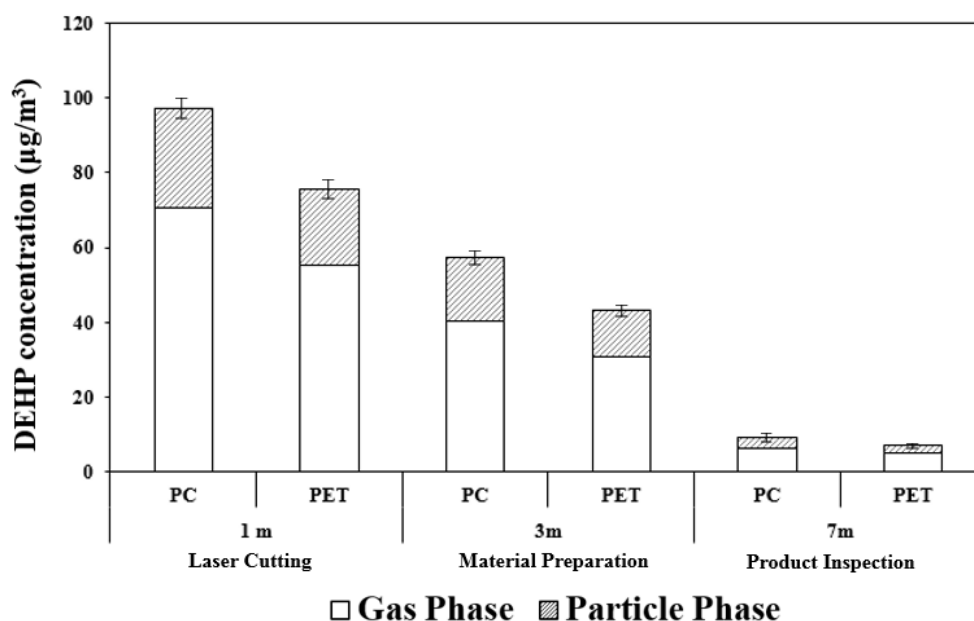


Fig. 3. DEHP emissions from cutting plastics at various distances.

(Vainiotalo *et al.*, 1990; Huang *et al.*, 2013). This might be because, to begin with, their plastics contained either longer or less amount of PAEs.

The results of this study also show that the ratios of gas-phase/total DEHP at the distances of 1 m, 3 m, and 7 m from the laser cutting equipment were 73%, 70%, and 69%, respectively, when cutting PC; and 73%, 71%, and 69%, respectively, when cutting PET. As the distance from the laser cutting equipment increased, so the ratio of gas-phase/total DEHP decreased, while the ratio of particle-phase/total DEHP increased. Different from the study result found in the source sampling (10 cm from the laser cutting point), DEHP can be detected in the both gas phase and particle phase under different laser powers. The reason for this might be the high temperature gas-phase DEHP formed by laser cutting were condensing and attaching to the surface of the particles in the air (Van Vaecck *et al.*, 1984).

#### Worker PAHs exposure assessment

With 240 W laser cutting of PC, and at distances of 1 m, 3 m, and 7 m from the laser cutting equipment, the measured concentrations of total gas-phase PAHs were  $157.0 \mu\text{g m}^{-3}$ ,  $73.64 \mu\text{g m}^{-3}$ , and  $10.68 \mu\text{g m}^{-3}$ , respectively, while for the total particle-phase PAHs the results were  $44.51 \mu\text{g m}^{-3}$ ,  $19.61 \mu\text{g m}^{-3}$ , and  $3.09 \mu\text{g m}^{-3}$  (Table 2). For PET, the total gas-phase PAHs were  $164.6 \mu\text{g m}^{-3}$ ,  $74.33 \mu\text{g m}^{-3}$ , and  $10.68 \mu\text{g m}^{-3}$  distances of 1 m, 3 m, and 7 m, respectively, while the total particle-phase PAHs were  $3.81 \mu\text{g m}^{-3}$ ,  $24.65 \mu\text{g m}^{-3}$ , and  $55.04 \mu\text{g m}^{-3}$  (Table 2). The results thus showed that the gas-phase, particle-phase, and total PAHs concentrations all decreased as the distance from the laser cutting equipment increased, as also seen with DEHP (Table 2). This trend coincides with a previous study reported by Adamczewska *et al.*, (2000). Moreover, the total PAHs concentrations emitted by PET cutting were higher than those by PC cutting at the same distances from the laser

cutting equipment. This might be attributed to the fact that higher temperature were observed during laser cutting of PET than those of PC, as previous studies have found that the heating temperature is related to the concentrations of emitted PAHs (Mastral *et al.*, 1995; Liu *et al.*, 2001).

In a previous study only some PAHs were found during laser cutting (Hietanen *et al.*, 1992). However, in this study 16 PAHs were observed. This is because the higher laser cutting power used in the earlier study resulted in temperatures high enough to completely burn and mitigate some of the PAHs (Durlak *et al.*, 1998). In addition, a previous study found that the numbers and concentrations of PAHs formed by laser cutting are higher than those formed by thermal fusion welding for plastics (Sims *et al.*, 1993). These results also imply higher exposure risk for workers conducting laser cutting of plastics.

The current study found that for both PC and PET the total concentrations of PAHs with the same ring number decreased as the distance from the laser cutting equipment increased (Fig. 4). At the same distance from the laser cutting equipment, we observed the 2- and 3-ring PAHs mainly in the gas phase and 5- and 6-ring PAHs principally in the particle phase. This is because that low-molecular-weight PAHs (2- and 3-ring) are more volatile and they have lower boiling points, and accordingly they exist mainly in the gas phase.

#### Worker Risk Assessment

The permissible exposure limit-time weighted average (PEL-TWA) of DEHP in the workplace is  $5 \text{ mg m}^{-3}$ , according to regulations published by the Ministry of Labor in Taiwan, as well as OSHA. The American Conference of Industrial Hygienists (ACGIH) sets the threshold limit value-time weighted average (TLV-TWA) at  $5 \text{ mg m}^{-3}$ , and the threshold limit value-short term exposure limit (TLV-STEL) at  $10 \text{ mg m}^{-3}$ . In this study, the concentrations

**Table 2.** PAHs emissions from PC and PET cutting at various distances.

PAHs	Rings	PC						PET					
		1 m		3 m		7 m		1 m		3 m		7 m	
		Laser Cutting	Material Preparation	Product Inspection	Laser Cutting	Material Preparation	Product Inspection	Laser Cutting	Material Preparation	Product Inspection	Laser Cutting	Material Preparation	Product Inspection
	g-phase	p-phase	g-phase	p-phase	g-phase	p-phase	g-phase	p-phase	g-phase	p-phase	g-phase	p-phase	
Nap	2-ring	65.98	0.14	31.5	0.06	5.02	0.01	71.59	0.14	30.87	0.07	4.3	0.01
Acpy	3-ring	23.75	0.4	10.43	0.16	1.44	0.03	24.2	0.45	10.58	0.21	1.65	0.04
Acp		28.6	0.22	13.55	0.09	1.89	N.D.	21.64	0.17	9.63	0.07	1.5	N.D.
Flu		14.89	0.1	7.12	0.04	1.04	N.D.	18.22	0.33	8.96	0.15	1.31	0.03
PA		7.77	4.54	3.74	2.11	0.54	0.37	11.38	5.3	5.6	2.33	0.77	0.47
Ant		2.85	5.13	1.45	2.39	0.23	0.4	2.6	4.07	1.28	1.72	0.18	0.3
FL	4-ring	5.22	4.73	2.25	2.09	0.32	0.35	2.82	3.51	1.42	1.5	0.19	0.25
Pyr		3.21	11.19	1.47	4.84	N.D.	0.8	5.92	11.63	3.09	5.47	0.42	0.88
BaA		2.79	8.65	1.2	3.6	0.19	0.61	3.64	9.21	1.69	4.06	0.24	0.65
CHR		1.66	5.49	0.79	2.37	N.D.	0.39	2	13.31	0.87	6.05	0.13	0.95
BbF	5-ring	0.19	1.96	0.09	0.92	N.D.	0.13	0.21	3.03	0.1	1.33	N.D.	0.22
BkF		0.13	1.23	0.06	0.63	N.D.	N.D.	0.1	1.33	0.09	0.57	N.D.	N.D.
BaP		N.D.	0.72	N.D.	0.3	N.D.	N.D.	0.17	1.39	0.08	0.61	N.D.	N.D.
IND	6-ring	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	0.05	0.5	0.02	0.21	N.D.	N.D.
DBA		N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	0.03	0.44	0.02	0.19	N.D.	N.D.
BghiP		N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	0.03	0.24	0.03	0.12	N.D.	N.D.
ΣPAHs		157	44.51	73.64	19.61	10.68	3.09	164.6	55.04	74.33	24.65	10.68	3.81
tPAH		201.5		93.25		13.77		219.6		98.98		14.49	

Note: g-phase: gaseous phase PAHs; p-phase: particulate phase PAHs.

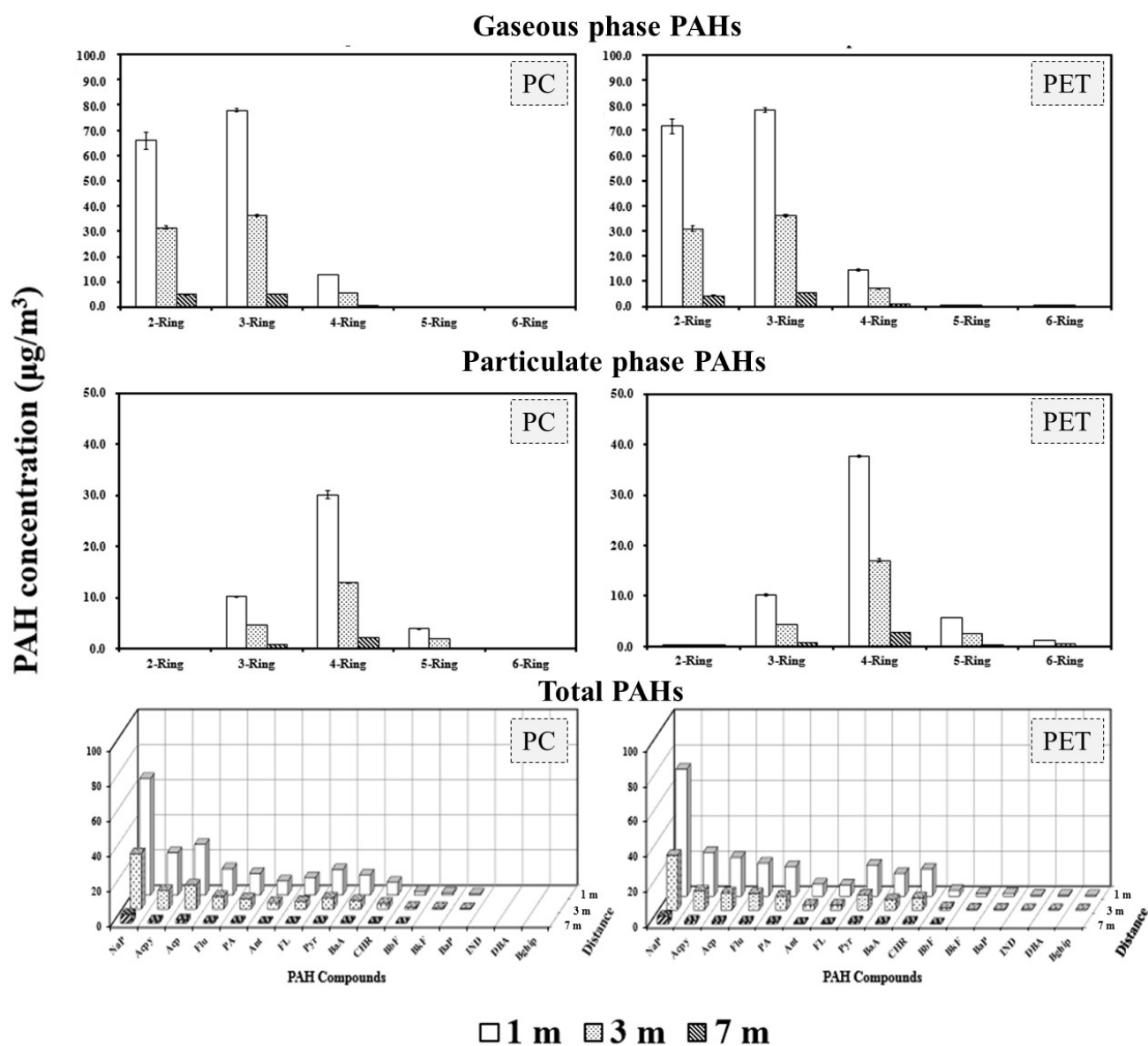


Fig. 4. PAHs emissions from plastic cutting at various distances.

of DEHP collected with 15 minutes sampling during laser cutting of PC or PET were all lower than the standard of TLV-STEL ( $10 \text{ mg m}^{-3}$ ) set by ACGIH (Fig. 3). These low concentrations may be due to the low content of DEHP in the plastics used in the focal TFT-LCD factory. TLV are health-based values and established by committees that review existing published and peer-reviewed literature in various scientific disciplines which focus on the inhalation exposure. Thus the DEHP exposure for workers shall still be regulated and the effective exposure controls and proper protections are recommended for airborne pollution (Chen *et al.*, 2015) since DEHP are widely added in articles for daily use that can enter to the human body by different routes of exposures in daily life. We further calculated the daily intake (DI) of DEHP for workers, and the workers' values of inhalation rate (IR) and body weight (BW) in the formula were obtained from the general population data provided by the Ministry of Health and Welfare (MOHW)

in Taiwan. The values of IR were  $12.7 \text{ m}^3 \text{ day}^{-1}$  and  $8.62 \text{ m}^3 \text{ day}^{-1}$  for male and female workers, respectively. Also the respective BWs used were 70.4 kg and 58.1 kg (MOHW, 2008). Table 3 shows that all estimated DI values of the workers observed in this study were below the tolerance dose of DEHP recommended by the US Consumer Product Safety Commission (CPSC). The DI values of males were found to be significantly higher than those of females. However, when cutting PC the DEHP DI value of  $5.85 \text{ } \mu\text{g kg}^{-1} \text{ day}^{-1}$  for male workers at 1 m from the operating laser cutter was slightly higher than  $5.8 \text{ } \mu\text{g kg}^{-1} \text{ day}^{-1}$ , the threshold level above which is believed to be harmful to male fertility under long-term exposure (CPSC, 2010). In addition, the non-carcinogenic hazard index (HI) of DEHP was calculated using the method recommended by the USEPA and the Scientific Committee on Toxicity, Ecotoxicity and the Environment (CSTEE). Although all estimated HI values of DEHP for the workers in the present study were below



1, the laser cutter operators (1 m) clearly had higher HI values of DEHP than their neighboring co-worker.

For PAHs, the OSHA regulations state that the total levels in the air should be under  $200 \mu\text{g m}^{-3}$ , and this is generally adopted as the standard for total PAH concentrations in indoor workplaces. This study found that, the exposure levels of total PAHs for workers operating the laser cutter exceeded the above regulated value, while exposure levels for other workers were below (Table 2). The toxicity equivalence of BaP (BaPeq) for all PAHs were calculated to estimate the health risk. The formula (Lifetime lung cancer risk = BaPeq  $\times$  Unit risk (UR)) was used to calculate the risk of exposure to the PAHs from the laser cutting of plastics, in which the UR of  $8.7 \times 10^{-2} (\mu\text{g m}^{-3})^{-1}$  proposed by the WHO was applied. The results showed that the highest lung cancer risk was found for the laser cutter operators (1 m) when cutting PET ( $3.59 \times 10^{-1}$ ). Among all workers studied the lowest lung cancer risk was found for the workers 7 m from the laser equipment when cutting PC (Table 4). Since general acceptable range of cancer risk is from  $10^{-6}$  to  $10^{-4}$ , all the workers investigated in this study had estimated lifetime lung cancer risks higher than  $10^{-4}$ . This means that, unless properly protected, all workers in the neighborhood of an operating laser cutter are facing a higher risk of developing lung cancer due to the exposure of a high level of PAHs emission from the laser cutting of plastics. Thus, the proper administrative control, such as respirator masks, shall be required for laser cutting task which could achieve a practical protection efficiency higher than 90% under fully sealed conditions, stated by Zhuanglei and Maosheng (2015).

## CONCLUSIONS

During the laser cutting of plastics, some endocrine disruptors, including DEHP and PAHs, are generated. If not treated properly, these reprotoxic and carcinogenic pollutants can cause health risk when inhaled by the workers. With regard to the laser cutting plastics, the results of health-risk assessments show that the related workers face considerable danger to their exposure to harmful substances. In order to address this issue we thus suggest that employers, especially for laser cutting operators, need effective personal protection, such as masks. Also, install local exhaust ventilation units must be installed in the workplace.

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