

Estimation of PAHs dry deposition and BaP toxic equivalency factors (TEFs) study at Urban, Industry Park and rural sampling sites in central Taiwan, Taichung

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Abstract

The concentrations of polycyclic aromatic hydrocarbons (PAHs) in gas phase and particle bound were measured simultaneously at industrial (INDUSTRY), urban (URBAN), and rural areas (RURAL) in Taichung, Taiwan. And the PAH concentrations, size distributions, estimated PAHs dry deposition fluxes and health risk study of PAHs in the ambient air of central Taiwan were discussed in this study. Total PAH concentrations at INDUSTRY, URBAN, and RURAL sampling sites were found to be 1650 ± 1240 , 1220 ± 520 , and 831 ± 427 ng/m³, respectively. The results indicated that PAH concentrations were higher at INDUSTRY and URBAN sampling sites than the RURAL sampling sites because of the more industrial processes, traffic exhausts and human activities. The estimation dry deposition and size distribution of PAHs were also studied. The results indicated that the estimated dry deposition fluxes of total PAHs were 58.5, 48.8, and 38.6 $\mu\text{g}/\text{m}^2/\text{day}$ at INDUSTRY, URBAN, and RURAL, respectively. The BaP equivalency results indicated that the health risk of gas phase PAHs were higher than the particle phase at three sampling sites of central Taiwan. However, compared with the BaP equivalency results to other studies conducted in factory, this study indicated the health risk of PAHs was acceptable in the ambient air of central Taiwan.

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1. Introduction

Dry deposition is an important pathway for the transfer of PAHs from air to land and water. Interest in atmospheric deposition has increased over the past decade due to concerns about the effects of the deposited material entering the environment and their further

health effect. The dry deposition can be measured by a smooth plate with a sharp leading edge that is point into the wind by a wind vane. Its collection surface was patterned after those used in wind tunnel studies, because this provided minimum air flow disruption and thus provides as estimation of the lower limit for dry deposition flux (Holsen et al., 1991). However, Sehmel (1980) and Noll and Fang (1989) developed mathematical model of particle deposition velocities for atmospheric particles. These models had already been applied in several studies (Sheu et al., 1997; Fang et al., 1999) for successful prediction of dry deposition flux for atmospheric particles.

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PAHs are formed during incomplete combustion or pyrolysis of organic material and in connection with the worldwide use of oil, gas, coal, and wood in energy production. Additional contributions to ambient air levels arise from tobacco smoking, while the use of heating sources can increase PAH concentrations in indoor air (WHO, 1987). PAHs have received increased attention in recent years in air pollution studies because some of these compounds are highly carcinogenic or mutagenic. In particular, benzo[*a*]pyrene (BaP) has been identified as being highly carcinogenic. To understand the extent of human exposure to BaP and other PAHs, reliable sampling and analytical methods are necessary (USEPA, 1999). Although atmospheric PAHs are partitioned between particulate matter and gas phase, they are associated predominantly with particulate matter. These indicate that particulate PAHs are considered to be significant hazardous substances to human health through breathing. In view of this health concern, monitoring the level of particulate PAHs in urban areas has become more important (Chetwittayachan et al., 2002). The highest concentrations of atmospheric PAH can be found in the urban environment, due to the increasing vehicular traffic and the scarce dispersion of the atmospheric pollutants. The risk associated with human exposure to atmospheric PAH is highest in the cities, considering the density of population (Caricchia et al., 1999). Despite the drastic reduction of urban particulate pollution in cities resulted from the improvement of coal usage and the shift toward other fossil fuels (oil or natural gas) for domestic heating, the densification of the urban net combined with population growth and increasing importance of traffic have contributed to reinforce urban particulate pollution. Furthermore, particles produced by cars are much smaller than coal particles and found in the breathable size fraction (Manoli et al., 2002). In practice they have

provided much information on the multi-ringed heavier PAH but have left the lighter vapor-phase PAH components rather neglected. Although these lighter compounds have weaker carcinogenic/mutagenic properties, they are the most abundant in the urban atmosphere and react with other pollutants to form more toxic derivatives (Park et al., 2002).

Ambient air PAHs in gas phase and particle bound were performed at Taichung Industrial Park (INDUSTRY), downtown of the Taichung City (URBAN) and rural site of Taichung City (RURAL). And the PAH concentrations, size distributions, estimated PAHs dry deposition fluxes and health risk of PAHs in the ambient air of central Taiwan were also discussed in this study.

2. Experimental methods

2.1. Sampling program

Table 1 indicates the sampling information and meteorological conditions during the sampling period. Three sampling sites, Taichung Industrial Park (INDUSTRY), rural site (RURAL), and urban site (URBAN) were selected to characterize the PAH concentrations in ambient air in central Taiwan, for this study. INDUSTRY represents the typical large-scale multi-industry in Taiwan. INDUSTRY was developed on 580 ha of land, and there are more than 800 factories at INDUSTRY, which included chemical industry, petroleum industry, plastic industry and electronics industry, etc. The sampling site is located in roof of a pharmaceutical factory (15 m in height), which is located in center of INDUSTRY. The second sampling site was RURAL as a background site to compare with the neighbor industrial park. RURAL is located in Taichung City which is surrounding by various trees and

Table 1
Sampling information and meteorological conditions in INDUSTRY, URBAN, and RURAL sampling sites

Sampling date	Temperature (°C)	Relative humidity (%)	Wind speed (m/s)	Wind direction	Atmospheric pressure (Pa)
1–3 August 2002	33	65	1.6	NW	1003.5
13–15 August 2002	39	63	1.3	N	1004.6
19–21 August 2002	38	63	0.9	N	1007.9
25–27 September 2002	28	65	1.8	NE	1012.1
7–9 October 2002	25	54	5.2	NW	1012.3
9–11 October 2002	31	57	2.0	NNE	1014.2
28–30 October 2002	28	58	1.7	N	1013.5
1–3 November 2002	27	71	2.3	N	1013.8
4–6 November 2002	24	44	1.3	N	1020.4
4–6 December 2002	25	64	0.7	NNW	1018.1
9–11 December 2002	16	59	3.5	N	1023.8
11–13 December 2002	20	68	3.5	N	1024.3
Mean	27.8	60.9	2.2	–	1014.0
Standard deviation	6.7	7.2	1.3	–	6.8

there are about 15000 students and faculty members. Taichung Veterans General Hospital Incinerator (combustion source) and Taichung Cong Road (the main line in Taichung City) in opposite were located of Tunghai University. The sampling heights were in the range of 1–1.5 m above ground level to simulate the breathing zone. The third sampling site was URBAN which represented the downtown site of Taichung City. There are residential area and heavy traffic highway around the sampling site. Sampling height in URBAN was about 10 m on the roof of Environmental Engineering building at the campus of URBAN which was close to the heavy traffic highway. The sources of the 21 PAHs are industrial combustion exhaust such as chemical industry, petroleum industry and plastic industry for INDUSTRY site. The sources of the 21 PAHs are traffic internal combustion exhausts for the URBAN site and the sources of the 21 PAHs are transferred from industrial and traffic nearby the RURAL site.

Samples were collected using three PS-1 samplers (GPS1 PUF Sampler, General Metal Work) which can collect particle size less than 50 μm efficiently with a pump drawing air through a tissue quartz filter (2500 QAT-UP, Dimension 102 mm) and a micro-orifice uniform deposit impactor (MOUDI) which can divide airborne particles in particle size of 0.056, 0.10, 0.18, 0.32, 0.56, 1.0, 3.2, 5.6, and 18 μm for characterize particle size distribution. Aluminum filter and Quartz filter were used for MOUDI and PS-1 sampling devices, respectively. Gas phase PAHs were sampled by a glass cartridge and inside the cartridge were the filter containing a 5 cm long polyurethane foam (PUF) plug, which in turn was followed by 3 cm thick packing of Amberlite XAD-16 resin (SIGMA, nonionic polymeric adsorbent, surface area 800 m^2/g), and finally by a 2 cm long PUF plug to collect the gas phase PAHs. The glass cartridge was cleaned by solvent before using. During sample transportation and storage, the PUF plug and resin were stored in a clean jar wrapped with aluminum foil, and filters were placed in sealed CD box. Filters were weighed before and after sampling to determine the amounts of particulate collected. Before sampling, filters were baked in an oven at 450 $^{\circ}\text{C}$ for 8 h to remove organic impurity. Glass cartridges were cleaned by sequential Soxhlet extractions with distilled-deionized water, methanol, dichloromethane (DCM) and a mixture of DCM/*n*-hexane (50/50, v/v) for 24 h in turn and finally dried in a no contaminate oven at 45 $^{\circ}\text{C}$ to remove residual solvent.

2.2. PAH analysis

For PAH analysis of the samples: after final weighing, all filters and glass cartridges were separately placed in appropriate Soxhlet extractors and extracted with a DCM/*n*-hexane mixture (50/50, v/v) for 24 h. The extract

was then concentrated under a rotary evaporator, cleaned and re-concentrated with ultra-pure nitrogen to exactly 1 ml using a procedure which was described previously by Lee et al. (1995). All extracts were analyzed using a gas chromatograph/mass selective detector (GC/MSD) (Varian GC3800 with Saturn MS2000) with an GC capillary column (30 $\text{m} \times 0.25 \text{ mm} \times 0.25 \mu\text{m}$, DB-5). A computer-controlled automatic sampler (Model 8200) was used in conjunction with the GC/MS system. All injections were splitless and volume was 1 μl . Injector and transfer line temperatures were 310 and 300 $^{\circ}\text{C}$, respectively. The temperature program used was: 35 $^{\circ}\text{C}$ holds 3 min, then to 180 $^{\circ}\text{C}$ at 25 $^{\circ}\text{C}/\text{min}$ and holds 2 min, then to 200 $^{\circ}\text{C}$ at 20 $^{\circ}\text{C}/\text{min}$ and hold 2 min, then to 300 $^{\circ}\text{C}$ at 2 $^{\circ}\text{C}/\text{min}$ and hold 6.4 min, total time 70 min.

Before analyzing, the calibration curves of 21 PAHs were measured and the R^2 of the calibration curve should be larger than 0.995 for analyzing ambient air samples. Method detection limit (MDL) was determined from selected the concentration slightly higher than the lowest concentration (10 ppb) of calibration curve. Repeat this concentration for seven times to estimate the standard deviation. Then, three times of the standard deviation was determined to be the value of MDL. At least 10% of the samples were analyzed with spiking amount of PAHs for recovery test.

The concentrations of the following PAHs were quantified in this study. Individual PAHs were according to their elution orders, recoveries (r) and method detection limits (mg/l) for PAHs analysis were as followed: naphthalene (Nap, m/z 128, $r = 88\%$, 0.059 mg/l), acenaphthylene (AcPy, m/z 152, $r = 93\%$, 0.091 mg/l), acenaphthene (Acp, m/z 154, $r = 89\%$, 0.084 mg/l), fluorene (Flu, m/z 166, $r = 91\%$, 0.072 mg/l), phenanthrene (PA, m/z 178, $r = 85\%$, 0.171 mg/l), anthracene (Ant, m/z 178, $r = 94\%$, 0.095 mg/l), fluoranthene (FL, m/z 202, $r = 98\%$, 0.091 mg/l), pyrene (Pyr, m/z 202, $r = 99\%$, 0.095 mg/l), cyclopenta(*c,d*)pyrene (CYC, m/z 226, $r = 99\%$, 0.117 mg/l), benzo(*a*)anthracene (BaA, m/z 228, $r = 95\%$, 0.116 mg/l), chrysene (CHR, m/z 228, $r = 101\%$, 0.531 mg/l), benzo(*b*)fluoranthene (BbF, m/z 252, $r = 92\%$, 0.110 mg/l), benzo(*k*)fluoranthene (BkF, m/z 252, $r = 101\%$, 0.329 mg/l), benzo(*e*)pyrene (BeP, m/z 252, $r = 77\%$, 0.047 mg/l), benzo(*a*)pyrene (BaP, m/z 252, $r = 86\%$, 0.183 mg/l), perylene (PER, m/z 252, $r = 86\%$, 0.046 mg/l), indeno(1,2,3-*cd*)pyrene (IND, m/z 276, $r = 89\%$, 0.074 mg/l), dibenzo(*a,h*)anthracene (DBA, m/z 278, $r = 91\%$, 0.054 mg/l), benzo(*b*)chrycene (BbC, m/z 278, $r = 90\%$, 0.067 mg/l), benzo(*ghi*)perylene (BghiP, m/z 276, $r = 95\%$, 0.093 mg/l), and coronene (COR, m/z 300, $r = 99\%$, 0.117 mg/l).

2.3. Toxic equivalency factors

The development and establishment of toxic equivalency factors (TEFs) for PAHs listed in Table 2 could

Table 2
Proposed toxic equivalency factors (TEFs) for individual PAHs

Compound ^a	CAS-Nr.	USEPA (1984)	Nisbet and LaGoy (1992)
Nap	91-20-3	0	0.001
AcPy	208-96-8	0	0.001
Acp	83-32-9	0	0.001
Flu	86-73-7	0	0.001
PA	5801-8	0	0.001
Ant	120-12-7	0	0.01
FL	206-44-0	0	0.001
Pyr	129-00-0	0	0.001
BaA	56-55-3	1	0.1
CHR	219-01-9	1	0.01
BbF	205-99-2	1	0.1
BkF	207-08-9	1	0.1
BaP	50-32-8	1	1
IND	193-39-5	1	0.1
DBA	53-70-3	1	1
BghiP	191-24-2	0	0.01

^a Full names of compounds are indicated in the text.

help to characterize more precisely the carcinogenic properties of PAH mixtures. USEPA separated PAHs into two subclasses consisting of carcinogenic and non-carcinogenic compounds. Benzo(a)pyrene (BaP) was used as a reference compound, a TEF of 1.0 was applied to all classified carcinogenic PAHs and a TEF of zero to the noncarcinogenic PAHs (USEPA, 1984). However, the available information indicated that the other carcinogenic PAHs have lower potency than BaP and that the EPA approach therefore leads to an overestimation of the risk. After that, further TEFs were proposed by Nisbet and LaGoy (1992) completed a new list of TEFs which seems to better reflect the actual state of knowledge on the relative potency of individual PAHs (Petry et al., 1996). In this study, Nisbet and LaGoy approach will be used to evaluate the human health risk with inhalatory exposure to PAHs in Taichung City, Taiwan.

2.4. Noll and Fang model for dry deposition modeling

The deposition velocities for the atmospheric particles by the dry deposition model were obtained by the following equations (Noll and Fang, 1989):

$$V_d = V_{st} + 1.12 \times U^* \times \exp(-30.36/D_p)$$

where V_{st} is the particle settling velocity (cm/s); U^* is the friction velocity (cm/s) and D_p is the particle diameter collected by MOUDI sampler (μm).

When $D_p > 5 \mu\text{m}$

$$V_{st} = V_{T,\text{stock}}$$

$$V_{T,\text{stock}} = (\rho_p D_p^2 g) / 18\mu$$

where $V_{T,\text{stock}}$ is the terminal settling velocity (cm/s); ρ_p is the density of particles (1.0 g/cm^3); g is the gravitational constant (980 cm/s^2) and μ is the absolute viscosity of air ($\text{g/cm}\cdot\text{s}$).

When $D_p < 5 \mu\text{m}$

$$V_{st} = V_{T,\text{stock}} \times K_c$$

where

$$K_c = 1 + 2\lambda [1.257 + 0.400 \exp(-0.55D_p/\lambda)] / D_p \quad \text{and} \\ \lambda = \mu / [0.499P(8M/\pi RT)^{0.5}]$$

where K_c is the Cunningham correction; λ is the mean free path (cm); P is the absolute pressure (Pa); R is the universal gas constant ($8.314 \text{ J/g}\cdot\text{mol}\cdot\text{K}$); M is the molecular weight (g/mol) and T is the absolute temperature (K).

Two meteorological parameters that influence an atmospheric turbulence are friction velocity (U^*) and surface roughness (Z_0). The relationship between these parameters for near neutral atmospheric stability condition is:

$$U = \frac{U^*}{k} \ln \frac{Z-d}{Z_0}$$

where U is the measured mean wind speed (cm/s) at height Z ; Z is the measured height above the ground (m); k is the Von Karman's constant (0.4); d is the datum displacement (m) and Z_0 is the surface roughness height (m). The measured heights Z were 15, 3, and 10 m for INDUSTRY, RURAL, and URBAN sampling site, respectively. The averaged structure heights were about 15, 5, and 15 m for INDUSTRY, RURAL, and URBAN sampling site, respectively and the datum displacements d were about 80% of the average structure height with the values of 12, 4, and 12 m for INDUSTRY, RURAL, and URBAN sampling site, respectively. In general, the roughness height Z_0 was 1/30 of the average structure height and the values of Z_0 were 0.5, 0.17, and 0.5 m for INDUSTRY, RURAL, and URBAN sampling site, respectively. The average measured wind speeds were about 1.8, 2.1, and 0.8 m/s for INDUSTRY, RURAL, and URBAN sampling site, respectively.

Previous studies (Sheu et al., 1996; Fang et al., 1999) indicated that the dry deposition was mainly contributed by coarse particles ($>10 \mu\text{m}$) and these studies can evaluate the dry deposition successfully by using Noll rotary impactor (NRI) which can collect airborne particles with particle diameter of 6.5–100 μm . Because lack of NRI sampler, thus we used PS-1 sampler for larger particles sampling in this study. Thus, combine the particle size distribution collected by PS-1 and MOUDI samplers the size distribution become 0.056, 0.10, 0.18, 0.32, 0.56, 1.0, 1.8, 5.6, 18, and 50 μm . The meteorological

logical parameters mentioned above were used to calculate the dry deposition velocities and the results indicated that the modeled dry deposition velocities (INDUSTRY, RURAL, and URBAN) were (0.0058, 0.0058, and 0.0058 cm/s), (0.29, 0.34, and 0.18 cm/s), and (20.7, 24.5, and 11.3 cm/s) for particle sizes 0.056–5.0, 5.0–18, and 18–50 μm , respectively.

3. Results and discussion

3.1. PAH concentrations in the ambient air

Measured mean 21 individual PAH concentrations in both gas and particle phases for INDUSTRY, URBAN, and RURAL sampling sites were displaced in Table 3, respectively. The total PAHs concentration at these sampling sites were found to be 1650 ± 1240 , 1220 ± 520 , and 831 ± 427 ng/m^3 for INDUSTRY, URBAN, and RURAL, respectively. During August to December sampling period, the highest total PAH concentrations were found to be 4620 ng/m^3 at 4–6 December 2002 at INDUSTRY sampling site. For other two sampling sites, URBAN, and RURAL, much higher total PAH concentrations were also found at the same day. This is because this sampling period was due to biomass burning and inverse temperature. Thus, because of the inverse temperature, the air pollutant such as PAHs and suspended particles from biomass burning accumulated

in the atmosphere of central Taiwan and caused these results. The total PAHs concentration in INDUSTRY was 1530 and 122 ng/m^3 for gas and particle phase, respectively and were about 1.5 and 1.03 times higher than the gas and particle phases in the URBAN sampling site and were about 2 and 1.5 times higher than the gas and particle phases in RURAL sampling site. Thus, the results in Table 3 also indicated that industrial operation processes and human activities were with higher possibility of total PAHs contamination in the environment. Due to fewer human activities in the rural area (RURAL), the measured total PAH concentrations were lower than the INDUSTRY and URBAN sampling sites. Previous study (Park et al., 2002) indicated selected PAHs (Nap, AcPy, Acp, and FLu) are associated with combustion source and the summation of these four PAH concentrations were occupied about 58%, 56%, and 57% for INDUSTRY, URBAN, and RURAL sampling sites, respectively. Thus, one of the mainly PAHs sources was the combustion source in all sampling sites of central Taiwan.

Table 4 indicated that the phase contributions of individual PAHs at three different sampling sites. The results indicated that the 2–4 rings PAHs such as Nap, AcPy, Acp, Flu, PA, Ant, FL, Pyr, CYC, BaA, and CHR mainly contributed in the gas phase. Because of the lower boiling points and higher volatility low molecular weight (LMW) PAHs such as 2-ring PAHs and medium molecular weight (MMW) PAHs such as 3–5 rings PAHs

Table 3
Mean concentrations of gas phase and particle bound individual PAHs in ambient air at three sampling sites ($n = 12$)

Compound	INDUSTRY		URBAN		RURAL	
	Gas (ng/m^3)	Particle (ng/m^3)	Gas (ng/m^3)	Particle (ng/m^3)	Gas (ng/m^3)	Particle (ng/m^3)
Nap	409	7.80	283	10.2	223	0.90
AcPy	177	7.10	118	8.30	126	3.30
Acp	196	6.20	137	6.10	47.4	1.10
Flu	129	9.80	85.8	9.90	73.3	3.40
PA	90.0	4.20	60.0	3.20	33.2	1.90
Ant	158	5.60	105	4.10	48.3	0.90
FL	80.5	3.90	53.7	5.20	31.3	4.70
Pyr	79.9	1.70	53.3	1.20	32.9	0.70
CYC	35.9	2.00	33.3	1.50	30.8	2.60
BaA	13.8	0.40	19.2	1.10	26.5	1.80
CHR	48.3	2.40	32.2	2.10	22.6	3.60
BbF	10.1	2.70	6.70	2.40	3.30	1.90
BkF	12.4	2.10	10.3	2.30	4.60	3.30
PER	33.8	23.3	32.5	21.5	24.6	10.9
BeP	35.3	6.90	23.5	7.80	16.0	8.90
BaP	4.70	4.30	3.50	2.90	1.60	1.50
IND	1.30	2.60	1.80	2.40	3.40	1.90
DBA	1.70	2.60	1.10	1.80	0.60	6.50
BbC	7.60	10.5	5.10	8.50	2.30	5.70
BghiP	2.10	4.60	2.40	3.10	1.70	4.00
COR	3.40	10.8	2.30	9.70	0.70	9.60
Total-PAHs	1530	122	1070	115	755	79.1

Table 4
Phase distributions (%) of individual PAHs at three sampling sites

Compound	INDUSTRY		URBAN		RURAL	
	Gas phase (%)	Particle phase (%)	Gas phase (%)	Particle phase (%)	Gas phase (%)	Particle phase (%)
Nap	98.1	1.90	96.5	3.50	99.6	0.40
AcPy	96.2	3.80	93.4	6.60	97.5	2.50
Acp	96.9	3.10	95.7	4.30	97.7	2.30
Flu	92.9	7.10	89.7	10.3	95.6	4.40
PA	95.5	4.50	94.9	5.10	94.3	5.70
Ant	96.5	3.50	96.2	3.80	98.0	2.00
FL	95.4	4.60	91.2	8.80	86.9	13.1
Pyr	97.9	2.10	97.8	2.20	97.9	2.10
CYC	94.7	5.30	95.7	4.30	92.2	7.80
BaA	97.2	2.80	94.6	5.40	93.6	6.70
CHR	95.3	4.70	93.9	6.10	86.3	13.7
BbF	78.9	21.1	73.6	26.4	63.5	36.5
BkF	85.5	14.5	81.7	18.3	58.2	41.8
PER	59.1	40.9	60.2	39.8	69.3	30.7
BeP	83.6	16.4	75.1	24.9	64.3	35.7
BaP	52.2	47.8	54.7	45.3	53.3	46.7
IND	33.3	66.7	42.9	57.1	64.2	35.8
DBA	39.5	60.5	37.9	62.1	8.5	91.5
BbC	42.0	58.0	37.5	62.5	28.8	71.2
BghiP	31.3	68.7	43.6	56.4	30.4	69.6
COR	23.8	76.2	19.2	80.8	6.8	93.2
Total-PAHs	92.6	7.40	90.3	9.70	90.5	9.50
LMW-PAHs	98.1	1.90	96.5	3.50	26.7	0.10
MMW-PAHs	95.9	4.10	94.2	5.80	94.2	5.80
HMW-PAHs	34.0	66.0	36.2	63.8	28.7	72.3
BbF + BaP + DBA	1.00	0.58	0.95	0.60	0.66	1.19

are more abundant in the vapor phase. The surface depositions of these PAHs are relatively lower in comparison to high molecular weight (HMW) PAHs such as 6–7 rings PAHs (Li and Ro, 2000). Thus, the 2–4 rings PAHs occupied about 96%, 95%, and 94% in the gas phase for INDUSTRY, URBAN, and RURAL sampling sites, respectively. However, the 6–7 rings PAHs only played about 40% in the gas phase in all sampling sites. Table 4 also showed the contribution of three most hazardous PAHs (BbF + BaP + DBA) in gas and particle phases. The results indicated that the contributions of BbF + BaP + DBA were about 1.00%, 0.95%, and 0.66% in the gas phase for INDUSTRY, URBAN, and RURAL sampling sites; were about 0.58%, 0.60%, and 1.19% in the particle phase for INDUSTRY, URBAN, and RURAL sampling sites, respectively. For gas phase, BbF + BaP + DBA contribution was higher due to industrial processes and human activities in INDUSTRY sampling site than that of URBAN and RURAL sampling sites. However, for particle phase, BbF + BaP + DBA contribution was higher in RURAL sampling site than that of URBAN and INDUSTRY sampling sites. This is because the BbF, BaP, and DBA were associated with airborne particles by longer trans-

formation from nearby heavy duty highway and incinerator in RURAL sampling site. For INDUSTRY and URBAN sampling sites, higher BbF + BaP + DBA contribution in gas phase than the particle phase indicated that the BbF, BaP, and DBA were come from direct exhaust in these two sampling sites.

3.2. PAHs particle size distribution

Total PAHs particle size distributions were measured by MOUDI sampler combined with PS-1 sampler and the cutting diameters were 0.056, 0.10, 0.18, 0.32, 0.56, 1.0, 3.2, 5.6, 18, and 50 μm . Fig. 1(a)–(c) indicated the total PAHs size distribution in INDUSTRY, URBAN, and RURAL sampling sites, respectively. The highest peak of total PAHs was appeared in the fine particle mode (0.10–0.56 μm) in INDUSTRY sampling site. However, the highest peaks were only appeared in particle size of 0.18–0.56 μm for URBAN and RURAL sampling sites. At the INDUSTRY sampling site, total PAHs were mostly associated with fine particles (<2.5 μm) and this result indicated that PAHs in the industrial ambient atmosphere originated mainly from emission of the industrial processes. This result also reflected some

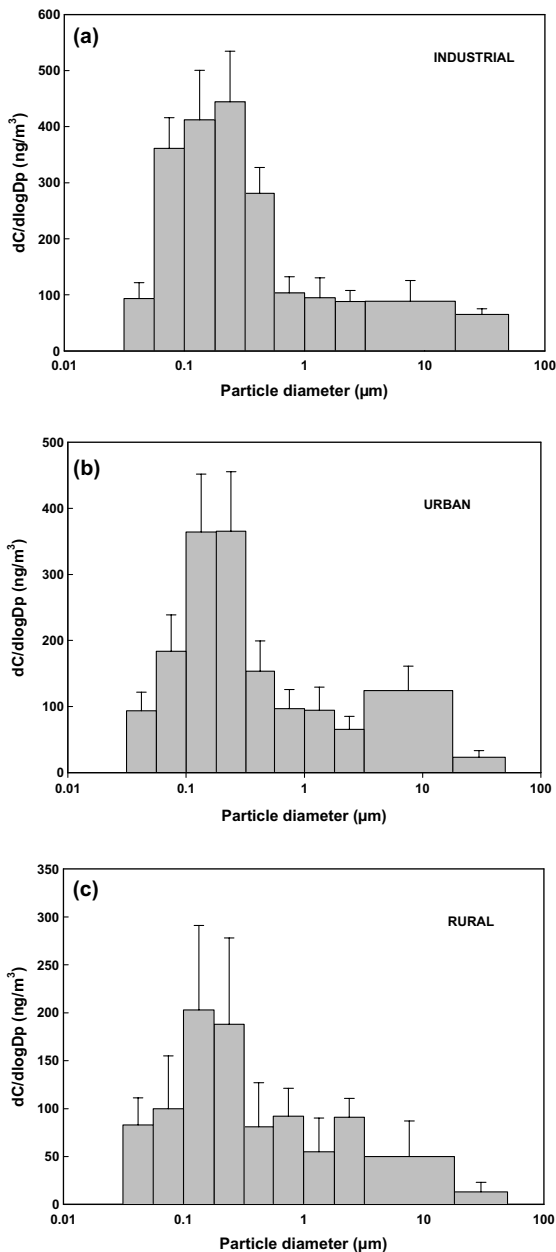


Fig. 1. Size distribution of total PAHs at INDUSTRY, URBAN, and RURAL sampling sites.

important information about the potential for health impact in the industrial area. At URBAN sampling site, the bimodal size distribution (0.18–0.56 and 5.6–18 μm) indicated that the total PAHs associated with fine particle mode were mainly from exhaust of traffics, however, the total PAHs combined with coarse particle mode were come from the re-suspended of the road dust which was belong to the coarse particles by the traffics. At the RURAL sampling site, the lower concentration

of total PAHs size distribution indicated that there were less PAHs sources in the RURAL sampling sites. However, the relative higher coarse particle size distribution (compared to INDUSTRY and URBAN) indicated that the total PAHs were come from the longer transport from nearby heavy duty highway and incinerator then associated with aged aerosols.

3.3. PAHs dry deposition estimation

PAHs dry deposition flux was a combination of both gas phase flux and particle phase flux, and given by: (Lee et al., 1996)

$$F_T = F_g + F_p = C_g \times V_{d,g} + F_p$$

where F_T is the PAHs dry deposition flux ($\mu\text{g}/\text{m}^2/\text{day}$) contributed by the summation of both the gas and particle phase, F_g is the PAHs gas phase dry deposition flux ($\mu\text{g}/\text{m}^2/\text{day}$), F_p is the particle phase dry deposition flux ($\mu\text{g}/\text{m}^2/\text{day}$), C_g is the PAHs concentration measured by PUF/XAD-16 cartridge of the PS-1 sampler (ng/m^3), $V_{d,g}$ is the dry deposition velocity of gas phase (cm/s), C_p is the PAH concentrations in the particle phase (ng/m^3) measured by the filter of PS-1 sampler and $V_{d,p}$ is the PAHs dry deposition velocity of particle phase (cm/s).

The estimation of particle bound PAHs dry deposition was followed by the equation:

$$\text{PAHs content } (\mu\text{g}/\text{g}) = \frac{F_{p,\text{PAHs}} (\mu\text{g}/\text{m}^2/\text{day})}{F_{T,\text{particles}} (\text{g}/\text{m}^2/\text{day})}$$

where PAHs content ($\mu\text{g}/\text{g}$) was calculated by PAH concentrations ($\mu\text{g}/\text{m}^3$) divided particle concentrations (g/m^3) and the results were displayed in Table 5; $F_{T,\text{particles}}$ ($\text{g}/\text{m}^2/\text{day}$) was the estimated dry deposition flux of total suspended particles by Noll and Fang model (Noll and Fang, 1989) and the calculated dry deposition fluxes of total particles were 2.02, 2.32, and 1.94 $\text{g}/\text{m}^2/\text{day}$ of INDUSTRY, URBAN, and RURAL sampling sites, respectively. Thus, by using the equation mentioned above the estimated dry deposition flux of particle bound PAHs can be calculated.

The dry deposition velocity of gaseous PAHs was in a range of 0.001–0.01 cm/s . And we selected 0.001 cm/s for the value of $V_{d,g}$ (Sheu et al., 1997). And the gas phase concentrations of PAHs were measured by PUF/XAD-16 cartridge of the PS-1 sampler in this study. Thus, the dry deposition fluxes for gas phase can be calculated. Once we sum up the calculated gas and particle phases PAHs, the estimated total PAHs dry deposition at these three sampling sites can then be obtained (Table 6).

For INDUSTRY sampling site, the calculated PAHs dry deposition fluxes were ranged from 0.17 to 12.3 $\mu\text{g}/\text{m}^2/\text{day}$ for 21 individual PAHs and the dry deposition flux of total PAHs was 58.5 $\mu\text{g}/\text{m}^2/\text{day}$. Higher

Table 5
Particle bound individual PAHs content ($\mu\text{g/g}$) in the ambient air of three sampling sites

Compound	INDUSTRY	URBAN	RURAL
Nap	159	197	14.9
AcPy	145	161	54.5
Acp	126	118	18.2
Flu	200	192	56.2
PA	85.9	62.0	31.4
Ant	114	79.4	14.9
FL	79.7	101	77.6
Pyr	34.8	23.2	11.6
CYC	40.9	29.0	42.9
BaA	8.18	21.3	29.7
CHR	49.1	40.7	59.5
BbF	55.2	46.5	31.4
BkF	42.9	44.5	54.5
PER	476	416	180
BeP	141	151	80.9
BaP	14.3	17.4	24.8
IND	53.1	46.5	31.4
DBA	53.1	34.8	107
BbC	214	164	132
BghiP	94.0	60.0	33.0
COR	221	189	158
Total-PAHs	2410	2190	1240

molecular weight PAHs such as 4–7 rings PAHs were occupied about 75% of total PAHs dry deposition flux. The calculated gas phase PAHs dry deposition flux at

Table 6
Estimation of dry deposition flux ($\mu\text{g/m}^2/\text{day}$) for individual PAHs for INDUSTRY, URBAN, and RURAL sampling sites

Compound	$F_T (F_p, F_g)$		
	INDUSTRY	URBAN	RURAL
Nap	0.77 (0.07, 0.70)	0.56 (0.07, 0.49)	0.51 (0.05, 0.46)
AcPy	0.42 (0.11, 0.31)	0.38 (0.18, 0.20)	0.27 (0.09, 0.18)
Acp	1.20 (0.86, 0.34)	1.13 (0.90, 0.23)	0.79 (0.56, 0.23)
Flu	3.69 (3.47, 0.22)	2.63 (2.48, 0.15)	2.44 (2.30, 0.14)
PA	1.32 (1.16, 0.16)	0.74 (0.64, 0.10)	0.87 (0.78, 0.09)
Ant	2.64 (2.37, 0.27)	1.63 (1.45, 0.18)	1.74 (1.66, 0.08)
FL	1.76 (1.62, 0.14)	1.93 (1.84, 0.09)	1.16 (1.09, 0.07)
Pyr	0.83 (0.69, 0.14)	0.30 (0.21, 0.09)	0.55 (0.46, 0.09)
CYC	0.86 (0.79, 0.06)	0.63 (0.57, 0.06)	0.57 (0.50, 0.07)
BaA	0.17 (0.14, 0.03)	0.37 (0.33, 0.04)	0.11 (0.08, 0.03)
CHR	1.04 (0.95, 0.09)	0.85 (0.80, 0.05)	0.68 (0.60, 0.08)
BbF	1.74 (1.72, 0.02)	1.13 (1.12, 0.01)	1.15 (1.14, 0.01)
BkF	1.36 (1.34, 0.02)	1.11 (1.09, 0.02)	0.90 (0.88, 0.02)
PER	12.3 (12.28, 0.06)	11.6 (11.52, 0.05)	8.14 (8.08, 0.06)
BeP	5.96 (5.90, 0.06)	4.56 (4.52, 0.04)	3.94 (3.91, 0.03)
BaP	0.37 (0.35, 0.02)	0.56 (0.55, 0.01)	0.24 (0.23, 0.01)
IND	2.05 (2.04, 0.002)	1.85 (1.85, 0.003)	1.35 (1.34, 0.01)
DBA	3.19 (3.19, 0.003)	1.18 (1.18, 0.002)	2.11 (2.10, 0.01)
BbC	6.09 (6.08, 0.01)	5.81 (5.80, 0.01)	4.02 (4.01, 0.01)
BghiP	2.83 (2.82, 0.004)	1.91 (1.90, 0.004)	1.86 (1.85, 0.01)
COR	7.84 (7.83, 0.01)	7.97 (7.96, 0.004)	5.18 (5.17, 0.01)
Total-PAHs	58.5 (55.8, 2.65)	48.8 (46.9, 1.85)	38.6 (36.9, 1.70)

INDUSTRY sampling site were ranged from 0.002 to 0.71 $\mu\text{g/m}^2/\text{day}$ for 21 individual PAHs and the dry deposition flux of gaseous $\sum 21$ PAHs was 2.65 $\mu\text{g/m}^2/\text{day}$. The calculated particle phase PAHs dry deposition flux at INDUSTRY sampling site were ranged 0.07–12.3 $\mu\text{g/m}^2/\text{day}$ for 21 individual PAHs and the dry deposition flux of particle bound $\sum 21$ PAHs was 55.8 $\mu\text{g/m}^2/\text{day}$. The gas and particle phases PAHs dry deposition flux occupied about 95.4% and 4.6% to the dry deposition flux of $\sum 21$ PAHs, respectively. The same phenomenon was also found at the URBAN and RURAL sampling sites. However, the dry deposition flux of total PAHs (48.8 and 38.6 $\mu\text{g/m}^2/\text{day}$) was lower than the INDUSTRY sampling site (58.5 $\mu\text{g/m}^2/\text{day}$). This result indicated that the industrial processes were the main PAHs dry deposition flux sources in central Taiwan.

3.4. BaP equivalency of particle and gas phase PAHs

Table 7 indicated that the gaseous PAH concentrations in different environments (INDUSTRY, RURAL, and URBAN) in BaP equivalents (Nisbet and LaGoy, 1992), given as geometric means. BaP occupied about a half of the total carcinogenic activity in INDUSTRY and URBAN with average values of 8.30 and 5.51 ng/m^3 . However, the highest BaP equivalent compound in RURAL site was BaA with an average value of 2.65 ng/m^3 and BaP concentration was only 1.60 ng/m^3 and occupied about 21.9% to the total carcinogenic activity.

Table 7
BaP toxic equivalency factors (TEFs) in INDUSTRY, RURAL, and URBAN sites

Compounds	INDUSTRY		RURAL		URBAN	
	Gas	Particle	Gas	Particle	Gas	Particle
Nap	0.41	0.0078	0.22	0.0009	0.28	0.0102
AcPy	0.18	0.0071	0.126	0.0033	0.12	0.0083
Acp	0.2	0.0062	0.047	0.0011	0.14	0.0061
Flu	0.13	0.0098	0.073	0.0034	0.086	0.0099
PA	0.09	0.0042	0.033	0.0019	0.06	0.0032
Ant	1.58	0.056	0.48	0.009	1.05	0.041
FL	0.08	0.0039	0.031	0.0047	0.054	0.0052
Pyr	0.08	0.0017	0.033	0.0007	0.053	0.0012
CYC	— ^a	— ^a	—	—	—	—
BaA ^b	1.38	0.04	2.65	0.18	1.92	0.11
CHR ^b	0.48	0.024	0.23	0.036	0.32	0.021
BbF ^b	1.01	0.27	0.33	0.19	0.67	0.24
BkF ^b	1.24	0.21	0.46	0.33	1.03	0.23
PER	—	—	—	—	—	—
BeP	—	—	—	—	—	—
BaP ^b	9	0.7	3.1	1.5	6.4	2.5
IND ^b	0.13	0.26	0.34	0.19	0.18	0.24
DBA ^b	1.7	2.6	0.6	6.5	1.12	1.8
BbC	—	—	—	—	—	—
BghiP	0.021	0.046	0.037	0.02	0.024	0.031
COR	—	—	—	—	—	—
∑21 PAHs	17	4.24	7.29	8.97	12.6	5.26

^aNo available TEFs.

^bThese compounds are classified as possible or probable human carcinogens by the IARC.

Georgiadis and Kyrtopoulos (1999) indicated that the range of airborne PAH an exposure examined in the various biomarker-based studies varies by several orders of magnitude. Total PAH concentrations are around <20, 20–200, and 100–1000 ng/m³ for rural, rural and workplace, respectively. And BaP concentrations are around <5, 5–50, and 100 ng/m³ for rural, urban, and workspace, respectively. Tsai et al. (2001) examined in a factory of Taiwan Industrial Park and the results indicated that the total gaseous PAHs and BaP concentrations were 1401 and 29.8 ng/m³. Petry et al. (1996) indicated that the sum of BaP equivalency were about 11857.2, 1812.8, 305.95, and 0.96 ng/m³ for coke plant, anode plant, graphite plant and city environment, respectively. These researches reflect that the higher total gaseous PAH concentrations and BaP concentration occur in industrial sampling site (INDUSTRY) due to industrial exhausts. And lower total gaseous PAH concentrations and BaP concentrations are indicated in the urban sampling site (URBAN) due to traffic exhausts. However, the lowest total gaseous and BaP concentrations are found in background sampling site (RURAL) and the major PAH sources may diffuse from nearby industrial and traffic sampling sites. The contributions of particle bound BaP to the total carcinogenic activity in particle bound PAHs were also showed in Table 7. Different from the gaseous PAH concentrations, the particle

bound BaP concentrations contributed only 16.5%, 16.7%, and 19.7% to the total carcinogenic activity in INDUSTRY, RURAL, and URBAN sampling sites, respectively. The BaP equivalency results indicated that the health risk of gas phase PAHs were higher than the particle phase in three sampling sites of central Taiwan.

4. Conclusions

The gas and particle phases PAHs concentration were measured by MOUDI and PS-1 sampler at three different sampling sites of central Taiwan. Estimation of PAHs dry deposition fluxes were applied Noll and Fang model, meanwhile the PAHs BaP equivalency was also estimated by the TEFs simultaneously in this study. The results indicated that PAH concentrations were higher at industrial park (INDUSTRY) and urban (URBAN) sampling sites than the rural (RURAL) sampling site due to the more industrial processes, traffic exhausts and human activities. The results also indicated that the estimated dry deposition fluxes of total PAHs were 58.5, 48.8, and 38.6 µg/m²/day at INDUSTRY, URBAN, and RURAL sampling sites, respectively. The BaP equivalency results indicated that the health risk of gas phase PAHs were higher than the particle phase at these three sampling sites of central Taiwan.

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