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## PAH emission from various industrial stacks

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### Abstract

The emission of polycyclic aromatic hydrocarbons (PAHs) from various industrial stacks (blast furnace, basic oxygen furnace, coke oven, electric arc furnace, heavy oil plant, power plant and cement plant) in southern Taiwan were investigated. PAH concentrations ( $\mu\text{g}/\text{N m}^3$ ) and PAH emission factors ( $\mu\text{g}/\text{kg}$  feedstock) were determined. In addition to these eight stationary industrial stacks, an industrial waste incinerator, a diesel engine and a gasoline-powered engine were selected and combined for the identification of source indicator-PAHs in this study. The qualitative contribution of PAHs to the ambient air by various sources was estimated by factor analysis. Combustion of heavy oil produced considerably higher 4, 5 and 6 + 7-ring PAH concentration than other stacks. In addition, the HMW (higher molecular weight) PAH concentrations were significantly higher for the coke oven, the electric arc furnace and heavy oil combustion. Measured total-PAHs emission factors of eight stationary sources were between 77.0 and 3970  $\mu\text{g}/\text{kg}$  feedstock, while BaP (the most carcinogenic PAH) emission factors were between 1.87 and 15.5  $\mu\text{g}/\text{kg}$  feedstock. Among these eight emission sources, the heavy oil plant had both the highest total-PAH and the highest BaP emission factor. Indicator PAHs of the cement plant were AcPy, Acp and Ant, which are all 3-ringed PAHs. However, the indicator PAHs of the industrial waste incinerator were IND and CHR. For mobile sources (diesel- and gasoline-powered vehicles), the indicator PAHs were mainly lower molecular weight PAHs (AcPy, FL and Flu). By using factor analysis, the cursorily qualitative analysis of PAH emission was found to be practicable. © 1998 Elsevier Science B.V. All rights reserved.

*Keywords:* Polycyclic aromatic hydrocarbon; Factor analysis; Emission factor

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## 1. Introduction

Several polycyclic aromatic hydrocarbons (PAHs) are known to be mutagenic and/or carcinogenic toward rodents, and thus they are potential human carcinogens [1]. PAHs and their derivatives are generated by incomplete combustion and/or pyro-synthesis of organic material arising, in part, from natural combustion such as forest fires and volcanic eruptions. For the most part, however, they are generated from emissions of human activities, like industrial production, transportation, waste incineration and so on. There are many investigations concerning PAH emission from mobile sources [2–8]. The PAH concentration and emission factor of vehicles are well understood, but only few reports have focused on stationary sources [9–15]. In addition, the emission factors should be updated after a certain period because of the improvement in production processes and air pollution control devices [16]. Emission factors for PAHs can be considered as the amounts of PAHs released per unit feedstock or per unit product. Emission factors are a useful guide for the estimation of air-pollutant release amounts, and are of great importance in the setting of national and international environmental policies, protection strategies and regulations. In particular, to ensure that expenditures on pollution control measures are properly targeted and warranted, it is important that emission factors be based on the most recent and accurate data [6]. In this study, the emission factors by  $\mu\text{g}$  of PAH mass emitted per kilogram of feedstock provided are reported.

For stationary sources, there are several investigations concerning PAH emission from industrial waste incinerators [9–13], but there are only a few studies for the emission from the stacks of industrial processes [14,15]. The quantities and characteristics of PAHs emitted from industrial stacks will depend on several factors: the type of input (fuel, additive, etc.), the manufacturing process, air pollution control devices, etc., [15]. For the same kind of industrial plant, the PAH emission might not be the same because of these various influencing factors. Among these factors, the fuel is the most important. PAH emission is primarily from the unburnt fuel [17], while the traditional air pollution control devices seem ineffective for the elimination of PAHs [18]. Therefore, PAH emission from the stacks of individual industrial processes vary over a wide range. Emission factors have long been a fundamental tool for air quality management. Data from direct emission tests or continuous emission monitors of specific sources are usually preferred for estimating a source emission. However, direct measurement data from individual sources are not always available and, even when they are, they may not reflect the variability of actual emissions over time. In spite of their limitations, emission factors are frequently the best or only method available for estimating air-pollutant emissions.

Factor analysis is a mathematical technique developed to examine the underlying structure that exists in large data sets. It is assumed that although many different parameters describing a system can be identified, there are really far fewer causal forces that result in the state of the system as it is observed [19]. It is the identification and interpretation of these fewer causal forces that factor analysis attempts to achieve.

The objective of this study is to investigate the PAH emission (including the PAH concentration and PAH emission factor) from eight industrial stacks in southern Taiwan.

In addition, the PAH concentration to receptor sites was analysed with the factor analysis model. The major contribution of PAH from various sources to the receptor sites is estimated by the factor analysis.

## 2. Experimental

### 2.1. Industrial stacks

Eight industrial stacks located in southern Taiwan, including a blast furnace, a basic oxygen furnace (BOF), a coke oven, an electric arc furnace (EAF), a heavy oil plant, a coal power plant and a cement plant were investigated. The sampling information is shown in Table 1. The eight stacks investigated by this study are located in the industries that cause major air pollution in southern Taiwan. The major air pollution sources at an integrated iron/steel plant include the following four manufacturing processes: (1) coke oven, (2) sintering, (3) iron blast furnace, and (4) steel production, including the basic oxygen furnace and electric arc furnace. The cement manufacturing process can be divided into the following four primary components: (1) raw material acquisition and handling, (2) kiln feed preparation, (3) pyroprocessing, and (4) finished cement grinding. The raw material processing operations differ somewhat for wet and dry processes, respectively. The dry process is used in this cement plant. Drying the cement raw material by the thermal energy was mainly supplied by hot exhausted gases from the pyroprocessing system. The stack of this raw-material operation process is labeled as 'cement 1' in this study. Another stack of this cement plant is from the pyroprocessing system, and is labeled as 'cement 2'. The feed prepared from the kiln feed process was transferred into the kiln for the pyroprocessing process. The kiln fuel was coal and its feed rate was 140 ton/h for this cement plant (Table 1).

In addition to the industrial stacks, the ambient PAH concentrations were measured. Four receptors (Tzuoo-Yng, Chyan-Jin, Eii-Ling and Nan-Shing) spread around these eight industrial stacks were selected. Ambient-air samples for the particle and gas phases of PAHs were collected by using a standard semivolatile sampling train (General Metal Works PS-1) [2].

### 2.2. PAH sampling system for stack flue gas

The modification of USEPA's sampling method 5 (MM5) (40CFR60) by Graseby was adapted for the sampling. The flue gas was sampled from the stack isokinetically by the PAH sampling system (Fig. 1). The PAH sampling system was equipped with a sampling probe, a cooling device, a glass cartridge, a pump, a flow meter and a control computer. A PAH sampling system with a tube-type glass fiber filter (cleaned by heating to 450°C) was used to collect particulate and particle-phase PAHs. A glass cartridge packed with XAD-2 resin and supported by a polyurethane foam (PUF) plug was used to collect the gas phase PAHs. After each sampling cycle the sampling train was rinsed with *n*-hexane.

Table 1  
Sampling information for the emission sources

Plant	Blast furnace	Basic oxygen furnace	Coke oven	Electric arc furnace	Heavy oil plant	Power plant	Cement 1 <sup>a</sup>	Cement 2 <sup>b</sup>
Sampling date	96/4/18	96/4/19	96/4/26	96/5/3	96/4/25	96/5/2	96/5/9	96/5/10
Feedstock	Coke 100 ton/h Liquid steel 212 ton/h Sinters 258 ton/h	Liquid steel 160 ton/h	Coal 1200 ton/h	Waste steel 40.0 ton/batch Heavy oil 2800 l/h Charcoal 0.500 ton/h	Fuel oil 35.7 l/h	Bituminous coal 103 ton/h	Cement raw material 159 ton/h	Kiln feed 140 ton/h
Product	213 ton/h	140 ton/h	27.0 ton/stove	35.0 ton/h	259 l/h	395 MW	159 ton/h	139 ton/h
APCD <sup>c</sup>	Bag house	Bag house	Bag house	Bag house	No	EP <sup>d</sup>	EP	EP
Flow rate of exhaust (m <sup>3</sup> /min)	5650	7760	2500	1880	360	20000	4770	3930
Exhaust velocity (m/s)	14.5	16.3	14.1	13.4	2.40	28.1	18.7	11.0
Exhaust temperature (°C)	72.0	54.0	76.0	86.7	247	177	103	142
Humidity (%)	5.60	5.70	5.10	4.20	7.30	8.70	19.4	3.50
Stack diameter (m)	3.25	3.50	2.20	2.00	2.49	5.03	2.74	3.40
Stack height (m)	26.6	23.6	30.0	26.0	15.0	130	59.8	33.0
O <sub>2</sub> (%)	20.8	20.6	20.6	21.1	5.80	7.80	11.2	10.2
TPM <sup>e</sup> (mg/m <sup>3</sup> )	3.80	4.20	18.0	3.00	33.0	4.20	55.0	4.60
SO <sub>x</sub> (ppm)	6.30	—	8.50	20.0	71.0	320	4.10	—
NO <sub>x</sub> (ppm)	14.0	—	7.80	43.0	—	292	284	—

<sup>a</sup>Cement 1: Drying of cement raw material.

<sup>b</sup>Cement 2: Pryoprocessing system.

<sup>c</sup>APCD: Air pollution control devices.

<sup>d</sup>EP: Electrostatic precipitator.

<sup>e</sup>TPM: Total particulate matter.

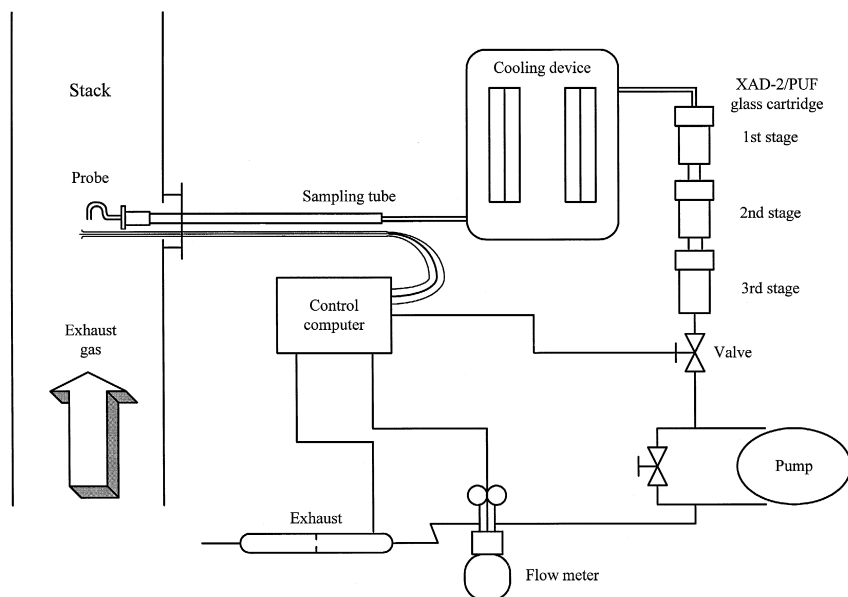


Fig. 1. PAH sampling system.

Breakthrough tests were investigated by three stages of XAD-2/PUF cartridge. Each stage of cartridge was analyzed individually and compared for the PAH mass collected. Breakthrough tests results showed that there was no significant PAH mass found to be collected in the cartridge of the third stage. All the experiments were repeated at least three times to make sure that the results were reproducible.

### 2.3. PAH analysis

PAH-containing filters and cartridges were Soxhlet extracted with a mixed solvent (*n*-hexane and dichloromethane, v:v = 1:1) for 24 h. The extract was then concentrated by purging with ultra-pure nitrogen to 2 ml for the cleanup procedure [2]. The collected eluant from the cleanup procedure was re-concentrated to 0.5 ml with nitrogen. A gas chromatograph (GC) (Hewlett-Packard 5890A) with a Hewlett-Packard capillary column (HP Ultra 2—50 m × 0.32 mm × 0.17 μm), a mass selective detector (MSD) (Hewlett-Packard 5972) and a computer workstation were used for the PAH analysis. The masses of molecular and fragment ions of PAHs were determined by using the scan mode for pure PAH standards. Qualification of PAHs was performed by using the selected ion monitoring (SIM) mode.

The concentrations of the following PAHs were determined: naphthalene (Nap), acenaphthylene (AcPy), acenaphthene (Acp), fluorene (Flu), phenanthrene (PA), anthracene (Ant), fluoranthene (FL), pyrene (Pyr), cyclopenta[*c,d*]pyrene (CYC), benz[*a*]anthracene (BaA), chrysene (CHR), benzo[*b*]fluoranthene (BbF), benzo[*k*]fluoranthene (BkF), benzo[*e*]pyrene (BeP), benzo[*a*]pyrene (BaP), perylene (PER), indeno[1,2,3-*cd*]pyrene (IND), dibenz[*a,h*]anthracene (DBA), benzo[*b*]chrysene (BbC), benzo[*ghi*]perylene (BghiP), and coronene (COR).

According to the International Agency for Research on Cancer (IARC) [20], the higher molecular weight PAHs are often more carcinogenic. PAHs can be classified by their numbers of aromatic ring as follows: 2-ring including Nap; 3-ring including AcPy, Acp, Flu, PA and Ant; 4-ring including FL, Pyr, BaA and CHR; 5-ring including CYC, BbF, BkF, BeP, BaP and PER; 6-ring including IND, DBA, BbC and BghiP; 7-ring including COR. PAHs having more aromatic rings, in general, represent higher molecular weights. PAHs can also be further classified into lower molecular weight (LMW containing two and 3-ringed PAHs), middle molecular weight (MMW containing 4-ringed PAHs) and higher molecular weight PAHs (HMW containing 5-, 6- and 7-ringed PAHs).

PAH recovery efficiencies were determined by processing a solution containing known PAH concentrations through the same experimental procedure used for the samples. This study showed that the recovery efficiency of PAHs varied between 0.72 and 1.13 and averaged 0.839. Mean relative standard deviation (RSD) (%) of recovery efficiencies were up to 18% and the value of potential error for PAHs analysis was normally estimated to be 20%. Blank tests for PAHs were accomplished by performing the same procedure as the recovery-efficiency tests without adding the standard solution before extraction. Analyses of field blanks including filters and PUF/XAD-2 cartridges found no significant contamination (GC/MS integrated area was less than detection limit).

### 3. Results and discussion

#### 3.1. Mass distribution of PAHs on the stack sampling system

When PAHs were collected by the stack PAH-sampling system, including the tube filter and XAD-2/PUF cartridge, they might also condense on the sampling pipe and the cooling device. If one of these four parts were excluded, the PAH concentrations might be underestimated. The mass distribution of PAHs in the four parts of the sampling system is listed in Table 2. Total-PAH mass in the gas phase was between 78.0% and 95.3% and averaged 92%. This is because the high temperature of stack flue gas results in the PAHs existing mainly in the gas phase. Because of their higher molecular weight and lower vapor pressure, more than 20.0% and 29.0% of MMW and HMW PAH mass, respectively, was in the particulate and was collected by the tube type filter. The mean fraction of individual PAH mass collected by the cooling water was between 1.55% (BbF) and 16.8% (FL), while that of pipe residual was between 0.435% (Nap) and 8.0% (COR). A considerable fraction of PAH mass existed in both the cooling water and the pipe residual. It is recommended that, in order to reduce the system error for measured PAH data, the PAH samples for the cooling water and pipe residual should be determined and included.

#### 3.2. PAH-homologue concentrations in the flue gas of industrial stacks

PAH-homologue concentrations of eight industrial stacks are shown in Fig. 2. Both the blast furnace and the BOF have higher Nap (2-ring PAH) concentrations, while the

Table 2

The mass distribution of PAHs in the whole sampling equipment

Fraction PAHs	Particulate phase (%)		Cooling water (%)		Pipe residual (%)		Gaseous phase (%)	
	Range	Mean	Range	Mean	Range	Mean	Range	Mean
Nap	0.151–3.95	1.71	0.275–8.64	2.31	0.008–1.93	0.453	89.0–97.8	95.5
AcPy	0.115–50.9	13.6	N.D.–4.13	2.04	0.006–2.73	0.853	47.1–97.0	83.8
Acp	8.13–44.1	16.8	1.67–9.20	3.77	0.051–5.95	1.49	44.6–86.2	78.0
Flu	0.380–27.6	8.28	0.740–4.59	1.72	N.D.–3.80	0.800	71.0–98.9	89.2
Ant	0.077–16.8	2.11	0.740–10.2	6.51	0.569–10.9	3.00	73.0–98.5	88.6
PA	0.684–19.2	8.19	1.21–7.12	3.36	N.D.–2.46	0.913	80.2–99.9	89.5
FL	0.444–6.46	3.61	1.34–52.2	16.8	1.01–13.6	7.08	41.0–90.7	71.8
Pyr	0.129–17.6	8.42	1.23–54.8	16.2	0.644–7.23	4.50	39.7–95.0	70.3
CYC	8.70–69.7	22.8	0.455–17.5	4.92	N.D.–6.89	1.45	28.8–88.3	72.5
BaA	9.36–62.9	31.5	2.74–11.5	6.09	N.D.–9.52	2.68	37.1–87.7	59.2
CHR	2.84–58.5	34.5	1.82–6.54	5.72	1.07–13.4	3.82	27.5–97.5	55.2
BbF	5.73–62.5	32.4	1.06–5.49	1.55	N.D.–2.67	0.756	32.0–99.9	70.8
BkF	4.28–89.8	29.0	0.434–11.0	4.84	N.D.–2.26	0.935	61.7–95.2	66.9
BeP	2.55–53.7	30.4	0.216–11.8	2.73	N.D.–10.0	3.44	35.8–89.2	65.7
BaP	4.19–89.8	26.8	0.144–12.2	3.62	0.080–2.53	0.619	46.3–92.4	69.8
PER	4.53–31.2	23.3	0.589–11.0	3.51	0.090–5.90	1.38	55.5–98.8	73.6
IND	3.84–47.2	31.1	0.717–11.2	7.36	N.D.–4.53	1.81	40.5–90.4	66.1
DBA	4.94–60.2	28.6	0.738–8.34	5.21	N.D.–4.79	2.26	48.4–89.5	62.4
BbC	10.9–55.7	28.8	1.34–26.6	7.77	N.D.–11.8	6.34	40.8–91.0	62.6
BghiP	7.15–89.3	35.8	1.32–20.6	5.96	N.D.–8.01	4.06	42.2–82.8	61.1
COR	11.4–87.8	37.7	0.854–6.62	3.45	N.D.–32.0	8.00	12.2–90.3	54.2
Total-PAHs	1.16–4.84	3.56	0.454–15.7	3.58	0.291–3.76	0.896	78.0–95.3	92.0

stack of the cement plant (cement 1 and cement 2) was dominant in 3-ring PAH homologues. The heavy oil plant produced considerable higher concentrations of 4- and 5-ring PAH-homologues than other stacks. However, the EAF, the heavy oil plant and the power plant have higher mean 6 + 7-ring PAH-homologue concentrations. These higher molecular weight PAHs would be more harmful to human beings.

The PAH-homologue mass distribution in various stacks is listed in Table 3. The flue gas is mainly the 2-ring PAHs for most stacks and the mass fraction of 7-ring PAH is the least. The HMW-PAH mass fraction was significantly higher for the heavy oil plant (19.9%), the EAF (15.0%), the power plant (12.0%) and the coke oven (11.8%). For that of the cement plants, the fraction of 3-ring PAHs averaged 28.2% of the total-PAH mass, which is much higher than other stacks.

### 3.3. PAH emission factors

PAH emission factors of these stacks are listed in Table 4. These PAH emission factors are on the basis of whole weight of feedstock, including fuel, material, additives, etc. The total-PAH emission factors are 77.0, 521, 241 and 179  $\mu\text{g}/\text{kg}$  feedstock for the blast furnace, the BOF, the coke oven and the EAF, respectively. BaP is the most carcinogenic PAH for these four emission sources. The BaP emission factors are 2.25, 3.07, 15.5, and 4.03  $\mu\text{g}/\text{kg}$  feedstock for the blast furnace, the BOF, the coke oven and

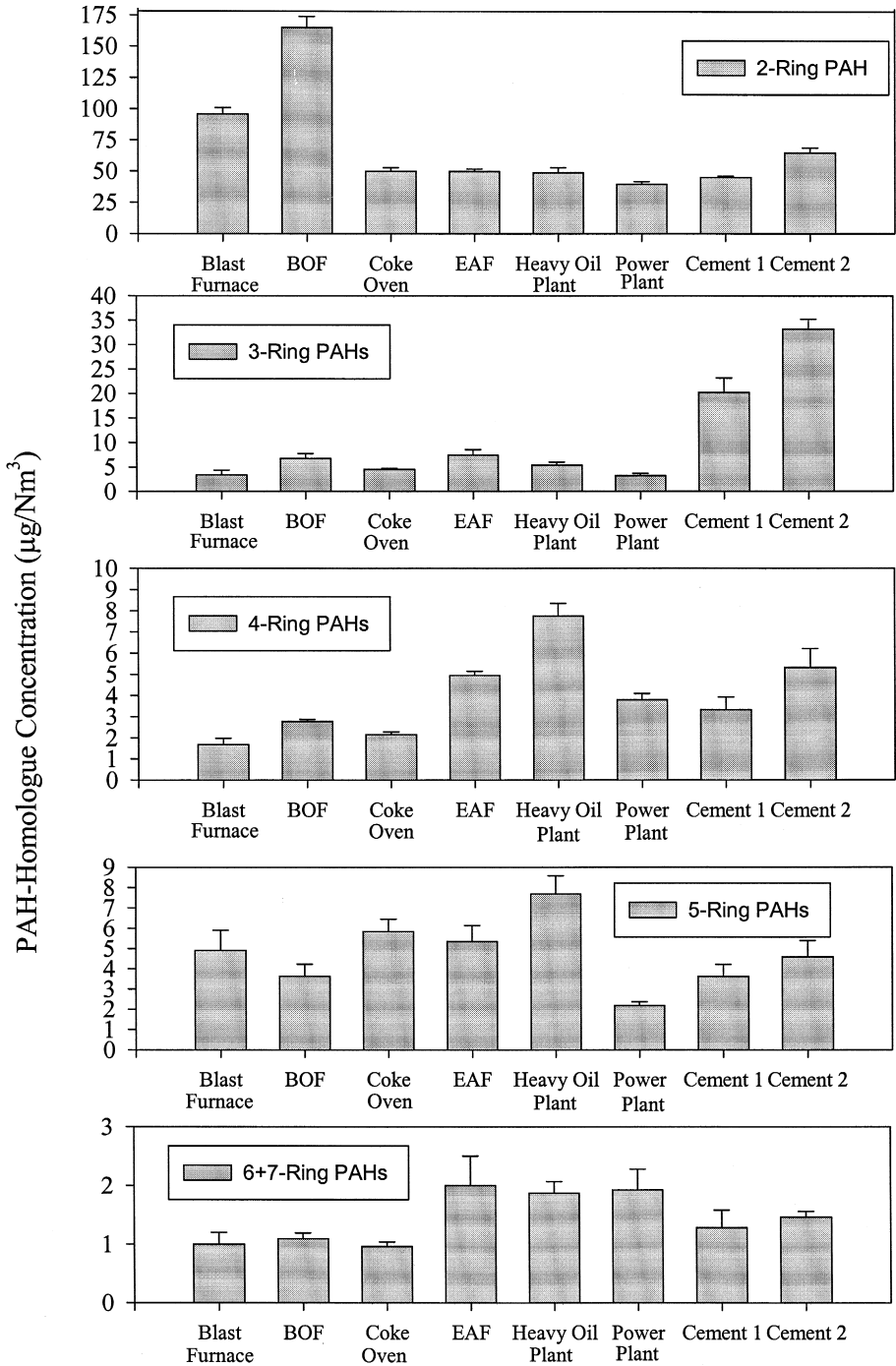


Fig. 2. PAH-homologue concentration of various industrial stacks.



Table 3

Mass distribution of PAH-homologue in the stack flue gas of various industrial processes (%)

PAHs	Blast furnace	BOF <sup>a</sup>	Coke oven	EAF <sup>b</sup>	Heavy oil plant	Power plant	Cement 1 <sup>c</sup>	Cement 2 <sup>d</sup>
2-ring	89.3	91.8	77.8	68.0	63.0	74.8	60.1	57.5
3-ring	3.13	3.78	7.04	10.2	7.01	6.05	26.9	29.4
4-ring	1.56	1.54	3.37	6.77	10.0	7.16	4.42	4.71
5-ring	5.05	2.28	10.3	12.3	17.5	8.35	6.89	7.13
6-ring	0.726	0.450	1.06	2.37	1.92	3.11	1.25	0.986
7-ring	0.210	0.159	0.432	0.369	0.501	0.538	0.456	0.307
LMW	92.5	95.6	84.9	78.2	70.0	80.8	87.0	86.9
MMW	1.56	1.54	3.37	6.77	10.0	7.16	4.42	4.71
HMW	5.99	2.89	11.8	15.0	19.9	12.0	8.59	8.43

<sup>a</sup>BOF: Basic oxygen furnace.<sup>b</sup>EAF: Electric arc furnace.<sup>c</sup>Cement 1: Drying of cement raw material.<sup>d</sup>Cement 2: Pyroprocessing system.

the EAF, respectively. Although the air pollution control devices for these four plants are all bag houses (Table 1), their PAH emission factors differ significantly from source to source. As has been mentioned, PAH emission factors are affected by fuel, manufacturing processes and air-pollution control devices. The feedstocks for combustion or heating processes are the major sources of PAH emission, which includes the feedstock of coal, liquid steel and sinter for the blast furnace, liquid steel for the BOF, coal for the coke oven, and both heavy oil and charcoal for the electric arc furnace.

Being more viscous and less volatile than distillate oil, the heavier residual oils (heavy oil) may need to be heated for ease of handling and to facilitate proper atomization. The total-PAH emission factor of this plant is 3970  $\mu\text{g}/\text{kg}$  residual oil, much greater than those of the integrated iron/steel plant. Additional reasons for this are that the feedstock is pure residual oil for this plant, that there are some stuff and additives in the feedstock for the previous plants, and that there are no air pollution devices for this heavy oil plant. The BaP emission factor for the heavy oil plant is 285  $\mu\text{g}/\text{kg}$  feedstock, 18.4 times higher than that of the coke oven and averaging 74.4 times of magnitude higher than the mean value of the blast furnace, the BOF, the coke oven, the EAF, the power plant and the cement plants.

The fuel of the power plant in this study was bituminous coal, which is by far the largest group and is characterized as containing lower fixed carbon and higher volatile matter than anthracite. For the power plant, the emission factor of total-PAHs and BaP was 602 and 8.64  $\mu\text{g}/\text{kg}$ -bituminous coal, respectively. The emission factor of BaP was approximately 500 times of magnitude higher than that with air pollution control devices reported by USEPA [21].

The total-PAH emission factors were 132  $\mu\text{g}/\text{kg}$  cement raw material for cement 1 and 184  $\mu\text{g}/\text{kg}$  kiln feed for cement 2, respectively (Table 4). As to the individual PAHs, the patterns of these two stacks were very similar, since the drying gas of cement 1 stack was from the exit gas of cement 2 stack.

Table 4  
Emission factors of PAHs ( $\mu\text{g PAHs/kg feedstock}$ )

PAHs	Blast furnace	BOF <sup>a</sup>	Coke oven	EAF <sup>b</sup>	Heavy oil plant	Power plant	Cement 1 <sup>c</sup>	Cement 2 <sup>d</sup>
Nap	69.1	480	190	128	2707	470	80.9	109
AcPy	0.667	4.21	4.10	9.44	81.3	14.3	11.3	2.50
Acp	0.683	7.16	3.06	2.40	60.3	10.1	20.9	37.3
Flu	0.442	2.68	3.34	3.70	54.8	4.41	2.55	7.05
PA	0.580	5.34	5.86	3.37	89.9	8.17	1.37	8.03
Ant	0.046	0.376	0.798	0.412	14.4	1.12	0.185	0.933
FL	0.194	1.41	1.29	0.84	24.6	3.89	0.703	0.759
Pyr	0.640	5.24	4.09	2.47	79.7	14.6	2.48	2.38
CYC	0.083	0.422	1.17	9.12	313	24.1	2.43	5.34
BaA	0.252	0.673	1.09	0.079	4.67	0.844	0.177	0.278
CHR	0.030	0.278	0.569	0.259	8.68	1.58	0.168	0.199
BbF	0.333	1.00	1.73	1.18	38.1	6.05	1.051	0.932
BkF	0.145	0.507	0.492	0.622	10.6	2.03	0.309	0.507
BeP	0.473	2.88	1.57	2.93	40.6	5.48	2.65	1.04
BaP	2.25	3.07	15.5	4.03	285	8.64	1.87	3.12
PER	0.338	3.10	2.93	5.01	52.1	3.74	0.632	2.13
IND	0.050	0.102	0.034	0.444	3.08	0.664	0.070	0.340
DBA	0.168	0.700	0.626	2.70	39.2	12.3	0.565	0.513
BbC	0.295	1.42	1.79	1.07	34.6	5.13	0.826	0.836
BghiP	0.049	0.134	0.130	0.254	5.65	1.47	0.222	0.184
COR	0.162	0.833	1.05	0.697	21.5	3.38	0.615	0.583
Total-PAHs	77.0	521	241	179	3970	602	132	184
LMW	71.5	500	207	148	3008	508	117	165
MMW	1.20	8.03	8.21	12.8	430	45.0	5.95	8.95
HMW	4.26	13.7	25.8	18.9	530	48.9	8.81	10.2

<sup>a</sup>BOF: Basic oxygen furnace.

<sup>b</sup>EAF: Electric arc furnace.

<sup>c</sup>Cement 1: Drying of cement raw material.

<sup>d</sup>Cement 2: Pyroprocessing system.

Among these eight stacks, the total-PAH emission factors are in this order: heavy oil boiler > power plant > BOF > coke oven > cement plant > EAF > blast furnace. The LMW-PAHs averaged 75.9% of total-PAH mass emission.

### 3.4. Indicatory PAHs

Many investigations have suggested that compositional differences in PAH resulting from the combustion of different fuels could be exploited for source identification [22–24]. As these PAHs have been characterized, they could be suggested as possible tracers [25]. Several studies have suggested that some specific PAHs or ratios between individual PAHs may be used for source identification [26,27]. Most investigations have focused their attention on particle-bound PAHs [25–27]. However, the mass of the total PAHs is mainly in the gas phase [2]. Therefore, both particle phase and gas phase PAHs

Table 5  
PAH concentrations and its relative standard deviation (RSD) in the ambient air of four receptors ( $n = 6$ )

Receptor	Tzuoo-Yng		Chyan-Jin		Eil-Ling		Nan-Shing	
	Mean (ng/m <sup>3</sup> )	RSD (%)	Mean (ng/m <sup>3</sup> )	RSD (%)	Mean (ng/m <sup>3</sup> )	RSD (%)	Mean (ng/m <sup>3</sup> )	RSD (%)
Nap	105	72.9	197	71.9	153	63.5	133	55.8
AcPy	19.9	75.1	19.9	124	23.2	96.0	24.5	87.0
Acp	25.0	175	4.86	30.8	9.94	77.6	8.41	42.7
Flu	8.21	93.5	5.04	21.8	6.43	34.7	4.92	35.4
PA	12.0	44.5	10.1	17.8	10.7	30.1	7.61	49.5
Ant	1.05	78.0	0.839	44.1	1.32	46.9	0.948	59.7
FL	3.03	68.7	7.47	67.0	1.92	62.2	19.3	121
Pyr	2.60	44.1	2.32	37.7	2.19	50.5	2.64	77.5
CYC	0.842	70.5	0.556	87.2	0.775	72.5	1.44	156
BaA	0.476	39.6	0.352	68.9	0.617	53.0	0.430	27.9
CHR	0.485	43.0	0.351	38.6	0.628	38.9	0.829	92.6
BbF	0.326	103	0.677	46.0	0.965	30.4	1.36	150
BkF	0.521	150	0.136	65.7	0.408	74.2	0.402	146
BeP	0.951	93.6	0.949	89.1	1.21	93.0	1.54	79.1
BaP	1.12	50.3	1.23	34.5	1.81	75.6	1.11	82.0
PER	0.826	103	1.56	86.7	1.94	107	1.54	97.4
IND	1.47	124	0.348	82.5	0.555	63.4	0.299	60.0
DBA	13.2	140	39.1	204	41.2	196	38.6	204
BbC	1.83	78.3	2.17	71.1	3.74	19.2	1.77	22.8
BghiP	1.22	101	2.23	86.7	2.69	68.6	3.29	85.1
COR	1.12	78.6	0.875	113	1.09	97.3	1.23	71.6
Total-PAHs	198	39.6	298	47.0	264	35.1	253	26.6

should be involved in the investigation of PAH emission. Measured PAH concentrations in the ambient air of four receptors are shown in Table 5.

Combustion source emissions can have an inherently high variation in the ratio of tracer compounds [28]. Because the same PAH may be generated by each different source, the value of using PAHs depends on how different the patterns of the PAHs are from each source. The following formula was applied to define the indicatory PAHs [29]:

$$\text{Ratio}_{ji} = \frac{(X_i/\sum X)_j}{(X_i/\sum X)_{\min}}$$

where:  $X_i$  is the  $i$ th individual PAH (gas phase plus particulate phase) concentration;  $(X_i/\sum X)_j$  is the quotient of  $i$ th individual PAH concentration divided by the summation of 21 PAH concentrations of emission source  $j$ ;  $(X_i/\sum X)_{\min}$  is the quotient of  $i$ th individual PAH concentration divided by the summation of 21 PAH concentrations which are the minimum of all the emission sources. A higher value of  $\text{Ratio}_{ji}$  means that the concentration of  $i$ th PAH from emission source  $j$  is higher than those of other sources.

Table 6  
 Indicatory PAHs for various major sources

Category		Detail information	Indicatory PAHs	References
Stationary sources	Steel industry	Blast	BaP, BaA	This study
		BOF <sup>a</sup>	PER, BeP	This study
		Coke	BaP, COR	This study
		EAF <sup>b</sup>	CYC, PER	This study
	Cement		AcPy, Acp, Ant	This study
	Power plant	Coal	CYC, DBA	This study
Heavy oil burner			CYC, BaP	This study
IWI <sup>c</sup>			IND, CHR	[30]
Mobile Sources	Diesel vehicle		AcPy, FL	[31]
	Gasoline-powered vehicle		Flu, CHR	[32]

<sup>a</sup>BOF: Basic oxygen furnace.

<sup>b</sup>EAF: Electric arc furnace.

<sup>c</sup>IWI: Industrial waste incinerator.

In addition to the eight stationary industrial stacks, an industrial waste incinerator, a diesel engine and a gasoline-powered engine were selected and combined for the identification of indicatory PAHs in this study. The highest two ratio values of PAHs for each source were recognized as the indicatory PAHs.

The determination of indicatory PAHs from emission sources is the first step for the apportionment of PAH contribution to the ambient air. Table 6 lists the indicatory PAHs of various sources. Nap is excluded from the factor analysis because the concentration is much higher than other PAHs. Anyway, in a strict sense, Nap is not polycyclic aromatic hydrocarbons; it is bicyclic. It is sometimes regarded as a volatile organic compound (VOC). The indicatory PAHs from these industrial stacks are primary 4- and 5-ringed PAHs (BaP, BaA, PER, BeP, CYC and DBA) except for the cement plant. The indicatory PAHs of the cement plant are AcPy, Acp and Ant, which are all 3-ringed PAHs, while those of the industrial waste incinerator are IND and CHR. For mobile sources (diesel- and gasoline-powered vehicles), the indicatory PAHs are mainly lower molecular weight PAHs (AcPy, FL and Flu).

### 3.5. Contribution of major PAHs to the receptor ambient air

Factor analysis (FA) is a technique which can be used to reduce the dimensionality of a data matrix by creating new variables from groupings of old ones, and therefore a number of minor sources grouped together may indicate combined sources. FA in this study was carried out using the statistical analysis system (SAS) software [33].

Factor loadings of the 'orthogonal or oblique transformations' solutions of the FA for the combined four receptors in southern Taiwan were obtained, and the major results are summarized in Table 7. The factors were retained as those having a variance > 1.0 after an orthogonal rotation [19]. The factor loadings greater than 0.80 were grouped together and regarded as major PAHs. The major PAHs of Factor 1 were AcPy and BbC. By the indicatory PAHs of emission sources proposed by this study (Table 6), the major

Table 7  
Result of factor analysis for four receptors ( $n = 20$ )

PAHs	Factor number			
	Factor 1	Factor 2	Factor 3	Factor 4
AcPy	<b>0.816</b> <sup>a</sup>	-0.043	0.275	-0.047
Acp	-0.176	0.039	<b>0.889</b>	-0.039
Flu	-0.065	0.034	<b>0.973</b>	-0.039
PA	0.210	0.032	<b>0.899</b>	0.065
Ant	-0.009	0.361	0.596	0.581
FL	0.054	-0.004	-0.154	-0.188
Pyr	0.335	0.791	0.392	0.012
CYC	-0.374	<b>0.878</b>	0.092	0.162
BaA	0.328	-0.009	0.021	0.703
CHR	0.243	<b>0.917</b>	0.160	0.140
BbF	-0.082	<b>0.931</b>	-0.120	0.208
BkF	0.575	-0.074	0.121	0.099
BeP	0.702	0.600	-0.151	0.113
BaP	-0.145	0.313	0.129	<b>0.839</b>
PER	0.306	0.300	-0.243	0.779
IND	0.001	0.001	0.115	0.018
DBA	-0.518	-0.226	-0.089	-0.246
BbC	<b>0.803</b>	0.264	-0.193	0.078
BghiP	0.363	0.564	-0.378	0.376
COR	0.678	-0.019	-0.162	-0.193
Eigenvalue	6.04	4.05	3.05	1.66
V <sup>b</sup>	6.04	4.05	3.05	1.66
% <sup>c</sup>	28.8	19.3	14.3	7.91
Major PAH	AcPy, BbC	CYC, CHR, BbF	Acp, Flu, PA	BaP
Pollution Sources	Diesel, Cement	IWI, Gasoline	Cement, Gasoline	Blast, Coke

<sup>a</sup>The bold text means that the factor loading is greater than 0.80.

<sup>b</sup>Variance explained by each factor.

<sup>c</sup>The percentage of variance explained by each factor.

pollution sources of Factor 1 were diesel vehicles and the cement plant; those of Factor 2 were the industrial waste incinerator (IWI) and gasoline powered vehicle; those of Factor 3 were the cement plant and gasoline powered vehicle; and those of Factor 4 were the blast furnace and the coke oven (Table 7).

In this study, the FA was also carried out for the four receptors separately, and the major results are listed in Table 8. For the receptor Tzuoo-Yng, only three factors were retained for orthogonal rotation and these three factors explained 94.0% of the variance. The major PAH pollution sources suggested by the FA were the BOF and the EAF for Factor 1, diesel- and gasoline-powered vehicles for Factor 2, the power plant and the industrial waste incinerator (IWI) for Factor 3 of receptor at Tzuoo-Yng. As to the receptor at Chyan-Jin, the pollution sources were predicted as diesel vehicles, the IWI and the blast furnace for Factor 1, the BOF for Factor 2 and gasoline-powered vehicles for Factor 3. These three factors accounted for 85.1% of the total variance. Chyan-Jin is located downtown in the city, which has heavy traffic; thus, the diesel and gasoline-powered vehicles are the major contributors of ambient air PAHs. Besides, the industrial

Table 8  
Results of factor analysis for the four receptors, individually

		Factor number			
		Factor 1	Factor 2	Factor 3	Factor 4
Receptor: Tzuoo-Yng					
% <sup>a</sup>		37.4	35.9	20.7	—
Major PAH	BkF, BeP, PER, BbC, BghiP		Acp, Flu, PA, Ant, FL	DBA, BbF, IND	—
Pollution					
sources	BOF, EAF		Diesel, Gasoline	Power plant, IWI	—
Receptor: Chyan-Jin					
%		43.5	25.7	15.9	12.8
Major PAH	Ant, FL, Pyr, BeP, CHR, BaA		PER, BbC, BghiP	PA, Flu	BkF
Pollution					
sources	Diesel, IWI, Blast		BOF	Gasoline	N.A. <sup>b</sup>
Receptor: Ell-Lin					
%		35.7	27.8	22.6	12.0
Major PAH	AcPy, BeP, BbC, IND,		Acp, PA, Flu, FL	Ant, BaA, BaP	BbF
Pollution					
sources	EAF, Cement, BOF, IWI		Diesel, Gasoline	Blast, Coke	N.A.
Receptor: Nan-Shing					
%		47.0	34.8	13.7	—
Major PAH	Ant, Pyr, BeP, PER, CHR, BbF, BaP, CYC		Flu, PA, IND, COR	Acp, FL	—
Pollution					
sources	Blast, Coke, Heavy oil plant, EAF, BOF		Gasoline, IWI	Diesel	—

<sup>a</sup>The percentage of variance explained by each factor.

<sup>b</sup>Not available.

waste incinerator (IWI) and steel mill are nearby. The Factor analysis also related BOF and blast furnace to the receptor. The FA result of this receptor fitted well with the actual situation. As to the receptors of Ell-Ling and Nan-Shing, they are located near the steel mill, the power plant and the industrial waste incinerator, and the FA results showed these two receptors received multiple sources of PAH emission.

It is of limited value if all the observed variables are more or less uncorrelated, and it has been recommended that at best, FA should be viewed only as an approximation to reality [34]. The PAH source apportionment was difficult to identify for this essential reason. However, in this study the cursory qualitative analysis of PAH emission by FA is shown to be reasonable.

#### 4. Conclusions

(1) The mass distribution of PAHs in the whole sampling equipment was 3.56% in the particulate phase, 3.58% in the cooling water, 0.896% in the pipe residual and 92% in the gas phase. It is recommended that, in order to reduce the system error for the measured PAH data, the PAH samples for the cooling water and pipe residual should be determined and included.

(2) Combustion of heavy oil produced considerably higher 4, 5 and 6 + 7-ring PAH concentrations than other stacks, and these PAHs would be more harmful to humans. The HMW PAH concentration was significantly higher for the coke oven, the electric arc furnace and heavy oil combustion.

(3) Measured total-PAHs emission factors are between 77.0 and 3970  $\mu\text{g}/\text{kg}$  feedstock, while BaP emission factors are between 1.87 and 15.5  $\mu\text{g}/\text{kg}$  feedstock. Among these eight emission sources, the heavy oil plant has both the highest total-PAH and BaP emission factors. PAH emission factors are affected by incoming fuel, the manufacturing processes and the air pollution control devices.

(4) Compositional differences in PAH resulting from the combustion of different fuels could be exploited for source identification. As these PAHs have been characterized, they could be suggested as possible tracers. Indicator PAHs from various emission sources were identified by this study. The indicator PAHs from these industrial stacks are primarily 4- and 5-ringed PAHs (BaP, BaA, PER, BeP, CYC and DBA) except for the cement plant. The indicator PAHs of the cement plant are AcPy, Acp and Ant, which are all 3-ringed PAHs. The indicator PAHs of the industrial waste incinerator are IND and CHR. The indicator PAHs of mobile sources (diesel- and gasoline-powered vehicles) are mainly lower molecular weight PAHs (AcPy, FL and Flu).

(5) The cursory, qualitative analysis of PAH emissions by FA used in this study was shown to be practicable.

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