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Journal of Hazardous Materials A69 (1999) 1–11

**Journal of
Hazardous
Materials**

www.elsevier.nl/locate/jhazmat

PAH emission from the industrial boilers

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Received 6 May 1998; received in revised form 12 April 1999; accepted 25 May 1999

Abstract

Polycyclic aromatic hydrocarbons (PAHs) emitted from 25 industrial boilers were investigated. The fuels used for these 25 boilers included 21 heavy oil, two diesel, a co-combustion of heavy oil and natural gas (HO + NG) and a co-combustion of coke oven gas and blast furnace gas (COG + BFG) boilers. PAH samples from the stack flue gas (gas and particle phases) of these 25 boilers were collected by using a PAH stack sampling system. Twenty one individual PAHs were analyzed primarily by a gas chromatography/mass spectrometer (GC/MS). Total-PAH concentration in the flue gas of 83 measured data for these 25 boiler stacks ranged between 29.0 and 4250 $\mu\text{g}/\text{m}^3$ and averaged 488 $\mu\text{g}/\text{m}^3$. The average of PAH-homologue mass ($F\%$) counted for the total-PAH mass was 54.7%, 9.47% and 15.3% for the 2-ring, 3-ring and 4-ring PAHs, respectively. The PAHs in the stack flue gas were dominant in the lower molecular weight PAHs. The emission factors (EFs) of total-PAHs were 13 300, 2920, 2880 and 208 $\mu\text{g}/\text{kg-fuel}$ for the heavy oil, diesel, HO + NG and COG + BFG fueled-boiler, respectively. Nap was the most predominant PAH occurring in the stack flue gas. In addition, the EF of 21 individual PAHs in heavy-oil boiler were almost the highest among the four various fueled-boilers except for those of FL and BkF in the diesel boiler. Furthermore, the EF of total-PAHs or BaP for heavy oil were both one order of magnitude higher than that for the diesel-fueled boiler. © 1999 Elsevier Science B.V. All rights reserved.

Keywords: PAH; Emission; Industrial boiler; Heavy oil; Diesel; Natural gas; Coke oven gas; Blast furnace gas

1. Introduction

Polycyclic aromatic hydrocarbons (PAHs) and their derivatives are widespread harmful compounds generated by incomplete combustion of organic material arising, in part, from natural combustion such as forest fires and volcanic eruptions but for the most

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important part from human activities [1–3]. Many investigations have focused on PAH emission from mobile sources [4–9] which are well understood, but far less research has concentrated on that from stationary sources [10–14]. Industry plays an important role in the development of Taiwan. The industrial boiler, the core of industry, is a necessary facility and a major stationary source of PAH emission in most of the industrial plants. The quantities and characteristics of PAHs emitted from industrial boilers will depend on several factors: the type of input (fuel, additive, etc.), air pollution control devices, etc. [15]. Choice of fuel is usually a matter of economics, but it will deeply influence the PAH emission, which comes primarily from the unburnt fuel [16]. Owing to the difficulty and danger of the stack sampling work, only a few previous reports have focused on the PAH emission from industrial boilers. However, coal-fired industrial boilers generally give a higher emission relative to the energy produced.

Davies et al. [12] investigated PAH emission from municipal incinerators, and the results showed that the greatest daily emission of PAH was near one order of magnitude in the solid residues higher than that in the stack gases. Kenji and Mikihiro [14] found that PAHs concentration increased logarithmically to the plastic content (0%–24%) in municipal waste when the operational temperature was 850°C. In addition, emission factors (EFs) for PAHs can be thought of as the amounts of PAHs released per unit feedstock or per unit product. EF can be used for the estimation of air-pollutant release amounts and can serve as the reference in the setting of national and international environmental policies, protection strategies and regulations. A weighted EF of seven types of coal-fired power plants was found to be 19 $\mu\text{g}/\text{kg}$ coal charged [17–19]. Biomass, an alternative fuel, has attracted great attention from the viewpoint of waste recycling. In a study of a small 2 MW hot water boiler, the combustion of wood and peat gave EFs of 2 and 15 mg PAH/kg fuel, respectively [2,20]. Oil-fired power plants in Sweden have been estimated to emit 10 μg PAH/kg oil [21]. Oil-fired intermediate boilers (6–8 MW) have an EF of 23 $\mu\text{g}/\text{kg}$ oil [17,18]. The intermediate boilers (1.2 MW) heated by premixed gas burners indicate an EF of 1 mg/kg gas burned [17,18].

The emission of PAHs from eight various stacks (blast furnace, basic oxygen furnace, coke oven, electric arc furnace, heavy oil plant and cement plant) in southern Taiwan was investigated by Yang et al. Total-PAH EFs of these eight stationary sources were between 77.0 and 3970 $\mu\text{g}/\text{kg}$ feedstock, while BaP (most carcinogenic PAH) EFs were between 1.87 and 15.5 $\mu\text{g}/\text{kg}$ feedstock [22].

The main objective of this study was to investigate the concentration and EF of 21 individual PAHs among 25 industrial boilers which consumed five different fuels: heavy oil, diesel, coal, natural gas and blast furnace gas. This information is not only required for PAH control, but also useful for the impact assessment on both ambient air quality and health.

2. Experimental section

2.1. Industrial boiler stacks

Totally, 25 industrial boiler stacks were investigated in this study. The information of these stacks is shown in Table 1. The fuels used for these boilers included heavy oil

Table 1
Sampling information for the boiler stacks

Stack no.	Inner diameter of stack (mm)	Fuel consumption rate (kg/h)	Gas flow rate in the stack (m ³ /s)	Temperature at the inlet of sampling probe (°C)	Number of samples
H-1	850	399	3.12	297	3
H-2	600	148	1.42	341	3
H-3	400	69.9	0.49	261	3
H-4	700	312	3.25	340	3
H-5	600	115	1.73	303	3
H-6	2100	4555	34.2	143	4
H-7	1600	1863	10.0	158	3
H-8	1400	3389	14.6	302	3
H-9	1000	296	2.43	227	3
H-10	900	212	1.45	344	4
H-11	500	78.1	0.92	311	3
H-12	700	1035	8.15	250	4
H-13	1800	1841	11.5	275	3
H-14	400	109	0.38	186	4
H-15	2200	1840	7.13	192	3
H-16	600	92.0	0.43	218	4
H-17	750	142	1.27	266	3
H-18	600	139	1.13	235	3
H-19	1000	656	5.05	303	3
H-20	600	312	1.18	278	4
H-21	1100	393	1.33	198	4
D-1	500	36.8	0.59	157	3
D-2	200	13.4	0.40	529	3
HG-1	2100	4050	49.2	143	4
CB-1	2500	80 600	174	170	3

(a) Fuel consumption rate of stack HG-1 = natural gas 2000 kg/h + heavy oil 2050 kg/h.

(b) Fuel consumption rate of stack CB-1 = coke oven gas 2000 kg/h + blast furnace gas 78 600 kg/h.

(c) Heat Capacity of Fuels, Heavy Oil (HO) = 9800 kcal/kg; Diesel = 10 330 kcal/kg; Natural gas (NG) = 10 960 kcal/kg = 9134 kcal/Nm³; Coke oven gas (COG) = 11 540 kcal/kg = 4553 kcal/Nm³; Blast furnace gas (BFG) = 605 kcal/kg = 792 kcal/Nm³.

(boiler H-1–H-21), diesel (boiler D-1 and D-2), co-combustion of heavy oil and natural gas, HO + NG (boiler HG-1), and co-combustion of coke oven gas and blast furnace gas, COG + BFG (boiler CB-1).

2.2. PAHs 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 (PSS) [22]. The PSS was equipped with a sampling probe with a filter holder, a cooling device, a two stage glass cartridges with PUF and XAD-2, a pump, and a flow meter. The pump in the PSS was installed after the flow meter to suction the gas sample. A sampling probe with a filter holder was connected to the

sampling port of the stack. This filter was used to collect particulate and particle-phase PAHs from the stack. A glass cartridge containing a 5 cm polyurethane foam (PUF) plug followed by 3.0 cm XAD-2 resin and finally a 2.0 cm PUF plug was used to collect the gas phase PAHs. A cooling device was installed between the filter holder and the glass cartridge holder to reduce the temperature of gas entering the glass cartridge lower than 28°C and to prevent the breakthrough of lower molecular weight PAHs from the glass cartridge.

The tube-type glass fiber filters were cleaned by both distilled–deionized water and solvent solution (a mixture of *n*-hexane and dichloromethane, v:v = 1:1) for 24 h in a Soxhlet extractor and weighed before and after sampling to determine the amount of particulate collected. PUF plugs and resin were always stored and transported in clean screw-capped jars with Teflon cap liners. Glass fiber filters were transported to and from the field in a prebaked glass bottle and were wrapped with aluminum foil.

Breakthrough tests were investigated by three stages of XAD-2 cartridge. These three stages of XAD-2 resin were analyzed individually and compared for the PAH mass collected in each layer. Three breakthrough tests were investigated in this study and no significant PAH mass was found to be collected in the third stage of XAD-2 resin.

2.3. PAH analysis

After sampling, the samples were removed from the PSS and brought back to the laboratory. The samples were put in a desiccator for 24 h to attain the moisture equilibrium. These samples were weighed with the microbalance to determine the mass of particulate collected. Next, they were extracted and then the extract concentrated, cleaned up, and reconcentrated before GC/MS analysis. The main steps required for PAHs analysis are described below.

2.4. Extraction

The glass fiber filters and PUF/XAD-2 samples were extracted, respectively, with solvent solution (a mixture of *n*-hexane and dichloromethane, v:v = 1:1) for 24 h in a Soxhlet extractor to separate PAHs from the particulate and PUF/XAD-2 cartridge, respectively.

2.5. Concentration, cleanup and reconcentration

The extract was purged with nitrogen (flow rate 1.0 L/min) to concentrate it to 2 ml for the following cleanup procedure. The cleanup procedure removes pollutants such as sulfur compounds which would coelute with PAHs from the clean-up column. The cleanup column (I.D. = 1 cm) contained glasswool in the bottom. Fifteen grams of 3% deactivated silica gel were mixed with 50 ml *n*-hexane and put into the cleanup column followed by 1 cm of anhydrous sodium sulfate. Next, 30 ml of hexane was added to wash the sodium sulfate and the silica gel. Just prior to exposure of the sodium sulfate layer to the air, the elution of the hexane was stopped by closing the stopcock on the

cleanup column and the eluate was discarded. Next, the concentrated sample was transferred onto the column, and the wall of the vessel was rinsed twice with 2 ml hexane. Next 200 ml of 6% diethylether in hexane was added to the column and allowed to flow through the column at a rate of 3–5 ml/min, and the eluant collected. The collected eluant from the clean up procedure was reconcentrated to exactly 0.5 ml with nitrogen (flow rate = 1.0 l/min).

2.6. Gas chromatography / mass spectrometer

The identification and quantification of PAHs was accomplished by using a GC (Hewlett-Packard 5890) with a mass selectivity detector (MSD) (Hewlett-Packard 5972A). This GC/MS was controlled by a computer workstation and was equipped with a Hewlett-Packard capillary column (HP Ultra 2–50 m × 0.32 mm × 0.17 μm), a HP-7673A automatic sampler, injection volume = 1 μl, splitless injection at 300°C, the ion source temperature = 310°C, oven temperature from 50°C to 100°C at 20°C/min; 100°C to 290°C at 3°C/min; hold at 290°C for 40 min. The primary and secondary ion number of PAHs was determined by using the scan mode for pure PAH standards. Then, the quantification of PAHs was performed by using the selectivity 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).

The GC/MS was calibrated with a diluted standard solution of sixteen PAH compounds (PAH Mixture-610M from Supelco) plus five individual PAHs (from Merck). The masses of PAHs were calculated by comparing the response factor of standard solution at the same GC/MS relative retention time (RRT). Analysis of serial dilution of PAH standards found that the limit of detection of GC/MS for individual PAH compounds was between 21 and 474 pg. For PSS, the limit of qualification was between 10.8 and 34.2 ng/m³. Ten consecutive injections of a PAH 610-M standard yielded an average relative standard deviation (RSD) of GC/MS integration areas of 6.6% with a range between 3.5% and 10.2%.

PAHs recovery efficiencies were determined by processing a solution containing known PAH concentrations through the same experimental procedure used for the samples. This study showed the recovery efficiency of PAHs varied between 0.732 and 1.14 and averaged 0.853. The blank tests for PAHs were accomplished by using the same procedure as the recovery–efficiency tests without adding the known standard solution before extraction. Analyses of field blanks, including the glass fiber filter and PUF/XAD-2 cartridge found no significant contamination (integrated area < detection limit). The quality assurance and quality control of all PAH samples were performed similarly with those reported by Yang et al. [22] and Sheu et al. [23].

2.7. Trial sampling

Prior to formal sampling, several trial samplings were investigated to do the breakthrough tests and to obtain the optimum duration of sampling. Normally, a sampling duration of 30 min is enough for the PAH analyses.

3. Results and discussion

3.1. Total-PAH concentration

The boiler H-18 was found to have the highest mean total-PAH concentration (gas + particle phases) ($3530 \mu\text{g}/\text{Nm}^3$), while the boiler D-2 had the lowest mean total-PAH concentration ($33.0 \mu\text{g}/\text{Nm}^3$) (Table 2). Total-PAH concentration in the flue gas of 83 measured data for these 25 boiler stacks ranged between 29.0 and $4250 \mu\text{g}/\text{Nm}^3$ and averaged $488 \mu\text{g}/\text{Nm}^3$. The mean total-PAH concentration for these 25 boiler stacks was $\sim 25\%$ of magnitude lower than those measured by previous study ($648 \mu\text{g}/\text{m}^3$) — the waste ion-exchange resin incineration [16]. The mean total-PAH

Table 2
Total-PAH concentration

Stack no.	Total-PAH concentration range ($\mu\text{g}/\text{Nm}^3$)	Total-PAH concentration mean ($\mu\text{g}/\text{Nm}^3$)	RSD (%)
H-1	151–171	164	6.80
H-2	590–908	710	24.1
H-3	242–658	398	56.7
H-4	45.3–73.0	58.0	23.9
H-5	88.3–96.0	93.0	4.70
H-6	147–187	161	14.1
H-7	165–272	221	24.3
H-8	124–247	165	42.9
H-9	300–520	388	30.0
H-10	102–279	212	37.0
H-11	138–222	175	24.5
H-12	1350–2730	1940	29.9
H-13	301–521	420	26.5
H-14	125–520	322	65.5
H-15	166–223	191	15.3
H-16	204–322	273	19.1
H-17	1280–2980	2170	39.9
H-18	2720–4250	3530	21.8
H-19	30.4–88.5	64.4	47.0
H-20	52.0–92.7	71.3	23.6
H-21	126–248	164	20.3
D-1	77.0–142.0	119.8	30.9
D-2	29.0–36.5	33.0	11.5
HG-1	65.5–165.3	103.3	65.9
CB-1	31.0–62.8	43.5	38.8

concentrations for different fuels, heavy oil, diesel, HO + NG, and COG + BFG, were 566, 76.4, 103.3 and 43.5 $\mu\text{g}/\text{m}^3$, respectively. It's interesting that the stack CB-1 had the highest fuel consumption rate (Table 1), but had the lowest mean total-PAH concentration (43.5 $\mu\text{g}/\text{m}^3$). The mean total-PAH concentration in the H-type stack (heavy oil) was approximately one order of magnitude higher than that in the CB-1 stack. The PAHs were emitted from the sources mainly due to incomplete combustion. Feeding fuels are one of the key factors affecting the PAH emission. COG + BFG were used as the fuels for the CB-1 boiler. Generally, gas-type fuels always obtained more complete combustion in the industrial boiler, while liquid fuels, particularly, heavy oils containing a larger more amount of PAHs, possessed only an incomplete combustion and thus resulted in a higher concentration of PAHs in the stack flue gas.

3.2. Fraction of PAH-homologue mass (*F*%) for the total-PAH mass

The PAH homologues grouped by the numbers of aromatic ring are 2-ring PAH for Nap, 3-ring PAHs for AcPy, Acp, Flu, PA and Ant, 4-ring PAHs for FL, Pyr, BaA and

Table 3

The fraction of PAH-homologue mass (*F*%) counted for the total-PAH mass

Stack no.	2-ring PAH (%)	3-ring PAHs (%)	4-ring PAHs (%)	5-ring PAHs (%)	6-ring PAHs (%)	7-ring PAH (%)
H-1	26.2	45.6	23.1	4.25	0.70	0.02
H-2	72.8	21.6	4.25	1.60	0.01	ND
H-3	79.1	6.57	12.8	1.64	0.13	0.003
H-4	63.0	7.19	20.6	8.99	0.31	0.12
H-5	52.2	3.42	41.8	2.33	0.11	0.09
H-6	93.3	4.01	0.39	0.97	0.78	0.51
H-7	38.5	8.77	9.13	35.1	8.33	0.12
H-8	18.2	20.8	19.4	19.1	20.3	2.40
H-9	22.6	5.99	29.1	30.6	10.8	0.90
H-10	42.4	11.5	14.6	24.0	7.29	0.20
H-11	44.6	7.65	15.5	22.6	9.32	0.29
H-12	93.3	2.50	1.54	1.52	1.06	0.05
H-13	40.7	8.28	11.7	19.8	18.7	0.77
H-14	59.6	5.60	12.3	13.1	9.04	0.20
H-15	44.7	9.92	12.0	15.9	17.1	0.11
H-16	74.7	3.89	2.39	13.2	5.82	0.07
H-17	95.9	0.64	0.41	1.89	1.18	ND
H-18	96.3	0.81	0.82	1.16	0.74	0.15
H-19	34.6	6.16	4.95	25.3	25.9	3.09
H-20	36.8	6.20	3.28	29.6	23.0	1.16
H-21	47.0	2.32	1.09	19.7	29.6	0.02
D-1	35.3	6.82	53.4	4.11	0.19	0.09
D-2	72.7	13.7	1.49	8.13	1.01	3.02
HG-1	64.3	24.8	7.89	2.80	ND	0.18
CB-1	17.9	1.90	78.4	1.79	0.01	ND
Mean	54.7	9.47	15.3	12.4	7.66	0.54

ND: non-detectable.

CHR, 5-ring PAHs for CYC, BbF, BkF, BeP, BaP, PER, DBA and BbC, 6-ring PAHs for IND and BghiP, and 7-ring PAH for COR. As is shown in Table 3, there are seven flue gases of boiler stacks-H-2, H-3, H-4, H-5, H-6, D-2 and HG-1, whose $F\%$ of 2-ring PAH mass was more than 50%. However, the stack H-1 was dominant in 3-ring PAHs (45.6%) and both stack D-1 and CB-1 were dominant in 4-ring PAHs (53.4% and 78.4%, respectively) (Table 3). The mean fraction of PAH-homologue mass ($F\%$) counted for the total-PAH mass was 54.7%, 9.47% and 15.3% for the 2-ring, 3-ring and 4-ring PAHs, respectively. The mean $F\%$ of 5-ring and 6-ring PAHs was 12.4% and 7.66%, respectively, while the 7-ring PAHs were only 0.54%. The summation $F\%$ of 5-ring, 6-ring and 7-ring PAHs was lower than 21%. These results revealed that the PAHs in the stack flue gas were primarily dominant in the lower molecular weight PAHs.

3.3. Emission factor of PAHs for various fueled-boilers

The mean EF of PAHs for four kinds of fueled-boilers presented by the unit of μg PAH/kg-fuel consumed are shown in Table 4. The mean EFs of total-PAHs were

Table 4

The mean emission factor of PAHs for the various fueled-boilers presented by the unit of μg PAH/kg-fuel consumed

PAHs	(μg PAH/kg-fuel consumed)			
	Heavy oil fueled-boiler	Diesel fueled-boiler	HO + NG fueled-boiler	COG + BFG fueled-boiler
Nap	10900	1263	1835	37.3
AcPy	68.8	21.4	10.1	0.05
Acp	68.9	47.3	22.9	0.10
Flu	340	68.3	72.5	1.55
PA	322	78.8	615	0.23
Ant	109	30.8	9.68	2.10
FL	381	1115	128	158
Pyr	357	108	86.8	4.68
CYC	30.8	4.25	7.00	0.33
BaA	33.1	8.10	3.55	ND
CHR	29.2	5.23	11.8	0.05
BbF	65.5	19.0	2.58	0.15
BkF	37.1	48.3	5.20	0.60
BeP	62.8	21.1	5.33	0.48
BaP	112	26.0	16.7	1.53
PER	38.2	10.2	8.93	0.10
IND	297	2.98	0.05	0.25
DBA	388	11.1	0.80	0.53
BbC	45.1	1.50	32.3	ND
BghiP	130	7.53	ND	ND
COR	24.7	20.3	5.13	ND
Total-PAHs	13300	2918	2879	208

ND: non-detectable.

13 300, 2918, 2879 and 208 $\mu\text{g}/\text{kg}$ -fuel for the heavy oil, diesel, HO + NG and COG + BFG fueled-boiler, respectively. The mean EF of total-PAHs for the heavy oil was 3.4 times higher than that measured by the previous study (3970 $\mu\text{g}/\text{kg}$ feedstock), but the EF of BaP, the most carcinogenic PAH [24], was 61% of magnitude lower than that in the previous study (285 $\mu\text{g}/\text{kg}$ feedstock) [22]. For the heavy-oil fueled boiler, there were 19 individual PAHs that have the EFs more than 30 $\mu\text{g}/\text{kg}$ -fuel consumed except the CHR and COR. For the diesel-fueled boiler, there were eight individual PAHs that have the EF more than 30 $\mu\text{g}/\text{kg}$ -fuel consumed; they were Nap (1263), FL (1115), Pyr (108), PA (78.8), Flu (68.3), BkF (48.3), Acp (47.3), and Ant (30.8 $\mu\text{g}/\text{kg}$ -fuel). For the HO + NG fueled-boiler, there were six individual PAHs that have the EFs more than 30 $\mu\text{g}/\text{kg}$ -fuel consumed; they were Nap (1835), PA (615), FL (128), Pyr (86.8), Flu (72.5) and BbC (32.3 $\mu\text{g}/\text{kg}$ -fuel). For the COG + BFG fueled-boiler, there were two individual PAHs that have the EFs more than 30 $\mu\text{g}/\text{kg}$ -fuel consumed; they were FL (158) and Nap (37.3 $\mu\text{g}/\text{kg}$ -fuel). These results indicate that the Nap is the most predominant PAH occurring in the stack flue gas. This is consistent with the results reported by Yang et al. [22]. However, the magnitude of EF

Table 5

The mean emission factor of PAHs for the various fueled-boilers presented by the unit of μg PAH/ 10^3 kcal of heat generated

PAHs	(μg PAH/ 10^3 kcal of heat generated)			
	Heavy oil fueled-boiler	Diesel fueled-boiler	HO + NG fueled-boiler	COG + BFG fueled-boiler
Nap	1110	51.9	74.8	17.0
AcPy	7.02	0.85	0.41	0.02
Acp	7.03	1.84	0.93	0.04
Flu	34.6	2.68	2.95	0.71
PA	32.9	3.50	25.1	0.10
Ant	11.1	1.23	0.39	0.96
FL	38.9	43.1	5.20	72.6
Pyr	36.4	4.21	3.53	2.14
CYC	3.14	0.18	0.29	0.15
BaA	3.37	0.33	0.14	ND
CHR	2.98	0.21	0.48	0.03
BbF	6.68	0.76	0.11	0.07
BkF	3.78	2.00	0.21	0.28
BeP	6.40	0.89	0.22	0.22
BaP	11.4	1.03	0.68	0.70
PER	3.90	0.43	0.36	0.05
IND	30.3	0.12	ND	0.01
DBA	39.6	0.46	0.03	0.24
BbC	4.60	0.07	1.31	ND
BghiP	13.3	0.33	ND	ND
COR	2.52	0.91	0.21	ND
Total-PAHs	1350	117	117	95.3

ND: non-detectable.

for the heavy-oil boilers reported in this study is approximately two order higher than that reported in the AP-42 of USEPA while the data of CYC, BeP, BaP, PER, BbC and COR reported in the USEPA are missing [25]. Furthermore, the EFs of 21 individual PAHs in the heavy-oil boiler were almost the highest among the four various fueled-boilers except for that of FL and BkF in the diesel boiler. In addition, the EFs of AcPy, CYC and PER for heavy-oil boiler reported in this study averaged 69.1% of magnitude lower than that in the previous study [22].

The mean EF of PAHs for four kinds of fueled-boilers presented by the unit of $\mu\text{g PAH}/10^3 \text{ kcal}$ of heat generated is shown in Table 5. The heat capacities of five different fuels are shown in Table 1. Mean EFs of total-PAHs were 1350, 117, 117 and $95.3 \mu\text{g}/10^3 \text{ kcal}$ of heat generated for the heavy oil, diesel, HO + NG and COG + BFG fueled-boiler, respectively. The EFs of total-PAHs and BaP by the unit of $\mu\text{g}/10^3 \text{ kcal}$ of heat generated for the heavy oil boiler were both approximately one order of magnitude higher than those for the diesel-fueled boiler. These results indicate that the fuel type and the PAH content in the fuel are two of the key factors affecting the PAH EFs from the industrial boilers [22].

According to AP-42 of USEPA [25], the EF was given a rating from A through E, with A being the best. Factor developed from A-rated source test data is taken from many randomly chosen facilities in the industrial population and the source category population is sufficiently specific to minimize variability. In this study, the EF of PAHs reported for the heavy oil-fueled boiler can be rated as "A", while the EF for the diesel, HO + NG and COG + BFG fueled-boilers, respectively, can be rated as "D" or "E". These results provide useful information for estimation of total amounts of PAH emission from the industrial boilers.

4. Conclusions

(1) Total-PAH concentration in the flue gas of 83 measured data for these 25 boiler stacks ranged between 29.0 and $4250 \mu\text{g}/\text{Nm}^3$ and averaged $488 \mu\text{g}/\text{Nm}^3$.

(2) The mean fraction of PAH-homologue mass ($F\%$) counted for the total-PAH mass was 54.7%, 9.47% and 15.3% for the 2-ring, 3-ring and 4-ring PAHs, respectively. The summation of $F\%$ of 5-ring, 6-ring and 7-ring PAHs was lower than 21.0%. The PAHs in the stack flue gas were primarily dominant in the lower molecular weight PAHs.

(3) The EFs of total-PAHs were 13 300, 2918, 2879 and $208 \mu\text{g}/\text{kg-fuel}$ for the heavy oil, diesel, HO + NG and COG + BFG fueled-boilers, respectively. Nap was the most predominant PAH occurring in the stack flue gas. In addition, the EFs of 21 individual PAHs in the heavy-oil boiler were the highest among the four various fueled-boilers except for those of FL and BkF in the diesel boiler.

(4) The EFs of total-PAHs and BaP by the unit of $\mu\text{g}/10^3 \text{ kcal}$ of heat generated for the heavy oil boiler were both approximately one order of magnitude higher than those for the diesel-fueled boiler. These results indicate that the fuel type and the PAH content in the fuel are two of the key factors affecting the PAH EFs from the industrial boilers

Acknowledgements

This research was supported by funds from the National Science Council, Taiwan, Grant No.NSC 84-2621-P006-017.

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