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Emissions of polycyclic aromatic hydrocarbons from fluidized and fixed bed incinerators disposing petrochemical industrial biological sludge

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ABSTRACT

This study investigated the emissions of polycyclic aromatic hydrocarbons (PAHs) from two fluidized bed incinerators (FLBI_A and FLBI_B) and one fixed bed incinerator (FIBI) disposing biological sludge generated from the petrochemical industries in Taiwan. The results of 21 individual PAHs (including low (LM-PAHs), middle (MM-PAHs) and high molecular weight PAHs (HM-PAHs)) were reported. The LM-PAHs mainly dominated the total-PAHs in the stack flue gases, whereas the LM- and HM-PAHs dominated the total-PAHs in the bottom fly, fly ash and WSB effluent. Due to high carcinogenic potencies (= total-BaP_{eq} concentrations) in the bottom ash (195 ng g^{-1}) and WSB effluent (20,600 ng L^{-1}) of the FIBI, cautious should be taken in treating them to avoid second contamination. Lower combustion efficiency and elevated fuel/feedstock (*F*/*W*) ratio for the FIBI led to the highest total emission factor of total-PAHs (38,400 μg kg^{-1}). Lower total-PAH removal efficiencies of wet scrubber (WSB) (0.837–5.89%), cyclone (0.109–0.255%) and electrostatic precipitator (ESP) (0.032%) than those reported elsewhere resulted in high fraction in PAH contributions from the stack flue gases. Lower total-PAH emission factor was found for FLBI_A (2380 μg kg^{-1} biological sludge) with higher combustion efficiency compared to those for FLBI_B (11,500 μg kg^{-1}) and FIBI (38,400 μg kg^{-1} biological sludge), implying that combustion efficiency plays a vital role in PAH emissions.

1. Introduction

Polycyclic aromatic hydrocarbons (PAHs) consisting of two or more benzene rings are generated from the incomplete combustion and/or pyrosynthesis of organic compounds [1,2]. Several individual PAHs, especially benzo[*a*]pyrene, have been recognized to be carcinogenic and mutagenic [3,4]. The PAH carcinogenicity is positively associated with corresponding molecular weight or aromatic rings [5]. Owing to higher molecular weights, particulate PAHs are therefore more carcinogenic than are gaseous PAHs [6]. However, the gaseous PAHs are usually the most abundant PAH group in the urban atmosphere, and more importantly, they can react with other pollutants to form more toxic PAH derivatives [6].

Due to their low solubility and high hydrophobicity, PAHs are adsorbed onto solid particles during wastewater treatment, resulting in sludge containing 1 and 10 mg kg^{-1} of PAHs [7]. Among the disposal alternatives, incineration has the advantages of waste volume reduction and heat recovery, but a large amount of ashes and stack flue gases containing PAHs are released. To date, there have been numerous investigations on the PAH emissions from waste incinerators [8–17]. The results indicated that the feedstock composition, the operating conditions (e.g., combustion temperature, amount of excess air and residence time), as well as the types and removal efficiencies of the air pollution control devices (APCDs) significantly affected the PAH yield during the incineration processes. Based on these influential factors, the PAH emissions from the stacks of various industrial activities vary over a wide range [16].

The objectives of this study were three folds. First, the PAH emissions from the stack flue gases, bottom and fly ashes and APCD effluents of fluidized and fixed bed incinerators (FIBI) disposing the biological sludge were determined in terms of concentrations and emission factors. Secondly, the carcinogenic potencies of PAHs were calculated according to the toxicity equivalency factors (TEFs) [18], and hence this study could be expanded into the perspective of

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Table 1
The background information of the incinerators in this study.

Background information	Type of incinerator		
	FLBI_A	FLBI_B	FIBI
Feedstock	Biological sludge	Biological sludge	Biological sludge
Feeding way	Continuous	Continuous	Batch
Feeding rate (kg h^{-1}) (*W*)	2000	912	415
Auxiliary fuel	Heavy oil	Heavy oil	Heavy oil
Feeding rate (kg h^{-1}) (*F*)	85	130	248
F/*W* ratio	0.043	0.143	0.598
Residence time (s)	5–8	1.5	2
Temperature (°C)			
Incineration chamber	870	800	800
Stack flue gas	130	30	65
Emission rate			
Stack flue gas (N m^3 min^{-1})	216	150	717
Bottom ash (kg h^{-1})	250	NA	40
Cyclone fly ash (kg h^{-1})	102	105	NA
ESP fly ash (kg h^{-1})	18	NA	NA
WSB effluent (m^3 h^{-1})	5	31.5	11.5

Note: NA: not available.

human health. Lastly, the PAH removal efficiencies of cyclone, electrostatic precipitator (ESP) and wet scrubber (WSB) were reported.

2. Experimental

2.1. Background information of incinerators

Two continuous-type fluidized bed incinerators (FLBI_A and FLBI_B), and one batch-type fixed bed incinerator disposing petrochemical industrial biological sludge in Taiwan were studied. The feeding rates of feedstock and auxiliary fuel (i.e., heavy oil in this study) for FLBI_A, FLBI_B and FIBI were 2000, 912 and 415 kg h^{-1}, respectively, as well as 85, 130 and 248 kg h^{-1}, respectively, resulting in the fuel/feedstock (*F*/*W*) ratios of 0.043, 0.129 and 0.598, respectively (Table 1). Other background information of three incinerators is summarized in Table 1

Cyclone, ESP and WSB have been known to perform higher removal efficiencies for particles, but lower removal efficiencies for gases. The cyclone, ESP and WSB were installed for the FLBI_A sequence, while the cyclone and WSB were installed for the FLBI_B in sequence. Nevertheless, the FIBI was equipped with the WSB only.

2.2. Sample collection

In this study, PAHs in the stack flue gas, bottom ash, fly ash and WSB effluent were determined. The stack flue gas was collected isokinetically with a PAH Sampling System (PSS), which has been proved comparable with the US EPA Modified Method 5 (MM5; 40CFR60) for collecting semi-volatile organic compounds (SVOCs). The gaseous PAHs were collected with two stages of glass cartridges packed with XAD-2 resin and supported by two polyurethane foams (PUFs) on the top and bottom. The particulate PAHs were collected with a pre-cleaned tube-type glass fiber filter (Whatman Glass Filter Thimble, 25 × 90 mm^2). The PAH contents (not reported here) found in the cooling water and sampling pipe residual (rinsed with *n*-hexane) were integrated into those in the stack flue gas, although knowing that their average total-PAH mass fractions (0.843 and 0.651%, respectively) were much smaller than those in the gaseous (93.9%) and particulate (4.60%) phases. Three sampling runs with a sampling interval of 3 months were conducted to collect a total of nine samples of stack flue gases for each incinerator. Each sampling run was performed for 20 min.

To obtain good representative samples, the bottom ash (from the FLBI_A and FIBI) and fly ashes (cyclone ash from the FLBI_A and FLBI_B; ESP ash from the FLBI_A) were collected twice with glass bottles (pre-treated with 10% HNO_3, rinsed with distilled water and wrapped with aluminium foil to avoid PAH decay) during the flue gas sampling period at intervals of 10 min and combined to a composite fly ash sample. Nine composite fly ash samples were measured for PAHs for each device. The WSB effluents were collected every 2 min (totally 10 times) concurrently with the flue gas sampling. Nine samples of effluents were collected for each device.

Breakthrough tests were investigated with three stages of XAD-2/PUF cartridge. The PAH mass in each cartridge was separately analyzed. The results showed that similar to previous study [8], the average total-PAH mass distributions for the first (70.2%), second (25.3%) and third (4.50%) stages of the cartridge sequentially decreased, suggesting that no significant PAH mass was detected in the third stage of the cartridge.

2.3. Sample analysis

PAH extraction and analysis of samples were performed according to Wang et al. [8]. Briefly, except samples in the cooling water, pipe residual and WSB effluents extracted using a liquid–liquid phase separation technique with 1:1 mixture of water and dichloromethane, other samples were separately Soxhlet extracted with 1:1 mixture of *n*-hexane and dichloromethane 24 h. All the extracts were then concentrated, cleaned-up and re-concentrated to exactly 1.0 mL. PAH contents were detected with a gas chromatography/mass spectrometry (GC/MS) (HP 5890A/5972) equipped with a capillary column (HP Ultra 2–50 m × 0.32 mm × 0.17 μm). The operating conditions of GC/MS and PAH determination can be found elsewhere [13].

Twenty one PAHs were categorized based on their molecular weights: low molecular weight (LM-) PAHs were two- and three-ringed PAHs including naphthalene (Nap), acenaphthylene (AcPy), acenaphthene (Acp), fluorene (Flu), phenanthrene (PA), anthracene (Ant); middle molecular weight (MM-) PAHs were four-ringed PAHs including fluoranthene (FL), pyrene (Pyr), cyclopenta(*c*,*d*)pyrene (CYC), benzo(*a*)anthracene (BaA), chrysene (CHR); high molecular weight (HM-) PAHs were five-, six- and seven-ringed PAHs including 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), dibenzo(*a*,*h*)anthracene (DBA), benzo(*b*)chrycene (BbC), benzo(*ghi*)perylene (BghiP) and coronene (COR). It is highlighted that BaA, CHR, BbF, BkF, BaP, IND, DBA and BghiP are classified as potential human carcinogens [19].

Five internal standards (Nap-d8, Acp-d10, PA-d10, CHR-d12 and PER-d12) were spiked to monitor analytical recovery efficiencies (ranging from 80.6 to 92.1%) and correct the original recovery efficiencies of the 21 individual PAHs (their corrected recovery efficiencies ranged from 75.9 to 107%). Analyses of field blanks, including the glass bottle, glass fiber filter and XAD-2/PUF cartridge showed no significant PAH contamination.

2.4. Carcinogenic potency

The carcinogenic potency of a given PAH compound can be expressed by the BaP_{eq}, which is the product of its toxic equivalency factor (TEF) and its concentration. The TEF list proposed by Nisbet and LaGoy [18] reflects well the actual state of knowledge on the toxic potency of each individual PAHs [20], and therefore was adopted in this study. The carcinogenic potency of the total-PAHs (i.e., total-BaP_{eq}) was the sum of individual BaP_{eq} of the 21 individual PAHs.

Table 2
Mean concentrations ($\mu g\,N\,m^{-3}$) of individual PAH compounds, total-PAHs, LM-PAHs, MM-PAHs, HM-PAHs and total-BaP_{eq} in the stack flue gas of FLBI_A, FLBI_B and FIBI.

Compound	FLBI_A ($n=9$)	FLBI_B ($n=9$)	FIBI ($n=9$)
Nap	52.5	674	85.6
AcPy	4.39	17.8	11.2
Acp	0.954	4.79	11.1
Flu	2.5	4.67	10.8
PA	135	118	25.8
Ant	0.707	9.14	1.7
FL	5.06	14.8	20.7
Pyr	1.33	21.7	14.4
CYC	0.215	1.31	2.15
BaA	0.18	3.09	4.95
CHR	0.038	4.64	8.75
BbF	1.86	1.34	5.82
BkF	0.116	2.66	3.95
BeP	0.516	10.3	8.42
BaP	0.522	24.0	19.4
PER	0.206	4.81	6.54
IND	0.043	15.2	11.3
DBA	0.085	36.1	8.45
BbC	0.130	5.11	8.22
BghiP	0.096	8.11	11.3
COR	10.5	0.182	1.91
LM-PAHs	196	828	146
MM-PAHs	6.61	44.2	48.8
HM-PAHs	14.3	109	87.5
Total-PAHs	217	982	282
Total-BaP_{eq}	0.932	62.9	31.0

Table 3
Mean concentrations ($ng\,g^{-1}$) of individual PAH compounds, total-PAHs, LM-PAHs, MM-PAHs, HM-PAHs and total-BaP_{eq} contained in the bottom ash, cyclone fly ash and ESP fly ash of FLBI_A, FLBI_B and FIBI ($n=9$).

Compound	FLBI_A			FLBI_B	FIBI
	Bottom ash	Cyclone fly ash	ESP Fly ash	Cyclone fly ash	Bottom ash
Nap	9.30	37.2	17.2	23.3	61.2
AcPy	0.723	2.91	4.21	9.16	13.7
Acp	1.51	1.30	1.49	12.7	18.1
Flu	0.300	2.10	1.42	8.83	8.09
PA	0.039	2.50	2.84	1.55	6.74
Ant	0.034	0.255	0.399	1.01	0.706
FL	0.018	0.392	0.523	0.554	2.36
Pyr	0.03	0.062	0.522	0.361	2.06
CYC	0.201	0.119	0.578	0.288	3.76
BaA	0.663	0.115	0.082	1.80	8.06
CHR	0.087	0.014	0.155	1.40	5.72
BbF	ND	3.28	0.205	2.01	12.2
BkF	0.411	1.95	0.609	3.45	8.74
BeP	2.93	4.54	4.41	1.32	9.15
BaP	0.051	4.96	3.13	4.31	40.8
PER	2.26	6.97	8.51	2.95	15.7
IND	0.962	0.054	0.103	13.8	ND
DBA	0.082	0.355	0.311	1.94	150
BbC	0.989	1.18	1.71	8.91	61.4
BghiP	0.449	0.145	0.268	0.922	115
COR	1.58	0.642	0.393	0.659	ND
LM-PAHs	11.9	46.3	27.6	56.6	109
MM-PAHs	0.798	0.583	1.28	4.12	18.2
HM-PAHs	9.92	24.20	20.2	40.6	417
Total-PAHs	22.6	71.0	49.1	101	543
Total-BaP_{eq}	0.351	5.89	3.60	8.50	195

Note: ND: not detectable.

3. Results and discussion

3.1. PAH concentrations in the stack flue gases

Table 2 shows the PAH concentrations (gaseous phase + particulate phase + cooling water + pipe residue) in the stack flue gases of three incinerators. The total-PAH concentration of the FLBI_B ($982\,\mu g\,N\,m^{-3}$) was 4.53 and 3.43 folds higher than those of the FLBI_A ($217\,\mu g\,N\,m^{-3}$) and FIBI ($286\,\mu g\,N\,m^{-3}$). Total-PAHs in the stack flue gases were contributed mostly by Nap and PA, which accounted for 86.4 and 80.7% for FLBI_A and FLBI_B, respectively, but only 39.4% for the FIBI (Table 2). Even though the lighter PAH compounds are less carcinogenic, they can react with other atmospheric pollutants to form more toxic derivatives [6] or bioaccumulate in the fish tissues [21]. Table 2 also shows the carcinogenic potencies associated with the PAH emissions. The total-BaP_{eq} concentrations in the stack flue gases demonstrated the trend (FLBI_B > FIBI > FLBI_A) similar to that for total-PAH concentrations for three incinerators. Four carcinogenic compounds, BbF, BaP, IND and DBA, were found to primarily contribute the total-BaP_{eq} concentrations. Their sums dominating 85.5, 98.2 and 95.3% of the total-BaP_{eq} concentrations for the FLBI_A, FLBI_A and FIBI, respectively, were somewhat similar, implying that the stack flue gases of three incinerators might contain similar carcinogenic potencies.

The PAH-homologue concentration distributions in the stack flue gases shared the same trend (LM-PAHs > HM-PAHs > MM-PAHs) for three incinerators. The above results also implied that the APCDs used in this study were not feasible to control the gaseous PAH emissions. The result that low concentrations of MM- and HM-PAHs for the FLBI_A was probably due to higher combustion efficiency (see Section 3.5) leading to more destruction of MM- and HM-PAHs to LM-PAHs.

3.2. PAH contents in the bottom ashes

No bottom ashes were generated from the FLBI_B, and therefore the PAH contents in the bottom ashes were only reported for the FIBI_A and FIBI. The total-PAH content in the bottom ash of the FIBI ($543\,ng\,g^{-1}$) was 24.0 folds higher than that of the FLBI_A ($22.6\,ng\,g^{-1}$) (Table 3). Wang et al. [9] found that the total-PAH input mass rate of the heavy oil was significant compared to that of the biological sludge, suggesting that higher *F*/*W* ratio resulted in higher PAH emission from incinerator. With better combustion efficiency for the fluidized bed incinerator than for the fixed bed incinerator [13], and lower *F*/*W* ratio for the FLBI_A (0.043) than that for the FIBI (0.598) (Table 1), the total-PAH content in the bottom ash of the FLBI_A was much lower than that of the FIBI.

It is also found that for the FIBI bottom ash, the HM-PAHs (especially DBA and BghiP) contributed to 76.7% ($417\,ng\,g^{-1}$) of the total-PAH content, and led to the high carcinogenic potency ($195\,ng\,g^{-1}$) (Table 3). In spite of high contribution of HM-PAHs (43.8%) to the FLBI_A bottom ash, the HM-PAH content was only $9.92\,ng\,g^{-1}$, resulting in a low carcinogenic potency of $0.351\,ng\,g^{-1}$. In addition, the total-PAH content of the FLBI_A was in the range of surface soil samples from urban areas of Hong Kong [23]. Therefore, high attention should be paid to the reutilization of the FIBI bottom ash.

3.3. PAH contents in the fly ashes

For the FLBI_A, both cyclone ($71.0\,ng\,g^{-1}$) and ESP ($49.1\,ng\,g^{-1}$) fly ashes (Table 3) contained higher total-PAH contents than did the bottom ash ($22.6\,ng\,g^{-1}$) because of higher temperature in the combustion chamber (870 °C) than in the cyclone (240 °C) and ESP (280 °C) and larger particle size of the bottom ash [22] than

Table 4
Mean concentrations (ng L^{-1}) of individual PAH compounds, total-PAHs, LM-PAHs, MM-PAHs, HM-PAHs and total-BaP_{eq} contained in the WSB effluent (liquid and solid phases) of FLBI_A, FLBI_B and FIBI (n = 9).

Compound	FLBI_A		FLBI_B		FIBI	
	Liquid phase	Solid phase	Liquid phase	Solid phase	Liquid phase	Solid phase
Nap	920	226	5190	722	8480	3520
AcPy	1010	95.8	6500	24.6	2440	514
Acp	189	16.1	3340	77.3	2810	666
Flu	58.5	0.059	2740	7.29	2450	466
PA	0.636	0.131	836	27.8	578	894
Ant	5.08	1.80	236	0.837	1090	ND
FL	4.75	0.798	141	9.59	169	538
Pyr	1.24	0.616	76.3	4.97	184	519
CYC	79.5	0.839	63.3	16.3	144	748
BaA	5.18	0.103	113	10.6	361	1200
CHR	8.27	1.12	542	63.6	449	2060
BbF	ND	ND	926	16.2	898	836
BkF	48.3	ND	737	33.5	637	3490
BeP	67.6	2.91	352	15.2	1030	1590
BaP	ND	6.97	1090	23.4	1720	5590
PER	51.6	12.6	1060	15.5	748	2380
IND	12.9	0.129	58.6	12.8	3660	5900
DBA	3.33	22.5	1510	ND	3230	8200
BbC	63.4	48.2	1680	1.70	472	4530
BghiP	3.71	ND	263	115	875	5580
COR	1660	123	103	17.8	152	135
LM-PAHs	2180	340	18800	860	17900	6060
MM-PAHs	19.4	2.64	872	88.8	1160	4320
HM-PAHs	1990	217	7840	267	13600	39000
Total-PAHs	4190	560	27600	1220	32600	49400
Total-BaP_{eq}	20.5	30.5	2860	32.9	5560	15000

Note: ND: not detectable.

those of the cyclone and ESP fly ashes. These led to more PAH vaporization from and less PAH adsorption onto the bottom ashes. Likewise, the ESP fly ash contained lower total- and HM-PAH contents than did the cyclone because the ESP had higher operating temperature (heating the flue gas) than had the cyclone as stated above, even though particle size of the ESP fly ash was smaller than that of the cyclone fly ash. This finding was consistent with that observed by Lee et al. [13]. Besides, the total-PAH content of the cyclone fly ash for the FLBI_B (101 ng g^{-1}) was found to be higher than that for the FLBI_A, indicating lower combustion efficiency for the FLBI_B than the FLBI_A as discussed in Section 3.5. The total-PAH contents of the cyclone and ESP fly ashes were found to be much smaller than those reported for batch hot mix asphalt plants (2030–3670 ng g^{-1}) [24] and medical waste incinerators (13,800–47,000 ng g^{-1}) [13], but were in the range of surface soil samples (7.0–410 ng g^{-1}) from urban areas of Hong Kong [23]. Furthermore, the carcinogenic potencies of both cyclone (5.10 ng g^{-1}) and ESP (4.79 ng g^{-1}) fly ashes were much lower than that of the FIBI bottom ash (195 ng g^{-1}). This implies that the bottom ash of FIBI was more hazardous to the environment than fly ash, and its engineering application and post-treatment requires serious concerns.

3.4. PAH concentrations in the WSB effluents

PAH concentrations in both liquid and solid phases of the WSB effluents were summarized in Table 4. The WSB effluents gained substantial PAH contents during their uses. The total-PAH concentration (82,000 ng L^{-1}) in the WSB effluent of the FIBI was significantly higher than those of the FLBI_A (4750 ng L^{-1}) and FLBI_B (28,820 ng L^{-1}). Similar trends could also be observed for the concentrations of LM-, MM- and HM-PAHs. These trends were probably related to the fact that only the WSB was installed for the FIBI, whereas three and two APCDs were installed for the FLBI_A and FLBI_B, respectively. Furthermore, the F/W ratio was the highest for the FIBI than those for the FLBI_A and FLBI_B (Table 1). It is therefore not surprising that the smallest total-PAH concentration was found in the WSB effluent of the FLBI_A with the exception of COR. Different levels of total-PAHs in the WSB effluents from the incinerations of animal carcass (10,500–45,300 ng L^{-1}) [10], livestock wastes (12,500–14,700 ng L^{-1}) [11] and medical wastes (62,200–124,000 ng L^{-1}) [13] have been reported in the literature.

Interestingly, the WSB effluents contained high concentrations of the LM- and HM-PAHs. Higher water solubility of LM-PAHs drove them to exist with larger quantity in the WSB effluents. HM-PAHs tended to be adsorbed onto the fine particles, and hence their moderately high concentrations could be attributed to the fine particles existing in the WSB effluents.

For the FLBI_A and FLBI_B, the total-PAH concentrations in the liquid phase (LP) were higher than those in the solid phase (SP) (LP/SP ratios = 7.48 and 22.6, respectively), whereas the solid phase dominated the total-PAH concentration of the FIBI (LP/SP ratio = 0.660) (Table 4). A more detailed insight was found that the LP/SP ratios of the HM-PAH and total-BaP_{eq} concentrations were 0.349 and 0.371 for the WSB effluent of the FIBI, whereas those ranged from 0.672 to 86.9 for the WSB effluents of the FLBI_A and FLBI_B. This suggests that more particles carrying HM-PAH and total-BaP_{eq} were removed by the APCDs installed for the FLBI_A (cyclone and ESP) and FLBI_B (cyclone) prior to the WSBs. It is also highlighted that the WSB effluent released from the FIBI only equipped with the WSB requires great care to avoid second contamination due to the high HM-PAH (52,600 ng L^{-1}) and total-BaP_{eq} (20,600 ng L^{-1}) concentrations. It is suggested that, for example, the suspended particles in the sedimentation tanks be solidified and the wastewater effluent be treated with activated carbons.

3.5. PAH emission factors

Table 5 shows the PAH emission factors reported as the micrograms of PAHs released per kilogram of biological sludge. The

Table 5
Emission factors ($\mu g\,kg^{-1}$ biological sludge) of LM-PAHs, MM-PAHs, HM-PAHs, total-PAHs and total-BaP_{eq} contained in the bottom ash, cyclone fly ash, ESP fly ash, WSB effluent and stack flue gas of FLBI_A, FLBI_B and FIBI ($n = 9$).

Compound	Bottom ash	Cyclone	ESP	WSB	Stack flue gas	Total
FLBI_A						
LM-PAHs	11.9	3.94	0.41	10.5	2130	2150
MM-PAHs	0.798	0.049	0.019	0.092	71.6	71.7
HM-PAHs	9.92	2.06	0.305	9.21	155	166
Total-PAHs	22.6	6.04	0.738	19.8	2360	2380
Total-BaP_{eq}	0.351	0.500	0.054	0.212	10.1	10.9
FLBI_B						
LM-PAHs	–	6.67	–	853	8670	9520
MM-PAHs	–	0.49	–	41.6	463	505
HM-PAHs	–	4.80	–	351	1140	1500
Total-PAHs	–	12.0	–	1245	10300	11500
Total-BaP_{eq}	–	1.00	–	125	659	784
FIBI						
LM-PAHs	7.64	–	–	660	18700	19400
MM-PAHs	1.28	–	–	151	6240	6400
HM-PAHs	29.2	–	–	1450	11200	12700
Total-PAHs	38.1	–	–	2260	36100	38400
Total-BaP_{eq}	13.7	–	–	568	3960	4560

Note: –: not applicable.

total emission factor was the sum of the emission factors of the bottom ash, fly ash, WSB effluent and stack flue gas. The result showed that the total emission factor of total-PAHs of the FIBI ($38{,}400\,\mu g\,kg^{-1}$) was 16.1 and 3.34 folds higher than those of the FLBI_A ($2380\,\mu g\,kg^{-1}$) and FLBI_B ($11{,}500\,\mu g\,kg^{-1}$). It is believed that better combustion efficiency was found for the fluidized bed incinerator than for the fixed bed incinerator [13]. Besides, elevated *F*/*W* ratio for the FIBI (Table 1) could also increase the total emission factor since our previous study [9] found a high total-PAH content ($601\,mg\,kg^{-1}$) for heavy oil. Therefore, it is not surprising to note that the FIBI had the highest total emission factor. On the other hand, Table 1 shows that the retention time, *F*/*W* ratio and incineration temperature of the FLBI_A and FLBI_B were 5–8 s, 0.043 and 870 °C, and 1.5 s, 0.143 and 800 °C, respectively. With longer retention time, less total-PAH content from the heavy oil based on the smaller *F*/*W* ratio and higher incineration temperature, it is believed that the combustion efficiency was higher for the FLBI_A chamber than that for the FLBI_B chamber, resulting in smaller total emission factor for the FLBI_A than that for the FLBI_B, despite the same type of incinerator. Besides, referring to the heavy oil feeding rates, it can be deduced that the biological sludge incinerated by the FLBI_B possibly contained higher moisture fraction, resulting in lower combustion efficiency. Similar explanations could be applied to overwhelmingly higher emission factors of HM-PAH and total-BaP_{eq} for the FIBI (12,700 and 4560 $\mu g\,kg^{-1}$, respectively) than those for the FLBI_A (166 and 10.9 $\mu g\,kg^{-1}$, respectively) and the FLBI_B (1500 and 784 $\mu g\,kg^{-1}$, respectively), reflecting that the carcinogenic potency associated with PAH emissions for the FIBI was higher than those for the FLBI_A and FIBI_B.

3.6. PAH removal efficiencies

Taking the FLBI_A as example, the PAH removal efficiencies of the APCDs used in this study were calculated as follows:

$$\eta_{Cyclone} = \left[\frac{ER_{Cyclone}}{ER_{Cyclone} + ER_{ESP} + ER_{WSB} + ER_{ST}}\right] \times 100\%$$

$$\eta_{ESP} = \left[\frac{ER_{ESP}}{ER_{ESP} + ER_{WSB} + ER_{ST}}\right] \times 100\%$$

$$\eta_{WSB} = \left[\frac{ER_{WSB}}{ER_{WSB} + ER_{ST}}\right] \times 100\%$$

$$\eta_{O} = 1 - [(1 - \eta_{Cyclone})(1 - \eta_{ESP})(1 - \eta_{WSB})]$$

where $\eta_{Cyclone}$, η_{ESP}, η_{WSB} and η_O are the PAH removal efficiencies (%) of the cyclone, ESP, WSB and overall APCDs, respectively, $ER_{Cyclone}$, ER_{ESP}, ER_{WSB} and ER_{ST} are the PAH emission rates ($mg\,min^{-1}$) from the cyclone, ESP, WSB and stack flue gas, respectively.

The overall total-PAH removal efficiencies of the APCDs were 1.12, 6.04 and 5.89% for the FLBI_A, FLBI_B and FIBI, suggesting the APCDs imposed limited effect on the removal of total-PAHs and carcinogenic PAH compounds from the incinerators (Table 6). Although this finding was quite consistent with the results obtained from two previous studies conducted on mechanical-grate and fixed-grate medical waste incinerators (15.2 and 15.4%, respectively) [13] and on batch hot mix asphalt plants (22.1%) [24], the overall total-BaP_{eq} removal efficiencies in this study (7.19, 16.1 and 12.5% for the FLBI_A, FLBI_B and FIBI, respectively) were overwhelmingly lower than those in their studies (83.6–84.2%, [13]; 93.7%, [24]).

The overall removal efficiencies of HM-PAHs that were mainly condensed on the particles were higher than those of LM- and MM-PAHs for all the APCDs. This finding was expected since LM-PAHs having lower boiling points and higher vapor pressures were predominantly found in the gaseous form and MM-PAHs were found both in the gaseous and particulate forms, and thus they were less efficiently collected by the APCDs particularly designated for particle removal.

For the FLBI_A and FLBI_B, both WSBs exhibited higher removal efficiencies on total-, LM-, MM-, HM-PAHs and total-BaP_{eq} than did the cyclone and ESP (except the MM-PAH removal efficiency of the cyclone was slightly higher than that of the WSB). For LM-PAHs having higher solubility and vapor pressure, it is not surprising that more LM_PAHs were scavenged by the WSB. For the FLBI_B, the WSB was also able to capture the fine particles containing MM- and HM-PAHs, which were not efficiently removed by the cyclone. Likewise, it can be observed that the FIBI having no other APCDs prior to the WSB demonstrated the similar total-PAH removal efficiencies. For the FLBI_A, most fine particles could be captured by the ESP, and thus the MM- and HM-PAH removal efficiencies of the WSB were

Table 6
Removal efficiencies (%)of the APCDs (cyclone, ESP, WSB and overall) on individual PAH compounds, total-PAHs, LM-PAHs, MM-PAHs, HM-PAHs and total-BaP_{eq} for FLBI_A, FLBI_B and FIBI (n = 9).

Compound	FLBI_A				FLBI_B			FIBI
	Cyclone	ESP	WSB	Overall	Cyclone	WSB	Overall	WSB
Nap	0.545	0.043	0.826	1.41	0.038	3.49	3.53	2.94
AcPy	0.476	0.096	8.81	9.33	0.236	60.3	60.4	5.38
Acp	0.883	0.178	7.59	8.57	0.765	74.7	74.9	6.32
Flu	0.727	0.073	0.916	1.71	0.618	70.8	71.0	5.52
PA	0.014	0.003	0.0002	0.017	0.016	2.96	2.97	1.22
Ant	0.259	0.065	0.649	0.971	0.131	9.69	9.80	12.2
FL	0.091	0.018	0.042	0.109	0.043	4.03	4.07	0.734
Pyr	0.035	0.069	0.056	0.104	0.030	1.54	1.57	1.04
CYC	0.368	0.369	13.0	13.6	0.403	20.2	20.6	8.22
BaA	0.510	0.051	1.12	0.510	0.548	14.2	14.6	6.38
CHR	0.223	0.446	11.1	11.1	0.185	35.0	35.1	5.83
BbF	1.47	0.025	0	1.49	0.379	74.4	74.5	6.05
BkF	9.32	0.685	13.8	22.4	0.676	54.4	54.7	18.4
BeP	6.30	0.840	5.08	11.8	0.112	12.9	13.0	6.29
BaP	6.50	0.870	0.877	8.13	0.162	16.1	16.2	7.53
PER	18.5	5.66	10.0	30.8	0.357	48.0	48.2	9.35
IND	0.990	0.380	10.0	10.9	1.02	1.93	2.92	15.5
DBA	4.74	0.498	10.0	14.7	0.047	14.7	14.7	22.6
BbC	5.06	1.33	24.3	29.1	0.817	57.7	58.0	11.6
BghiP	0.939	0.474	1.42	1.41	0.137	16.2	16.3	11.0
COR	0.041	0.004	6.16	6.20	0.971	73.5	73.8	3.13
LM-PAHs	0.183	0.018	0.491	0.691	0.071	8.94	9.00	3.41
MM-PAHs	0.090	0.028	0.070	0.188	0.096	8.23	8.32	2.37
HM-PAHs	1.25	0.192	5.62	6.98	0.323	23.7	24.0	12.2
Total-PAHs	0.255	0.032	0.837	1.12	0.109	5.94	6.04	5.89
Total-BaP_{eq}	4.61	0.553	2.16	7.19	0.123	16.0	16.1	12.5

lower than those of the FLBI_B, and only slightly higher than those of the cyclone and ESP. Besides, total-BaP_{eq} were mainly contributed by both MM- and HM-PAHs, and therefore the total-BaP_{eq} removal efficiencies of the WSBs were also larger than those of the cyclone and ESP.

Similarly, Lee et al. [13] also found that all PAH removal efficiencies of the ESP were consistently lower than those of the WSB. According to Lee et al. [13], it could be due to the generation of finer particles that might be more efficiently collected by the WSB than by the ESP. However, in this study, it was proven that the ability of the WSB to remove both gaseous and particulate phase PAHs led to the above result.

4. Conclusions

In this study, LM-PAHs (Nap and PA) dominated the total-PAHs in the stack flue gas, while LM-PAHs and HM-PAHs held similar importance in the bottom ash, fly ash and WSB effluent. High total-BaP_{eq} concentrations (equivalent to carcinogenic potencies) of bottom ash and WSB effluent of the FIBI reflect a need of proper post-treatment prior to their release. The highest PAH emission factors were also found for the FIBI, implying that it would pose higher risk on human health than would other two incinerators. Despite slightly higher PAH removal efficiency for the WSB than for the cyclone and ESP, relatively low PAH removal efficiencies (overall total-PAH and total-BaP_{eq} removal efficiencies = 1.12–6.04 and 7.19–16.0%, respectively) were still found in this study since the APCDs predominantly removed particulate matters, whereas greater amount of PAHs were found in the form of gaseous form. Overall, the impact of the PAHs released from biological sludge incineration has been found to be possibly significant on human according to the high total-BaP_{eq} levels. In this study, it is found that the PAH emissions relied on the PAH content in the auxiliary fuel and incineration conditions. It is recommended that continuous feeding way for feedstock, longer residence time, lower F/W ratio, higher combustion temperature and lower moisture fraction can remarkably reduce the PAH emissions from the incineration processes. In addition, the installation of APCDs with higher removal efficiencies of gaseous and particulate PAHs can warrant the PAH reduction before the flue gas is released.

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