# Emission of polycyclic aromatic hydrocarbons (PAHs) from the liquid injection incineration of petrochemical industrial wastewater

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## Abstract

This study investigated the emission of polycyclic aromatic hydrocarbons (PAHs) from stack flue gas and air pollution control device (APCD) effluent of the liquid injection incinerator (LII) disposing the petrochemical industrial wastewater, and PAH removal efficiencies of wet electrostatic precipitator (WESP) and wet scrubber (WSB). The PAH carcinogenic potency were investigated with the benzo(a)pyrene equivalent concentration ($BaP_{eq}$). The remarkably high total-$BaP_{eq}$ concentration ($220\,\mu g\,Nm^{-3}$) in the stack flue gas was much higher than those of several published emission sources, and indicated the possible influence on its surrounding environment. The total-PAH emission factors of the WESP, WSB and stack flue gas were 78.9, 95.7 and $30,900\,\mu g\,L^{-1}$ wastewater, respectively. The removal efficiencies of total-PAHs were 0.254, 0.309 and 0.563% for WESP, WSB and overall, respectively, suggesting that the use of both WESP and WSB shows insignificant PAH removal efficiencies, and 99.4% of total-PAHs was directly emitted to the ambient air through the stack flue gas. This finding suggested that the better incineration efficiencies, and APCD removal efficiencies for disposing the petrochemical industrial wastewater are necessary in future.
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*Keywords:* Polycyclic aromatic hydrocarbon (PAH); Liquid injection incinerator; Benzo(a)pyrene equivalent concentration ($BaP_{eq}$); Emission factor

## 1. Introduction

Incineration is considered as one of the best available techniques to dispose various kinds of wastes [1], and to reduce the volume and quantity of the toxic compounds [2]. However, incineration always results in the risk of unwanted pollution. Among the contaminants resulted from incomplete combustion of organic materials are polycyclic aromatic hydrocarbons (PAHs) which consists of two to seven fused benzene rings. Several PAHs are known to be mutagenic and/or carcinogenic [3], and hence understanding the PAH emission is necessary.

The quantitative and qualitative characteristics of PAHs emitted from industrial stacks are associated with the input type, the manufacturing process, and air pollution control devices

(APCDs) [4]. A number of studies examined the PAH emission from combusting various types of waste and fuels [5–17]. The PAH emission from the medical waste incinerators with higher plastic content were much greater than that from municipal waste incinerators [11,15]. Suitable quantity of oxygen would diminish the yield of PAHs and enhance the combustion efficiency [16]. The incineration temperature and residence time exerted marked effects on the PAH emission [18]. While our previous study [19] found that the use of waste terephthalic acid (TPA) as a co-fuel could save the consumption of heavy oil and reduce the PAH emissions during the combustion process in the fluidized-bed incinerator, the traditional APCDs have relatively low PAH removal efficiencies [20].

Petrochemical industry plays an important role in Taiwan economy, but it also produces a variety of wastes (e.g., wastewater containing toxic organic compounds) through the manufacturing processes. A method of incineration of liquid hazardous waste by high-rate injection into a combustion chamber has been

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used. This liquid injection incineration (LII) has the advantages of low capital and maintenance cost, and exclusive application for pumpable liquid waste, including some low-viscosity sludges and slurries [21]. Emission factors of 19 PAHs emitted from the LII equipped with baghouse and wet scrubber for mixed liquid industrial waste have been reported [22]; however, the waste type was not clearly characterized. It appears that no assessment has been made on the PAH emission from the LII for incinerating manufacturing wastewater in the petrochemical industry.

This study investigated the PAH emission from stack flue gas and APCD effluent of the LII disposing the petrochemical industrial wastewater, and PAH removal efficiencies of two types of APCDs. The carcinogenic potency of PAHs was also included in accordance with the benzo(a)pyrene equivalent concentrations (BaP$_{eq}$) [23], and hence this study was expanded into the perspective of human health.

## 2. Experimental

### 2.1. Brief description of the LII

In this study, a continuous-type (feeding rate = 4500 kg h$^{-1}$, incineration temperature = 850–900 °C) LII used for incinerating manufacturing wastewater operated at a petrochemical industry in southern Taiwan was selected. Heavy oil (feeding rate = 140 kg h$^{-1}$) was adopted as auxiliary fuel. This LII was equipped with a wet electrostatic precipitator (WESP) and a wet scrubber (WSB) which was installed in series. Other background information of the incinerator is summarized in Table 1.

### 2.2. Sample collection

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 sampling semi-volatile organic compounds (SVOCs). This PSS has been successfully used for sampling PAHs in different industrial stacks [7,9,24]. The PSS was equipped with a sampling probe, a set of cooling devices, a set of XAD-2/PUF glass

Table 1
The background information of the liquid injection incinerator (LII)

| Background information | LII |
| --- | --- |
| Feedstock | Manufacturing wastewater |
| Feeding way | Continuous |
| Feeding rate (kg h$^{-1}$) | 4500 |
| Auxiliary fuel | Heavy oil |
| Feeding rate (kg h$^{-1}$) | 140 |
| Temperature (°C) | |
| Incineration | 850–900 |
| Stack flue gas | 105 |
| Emission rate | |
| Stack flue gas (Nm$^3$ min$^{-1}$) | 1800 |
| WESP effluent (m$^3$ h$^{-1}$) | 30.1 |
| WSB effluent (m$^3$ h$^{-1}$) | 28.9 |

cartridges, and a pump, a flow meter, and a controlled computer. The gas phase PAHs were collected with two stages of glass cartridges which were packed with XAD-2 resin and supported by two polyurethane foams (PUFs) on the top and bottom. The particulate phase PAHs contained in the flue gas were collected with a tube-type glass fiber filter (Whatman Glass Filter Thimble, 25 mm × 90 mm). The total-PAH mass (not reported here) in the cooling water and sampling pipe residual (rinsed with *n*-hexane) were included in this study, although 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%) phase. The WSB and WESB effluents were collected every 2 min (totally 10 times) concurrently with the stack sampling to obtain good representative samples with glass bottles (pre-treated with 10% HNO$_3$, rinsed with distilled water, and wrapped with aluminium foil to avoid PAH decay).

Breakthrough tests were investigated with three stages of XAD-2/PUF cartridge, each of which was individually analyzed and compared in terms of the PAH mass collected. The results showed that 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. Totally nine PAH samples were collected, and each was sampled with a duration of 20 min.

### 2.3. Sample analysis

The PAHs contained in the cartridges and filters were Soxhlet extracted with the mixture of *n*-hexane and dichloromethane (v:v = 1:1) for 24 h, while those contained in the cooling water and pipe residual were extracted using the liquid/liquid phase separation technique with the mixture of water and dichloromethane (v:v = 1:1). The extract was then concentrated, cleaned-up and re-concentrated to exactly 1.0 mL. The detailed analytical procedures have been described elsewhere [25]. 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) and a HP 7673 A automatic sampler. The operating conditions of GC/MS and determination of PAHs can be found elsewhere [11].

The concentrations of 21 PAHs species were determined. They were categorized into three different molecular weight ranges: low molecular weight (LMW) PAHs are two- and three-ringed PAHs including naphthalene (Nap), acenaphthylene (AcPy), acenaphthene (Acp), fluorene (Flu), phenanthrene (PA), anthracene (Ant); middle molecular weight (MMW) PAHs are four-ringed PAHs including fluoranthene (FL), pyrene (Pyr), cyclopenta(c,d)pyrene (CYC), benzo(a)anthracene (BaA), chrysene (CHR); high molecular weight (HMW) PAHs are 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)chrysene (BbC), benzo(ghi)perylene (BghiP),

and coronene (COR). Of the 21 individual PAHs, BaA, CHR, BbF, BkF, BaP, IND, DBA and BghiP were listed as potential human carcinogens [26]. The PAH carcinogenicity is positively associated with corresponding molecular weight or aromatic rings [3].

Five internal standards (Nap-d8, Acp-d10, PA-d10, CHR-d12 and PER-d12) were added in the recovery tests to determine the final concentrated volumes and injected quantities before injection. The recovery efficiencies of these five internal standards and 21 individual PAH compounds were determined with a solution containing known PAH concentrations following the same experimental procedures. The recovery efficiencies (ranging from 80.6 to 92.1%) of these five internal standards were used to correct the original recovery efficiencies of the 21 individual PAH compounds (their corrected recovery efficiencies ranged from 75.9 to 107%). The blank tests for PAHs were accomplished following the same procedure as the recovery-efficiency tests without adding the known standard solution before extraction. Analyses of field blanks, including the glass bottle, glass fiber filter and XAD-2/PUF cartridge showed no significant 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 equivalent factor (TEF) and its concentration. The TEF list proposed by Nisbet and LaGoy [23] reflects well the actual state of knowledge on the toxic potency of each individual PAH compound, and thus was adopted in this study. The carcinogenic potency of the total-PAHs (i.e., total-$BaP_{eq}$) was the sum of individual of the 21 PAH compounds.

## 3. Results and discussion

### 3.1. Stack flue gas

Table 2 shows the concentrations of 21 individual PAHs and total-PAHs (i.e., the sum of the concentrations of 21 PAH species) in the stack flue gas. The average total-PAH concentration was 971 $\mu g\,Nm^{-3}$ and the range was between 362 and 1790 $\mu g\,Nm^{-3}$ (R.S.D. = 46.3%). This average was much higher than that of the fixed grate waste incinerator (FG-MWI) mainly used the special medical waste (587 $\mu g\,Nm^{-3}$) [11] and waste ion-exchange resin incineration (648 $\mu g\,Nm^{-3}$) [6], but lower than that of the mechanical grate waste incinerator (MG-MWI) used for general medical waste (1290 $\mu g\,Nm^{-3}$) [11]. The intrinsic divergence of the feedstock composition (e.g., high molecular compounds and phenyl compounds) could lead to these differences.

Contrary to previous finding that the PAH emission from the combustion process was consistently dominated by LM-PAHs [10,11], LM-PAHs (436 $\mu g\,Nm^{-3}$) and HM-PAHs (444 $\mu g\,Nm^{-3}$) showed similar average concentration in this study (Table 2). Among the HM-PAH compounds, IND (130 $\mu g\,Nm^{-3}$) and DBA (178 $\mu g\,Nm^{-3}$) showed especially high concentrations. This finding is notably significant in terms

Table 2
The range, mean, and R.S.D. of the concentrations for 21 individual PAHs, LM-PAHs, MM-PAHs, HM-PAHs and $BaP_{eq}$ in the stack flue gas ($n = 9$)

| Compound | Range ($\mu g\,Nm^{-3}$) | Mean ($\mu g\,Nm^{-3}$) | R.S.D. (%) |
|---|---|---|---|
| Nap | 181–633 | 373 | 41.5 |
| AcPy | 5.52–27.1 | 14 | 48.7 |
| Acp | 3.54–23.8 | 13.9 | 46.8 |
| Flu | 2.89–11.9 | 8.64 | 32.2 |
| PA | 9.32–26.4 | 20 | 25.3 |
| Ant | 2.81–14.4 | 5.3 | 71.2 |
| FL | 6.44–22.1 | 11.8 | 44.2 |
| Pyr | 12.0–211 | 63.5 | 107 |
| CYC | 1.38–8.24 | 4.09 | 57.6 |
| BaA | 1.69–13.6 | 6.46 | 78.6 |
| CHR | 2.12–21.9 | 10.8 | 57.2 |
| BbF | 1.27–14.8 | 7.99 | 66.5 |
| BkF | 1.78–12.2 | 6.94 | 51.0 |
| BaP | 12.2–29.5 | 19.9 | 32.0 |
| BeP | 14.4–46.4 | 26.7 | 45.7 |
| PER | 4.68–23.7 | 12.4 | 59.3 |
| IND | 2.94–348 | 130 | 109 |
| DBA | 7.44–447 | 178 | 85.3 |
| BbC | 1.97–116 | 31.7 | 115 |
| BghiP | 1.46–72.7 | 25.7 | 92.4 |
| COR | 0.381–6.64 | 1.42 | 142 |
| Total-PAHs | 362–1790 | 971 | 46.3 |
| LM-PAHs | 205–737 | 435 | 40.8 |
| MM-PAHs | 22.2–268 | 92.5 | 90.5 |
| HM-PAHs | 135–788 | 444 | 43.8 |
| Total-$BaP_{eq}$ | 22.8–534 | 220 | 81.3 |

of human health. HM-PAHs are known to be more carcinogenic [3], and six of them (i.e., BbF, BkF, BaP, IND, DBA and BghiP) have been listed as potential human carcinogens [26]. This resulted in higher carcinogenic potency in the application of the LII. Petrochemical wastewater could contain high levels of oil and grease (30–600 $mg\,L^{-1}$), phenol (200 $mg\,L^{-1}$) and benzene (100 $mg\,L^{-1}$) [27]. The formation of LM-PAHs and MM-PAHs with benzene, phenyl and biphenyl as growth species, and the contribution of LM- and MM-PAHs to formation of HM-PAHs have been confirmed ([28] and references therein). These phenyl and high molecular compounds might provide higher possibility for PAHs to be synthesized during the incomplete combustion process and it also explained the high HM-PAHs emission in this study. Of the 21 individual PAHs, Nap (38.4% of total-PAHs) dominated the PAH emission from the LII since it has high volatility.

Total-$BaP_{eq}$ concentrations ranged between 22.8 and 534 $\mu g\,Nm^{-3}$ with an average of 220 $\mu g\,Nm^{-3}$ (Table 2). Similar to the result found by Mi et al. [9], total-$BaP_{eq}$ was contributed mainly by the three carcinogenic compounds—BaP (24.1 $\mu g\,Nm^{-3}$), IND (11.8 $\mu g\,Nm^{-3}$) and DBA (160 $\mu g\,Nm^{-3}$) (not reported here). It is noted that PAHs with higher molecular weights are known with higher carcinogenic potencies. Based on this fact and measured PAH concentrations, this average value was much higher than those for the batch mixer (0.629 $\mu g\,Nm^{-3}$), preheating boiler (0.112 $\mu g\,Nm^{-3}$) and discharging chute (0.950 $\mu g\,Nm^{-3}$) from batch hot mix asphalt

Table 3
The range, mean, and R.S.D. of the concentrations for 21 individual PAHs, LM-PAHs, MM-PAHs, HM-PAHs and BaP$_{eq}$ and the ratio distributed in the liquid and solid phases in the WESP effluent ($n = 9$)

| Compound | Liquid phase | | | | Solid phase | | | |
|---|---|---|---|---|---|---|---|---|
| | Range (ng L$^{-1}$) | Mean (ng L$^{-1}$) | R.S.D. (%) | Ratio (%) | Range (ng L$^{-1}$) | Mean (ng L$^{-1}$) | R.S.D. (%) | Ratio (%) |
| Nap | 1620–2230 | 1,880 | 17.0 | 71.7 | 652–853 | 740 | 13.9 | 28.3 |
| AcPy | 691–1250 | 973 | 28.7 | 73.5 | 237–445 | 350 | 30.0 | 26.5 |
| Acp | 997–1420 | 1,210 | 17.4 | 79.8 | 194–374 | 306 | 32.0 | 20.2 |
| Flu | 980–1190 | 1,080 | 10.1 | 86.4 | 151–199 | 169 | 15.8 | 13.6 |
| PA | 11.1–518 | 306 | 86.0 | 92.1 | ND–77.0 | 26.2 | 168 | 7.93 |
| Ant | ND–565 | 188 | 173 | 65.2 | 27.6–167 | 101 | 69.3 | 34.8 |
| FL | 0.842–72.0 | 44.5 | 85.9 | 54.7 | 18.9–60.6 | 36.8 | 58.5 | 45.3 |
| Pyr | 94.5–134 | 108 | 20.4 | 70.8 | 20.2–78.8 | 44.6 | 68.3 | 29.2 |
| CYC | 103–240 | 161 | 44.1 | 58.4 | ND–288 | 115 | 133 | 41.6 |
| BaA | 151–760 | 359 | 96.5 | 69.3 | ND–478 | 159 | 173 | 30.7 |
| CHR | 172–399 | 285 | 39.8 | 52.0 | 187–353 | 263 | 31.8 | 48.0 |
| BbF | 289–496 | 367 | 30.6 | 87.6 | ND–88.8 | 51.9 | 89.1 | 12.4 |
| BkF | ND–58.9 | 28.9 | 50.1 | 44.8 | ND–74.5 | 35.6 | 105 | 55.2 |
| BaP | 429–729 | 540 | 30.6 | 79.6 | 76.3–238 | 138 | 63.2 | 20.4 |
| BeP | 778–1020 | 895 | 13.4 | 72.8 | 204–540 | 334 | 54.1 | 27.2 |
| PER | 446–866 | 652 | 32.3 | 79.7 | 137–210 | 166 | 23.6 | 20.3 |
| IND | 672–4530 | 2,130 | 98.2 | 48.3 | 1610–3030 | 2,280 | 31.3 | 51.7 |
| DBA | 201–2690 | 1,400 | 89.2 | 29.8 | 2460–4090 | 3,300 | 24.7 | 70.2 |
| BbC | 96.9–500 | 328 | 63.4 | 26.9 | ND–2570 | 889 | 163 | 73.1 |
| BghiP | 72.4–544 | 259 | 96.9 | 12.9 | ND–3000 | 1,740 | 89.4 | 87.1 |
| COR | 115–223 | 171 | 31.7 | 86.8 | ND–53.6 | 26.0 | 103 | 13.2 |
| Total-PAHs | 10,900–16,900 | 13,300 | 23.6 | 54.2 | 8300–14,500 | 11,300 | 27.5 | 45.8 |
| LM-PAHs | 4970–6190 | 5,630 | 11.0 | 76.9 | 1410–2040 | 1,690 | 19.0 | 23.1 |
| MM-PAHs | 478–619 | 797 | 54.7 | 61.3 | 288–731 | 503 | 44.1 | 38.7 |
| HM-PAHs | 4610–10,500 | 6,900 | 46.1 | 43.2 | 6170–12,600 | 9,080 | 35.8 | 56.8 |
| Total-BaP$_{eq}$ | 1340–3950 | 2,600 | 49.9 | 37.4 | 3030–4480 | 3,910 | 18.8 | 62.6 |

*Note*: ND: Non-detectable.

plants [10]. The remarkably high total-BaP$_{eq}$ concentration emitted from the LII indicated the possible influence on its surrounding environment.

### 3.2. Effluent from the wet electrostatic precipitator

The PAH concentrations of the WESP effluent were measured in both liquid and solid phases (Table 3). The liquid-phase and solid-phase total-PAH concentrations ranged between 10,900 and 16,900 ng L$^{-1}$ (average = 13,300 ng L$^{-1}$), and between 8300 and 14,500 ng L$^{-1}$ (averaged = 11,300 ng L$^{-1}$), respectively. LM-PAHs and MM-PAHs were mostly dissolved in the liquid phase (76.9 and 61.3%, respectively), whereas HM-PAHs were slightly prone to be adsorbed onto suspended solids (56.8%) (Table 3). Likewise, the total-BaP$_{eq}$ concentration was higher in the solid phase (3910 ng L$^{-1}$) than that in the liquid phase (2600 ng L$^{-1}$). Therefore, the carcinogenic potency of the solid phase was 1.67 times higher than that of the liquid phase.

The PAH homologue distributions of the WESP effluent in the liquid phase (LM-PAHs:MM-PAHs:HM-PAHs = 42.3:6.0:51.7%) were significantly different from those in the solid phase (LM-PAHs:MM-PAHs:HM-PAHs = 15.0:4.5:80.5%) (Table 3). Both distributions were significantly different from that in the stack flue gas (LM-PAHs:MM-PAHs:HM-PAHs = 44.8:9.52:45.7%), but all distributions demonstrated

high fraction of HM-PAHs, resulting in high carcinogenic potency in the WESP effluent emitted from the LII.

### 3.3. Effluent from the wet scrubber

In this study, the solid-phase samples of the WSB (equipped after the WESP) effluent were not collected since most particles were already removed by the WESP. As shown in Table 4, the total-PAH concentration of the WSB (liquid-phase) effluent averaged 29,800 ng L$^{-1}$ and ranged between 17,200 and 44,600 ng L$^{-1}$. Most PAHs collected in the WSB effluent were HM-PAHs, which averaged 18,600 ng L$^{-1}$, while the mean concentrations of LM-PAHs and MM-PAHs were 9500 and 1710 ng L$^{-1}$, respectively. Similar to the WESP effluent in the liquid phase, the PAH homologue distribution of the WSB effluent show the concentration trend as HM-PAHs > LM-PAHs > MM-PAHs (LM-PAHs:MM-PAHs:HM-PAHs = 31.9:5.7:62.4%). Although most particles were already removed by the WESP, the distribution of HM-PAHs for the WSB effluents in the liquid phase (62.4%) was higher than that for WESP effluents in the liquid phase (51.7%) probably because of the HM-PAH contribution of the dissolved solid. The WSB effluent was more carcinogenic compared with the WESP based on their mean BaP$_{eq}$ concentrations (Tables 3 and 4). This result indicated that the WSB effluent needs more efforts to be detoxified before it is discharged.

Table 4
The range, mean, and R.S.D. of the concentrations for 21 individual PAHs, LM-PAHs, MM-PAHs, HM-PAHs and $BaP_{eq}$ in the WSB effluent ($n = 9$)

| Compound | Range (ng L$^{-1}$) | Mean (ng L$^{-1}$) | R.S.D. (%) |
|---|---|---|---|
| Nap | 3030–3900 | 3600 | 14.0 |
| AcPy | 968–2150 | 1650 | 37.0 |
| Acp | 1220–2380 | 1860 | 31.7 |
| Flu | 1310–1750 | 1570 | 14.4 |
| PA | 13.0–785 | 513 | 84.5 |
| Ant | ND–686 | 312 | 111 |
| FL | 90.6–111 | 97.7 | 11.7 |
| Pyr | 116–164 | 143 | 17.4 |
| CYC | 114–614 | 381 | 66.1 |
| BaA | 456–559 | 512 | 10.2 |
| CHR | 121–2270 | 953 | 121 |
| BbF | ND | ND | NA |
| BkF | 814–2130 | 1330 | 52.5 |
| BeP | 901–2320 | 1460 | 52.0 |
| BaP | 1180–3800 | 2170 | 65.6 |
| PER | 669–1700 | 1230 | 42.3 |
| IND | 2470–8980 | 5280 | 63.4 |
| DBA | 817–11,300 | 5200 | 105 |
| BbC | ND–1830 | 807 | 116 |
| BghiP | 162–1650 | 670 | 126 |
| COR | 70.6–171 | 113 | 45.8 |
| Total-PAHs | 17,200–44,600 | 29,800 | 46.4 |
| LM-PAHs | 3640–11,700 | 9500 | 28.0 |
| MM-PAHs | 783–3100 | 1710 | 72.2 |
| HM-PAHs | 9860–29,900 | 18,600 | 54.8 |
| Total-BaP$_{eq}$ | 2390–16,400 | 8120 | 90.2 |

*Note*: ND: Non-detectable.

Table 5
The PAH emission factors ($\mu$g L$^{-1}$ wastewater) of the WESP, WSB and stack flue gas, and overall PAH emission factors of the LII found in this study ($n = 9$) and in the literature

| Compound | WESP | WSB | Stack flue gas | Overall | Johnson et al. [22] |
|---|---|---|---|---|---|
| Nap | 8.4 | 11.6 | 11,900 | 11,900 | – |
| AcPy | 4.24 | 5.27 | 445 | 455 | 2.70 |
| Acp | 4.86 | 5.96 | 442 | 453 | 3.60 |
| Flu | 3.99 | 5.02 | 275 | 284 | 6.70 |
| PA | 1.07 | 1.64 | 635 | 637 | 50.2 |
| Ant | 0.926 | 1.00 | 138 | 140 | 5.80 |
| FL | 0.26 | 0.313 | 376 | 377 | 24.8 |
| Pyr | 0.49 | 0.459 | 2,020 | 2,020 | 14.0 |
| CYC | 0.885 | 1.22 | 122 | 124 | – |
| BaA | 1.66 | 1.64 | 205 | 208 | 3.00 |
| CHR | 1.76 | 3.05 | 341 | 346 | 5.50 |
| BbF | 1.34 | ND | 254 | 255 | 2.50 |
| BkF | 0.114 | 4.28 | 220 | 225 | – |
| BeP | 2.17 | 4.67 | 632 | 638 | 1.00 |
| BaP | 3.94 | 6.96 | 847 | 858 | 1.00 |
| PER | 2.62 | 3.96 | 394 | 400 | 0.300 |
| IND | 14.2 | 16.9 | 4,150 | 4,180 | 1.90 |
| DBA | 15 | 16.7 | 5,640 | 5,680 | 0.600 |
| BbC | 3.9 | 2.59 | 1,010 | 1,013 | – |
| BghiP | 6.42 | 2.15 | 817 | 825 | 2.10 |
| COR | 0.633 | 0.363 | 43.6 | 44.6 | 1.30 |
| Total-PAHs | 78.9 | 95.7 | 30,900 | 31,000 | NA |
| LM-PAHs | 23.0 | 30.0 | 13,800 | 13,900 | NA |
| MM-PAHs | 4.17 | 5.46 | 2,940 | 2,950 | NA |
| HM-PAHs | 51.2 | 59.7 | 14,100 | 14,200 | NA |
| Total-BaP$_{eq}$ | 20.9 | 26.0 | 7,000 | 7,050 | NA |

*Note*: (–), Not available; NA, non-applicable.

## 3.4. Emission factors

Emission factor is a useful tool for estimating the emission of air pollutants, and of great importance in the setting of the national environmental protection regulations. Table 5 shows the PAH emission factors (microgram of PAHs per liter of wastewater) of the WESP, WSB and stack flue gas. The results showed that the total-PAH emission factors of the WESP, WSB and stack flue gas were 78.9, 95.7 and 30,900 $\mu$g L$^{-1}$ wastewater, respectively, and the overall total-PAH emission factor of the LII was 31,000 $\mu$g L$^{-1}$ wastewater. On average, the PAH emission factors found in this study were two to five orders of magnitude higher than those reported by Johnson et al. [22] for the LII equipped with baghouse and wet scrubber for incinerating mixed liquid industrial waste (not clearly characterized) (Table 5).

Approximately 35,640 t year$^{-1}$ of the wastewater was discharged from the petrochemical industry in this study, and thus approximately 1100 kg of total-PAHs was emitted from the stack in a year. Owing to small fractions of total-PAHs distributed into the effluents of the WESP and WSB, the total-PAH mass emitted from the LII was similar to that emitted from the stack. Applying the same amount of wastewater discharge, a total of 30.2 kg of BaP was emitted from the stack in a year.

The emission factors of the WESP and WSB shared the same trend (HM-PAHs > LM-PAHs > MM-PAHs), while the stack flue gas showed the similar emission factors for HM-PAHs and LM-PAHs, and followed by MM-PAHs. Since the emission factors of the stack flue gas were remarkably large, it was not surprising that the emission factors of the LII followed the same trend as that found for the stack flue gas.

Likewise, the total-BaP$_{eq}$ emission factor of the stack flue gas was also much larger (7000 $\mu$g L$^{-1}$ wastewater) than those of the WESP (20.9 $\mu$g L$^{-1}$ wastewater) and WSB (26.0 $\mu$g L$^{-1}$ wastewater), while that of the LII was approximately 7050 $\mu$g L$^{-1}$ wastewater.

## 3.5. PAH removal efficiencies

In this study, the PAH removal efficiencies of the WESP and WSB were calculated as follows:

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

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

$$\eta_O = 1 - [(1 - \eta_{WESP})(1 - \eta_{WSB})]$$

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

Table 6
PAH removal efficiencies of the WESP, WSB and overall on 21 individual PAHs, LM-PAHs, MM-PAHs and HM-PAHs

| Compound | WESP (%) | WSB (%) | Overall (%) |
|---|---|---|---|
| Nap | 0.071 | 0.097 | 0.168 |
| AcPy | 0.932 | 1.17 | 2.091 |
| Acp | 1.07 | 1.33 | 2.388 |
| Flu | 1.41 | 1.79 | 3.176 |
| PA | 0.167 | 0.258 | 0.425 |
| Ant | 0.663 | 0.721 | 1.379 |
| FL | 0.069 | 0.083 | 0.152 |
| Pyr | 0.024 | 0.023 | 0.047 |
| CYC | 0.713 | 0.991 | 1.697 |
| BaA | 0.798 | 0.794 | 1.585 |
| CHR | 0.507 | 0.887 | 1.390 |
| BbF | 0.527 | 0.00 | 0.527 |
| BkF | 0.051 | 1.90 | 1.954 |
| BeP | 0.341 | 0.734 | 1.072 |
| BaP | 0.459 | 0.815 | 1.270 |
| PER | 0.655 | 0.995 | 1.643 |
| IND | 0.339 | 0.406 | 0.743 |
| DBA | 0.265 | 0.295 | 0.559 |
| BbC | 0.385 | 0.256 | 0.640 |
| BghiP | 0.778 | 0.262 | 1.038 |
| COR | 1.42 | 0.825 | 2.232 |
| Total-PAHs | 0.254 | 0.309 | 0.563 |
| LM-PAHs | 0.170 | 0.220 | 0.390 |
| MM-PAHs | 0.141 | 0.185 | 0.326 |
| HM-PAHs | 0.360 | 0.420 | 0.778 |

The removal efficiencies of total-PAHs, LM-PAHs, MM-PAHs and HM-PAHs for the WSB were consistently larger than those for the WESP with the exception of few PAH compounds (i.e., Pyr, BaA, BbF, BbC, BghiP and COR) (Table 6). Lee et al. [11] also found that the WSB had better PAH removal efficiencies over the ESP. It should be highlighted that their PAH removal efficiencies were significantly higher than those in this study, probably owing to the different feedstock type in two studies. Theoretically, the incineration of wastewater generated much smaller particle mass than those of medical wastes [11]. It is therefore expected that the WESP and WSB designed exclusively for particle collection had less possibility to collect high amount of particulate PAHs in this study.

The removal efficiencies of the 21 individual PAHs ranged between 0.024 and 1.42% (0.254% for total-PAHs), between 0 and 1.90% (0.309% for total-PAHs), and between 0.047 and 3.18% (0.563% for total-PAHs) for the WESP, WSB and overall, respectively, suggesting that the use of both WESP and WSB shows insignificant PAH removal efficiencies for the LII, and 99.4% of total-PAHs was directly emitted to the ambient air through the stack flue gas.

## 4. Conclusions

The use of the LII for incinerating the petrochemical industrial wastewater was found to produce high HM-PAH concentrations and carcinogenic potency. The average total-$BaP_{eq}$ concentrations ($220 \, \mu g \, Nm^{-3}$) was much higher than those for the batch mixer ($0.629 \, \mu g \, Nm^{-3}$), preheating boiler ($0.112 \, \mu g \, Nm^{-3}$) and discharging chute ($0.950 \, \mu g \, Nm^{-3}$) from batch hot mix asphalt plants. The removal efficiencies of total-PAHs were 0.254, 0.309 and 0.563% for the WESP, WSB and overall, respectively. This resulted in the total-$BaP_{eq}$ emission factor of the stack flue gas was also much larger ($7000 \, \mu g \, L^{-1}$ wastewater) than those of the WESP ($20.9 \, \mu g \, L^{-1}$ wastewater) and WSB ($26.0 \, \mu g \, L^{-1}$ wastewater), while that of the LII was approximately $7050 \, \mu g \, L^{-1}$ wastewater. This finding suggested that the better incineration efficiencies (e.g., the destruction of benzene rings), and APCD removal efficiencies for disposing the petrochemical industrial wastewater are necessary in future.

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