Characteristics of PM and PAHs Emitted from Oil-fired Process

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ABSTRACT

Sampling and analysis of NO₂, SO₂, filterable particulate matter (FPM), FPM₂.₅, condensable particulate matter (CPM), and polycyclic aromatic hydrocarbons (PAHs) emitted from an oil-fired boiler equipped with efficiency of electrostatic precipitator (ESP) as air pollution control devices (APCDs) were conducted. Moreover, the emission characteristics of these pollutants were also evaluated at two loadings, i.e., low (30%) and high (80%) capacities. The results show that the NO concentration (90 ppm) emitted from the oil-fired boiler at low loading was lower than that of the high loading (176 ppm) while SO₂ concentrations are close under two loading conditions. In terms of particulate matter, the concentrations of FPM, FPM₂.₅, and CPM measured in the stack at low loading were 0.2, 0.1, and 51.2 mg Nm⁻³, respectively. As the boiler loading was increased from 30% to 80%, the concentrations of FPM, FPM₂.₅, and CPM increased to 1.1, 0.6, and 65.0 mg Nm⁻³, respectively. The total concentrations of PAHs in high loading and low loading oil-fired boilers were 28.3 and 24.4 μg Nm⁻³, respectively, and the contribution of gas-phase PAHs to the total PAHs was higher than 90%. Regarding the distribution of PAHs species, Nap is the dominant congener of the oil-fired boiler while BcFE is the major contributor for toxic equivalent concentrations. In addition, air pollutant emission factors reported in literatures were compiled and compared those obtained in this study. The results show that the emission factors of PAHs and FPM obtained for this oil-fired boilers are lower than the values measured in other studies.

Keywords: Oil-fired boiler, PM₂.₅, Condensable particulate matter, Polycyclic aromatic hydrocarbons (PAHs)

1 INTRODUCTION

More than 80% of the energy used worldwide comes from (Armaroli and Balzani, 2011). Oil is a common fossil fuel which is used in various industries to generate steam, heat and electricity (Yang et al., 2018a). Bhanarkar et al. (2005) mentioned that low-sulfur fuel oil (LSFO) is one of the main fuels for power generation, accounting for 2.9% of global electricity generation in 2018 (IEA, 2020). However, oil-fired power plants release a number of harmful substances to the environment, including PM, NOₓ, SOₓ, polycyclic aromatic hydrocarbons (PAHs), which adversely affect the ambient air quality and human health.

Fossil fuel combustion is one of the largest sources of sulfur oxides and PM₂.₅ (Maciejczyk et al. 2021). PM₂.₅ significantly reduces visibility and leads to the formation of atmospheric haze (Li et al., 2018b; Wang et al., 2020). Epidemiological studies indicate that particles originating from burning of fossil fuels are particularly harmful to human health (Laden et al., 2000; Lanki et al., 2006; Penttinen et al., 2006). In addition, toxicological studies have shown that PM₂.₅ can adsorb toxic substances such as PAHs, and affect human health through inhalation and respiratory deposition.
PM emitted from stationary sources can be classified into filterable particulate matter (FPM) and condensable particulate matter (CPM). FPM$_{2.5}$ refers to the solid or liquid particles discharged from the stack, which can be directly captured by the filter of the sampling train. U.S. EPA Method 202 defines CPM as the gas-phase pollutants that cools and dilutes in ambient air after emitting from the stack, condenses and reacts to form solid or liquid PM (U.S. EPA, 2016). Therefore, gaseous substances can also be regarded as the precursors of derivatized aerosol. The aerodynamic diameter of CPM is generally less than 2.5 µm, so CPM and FPM$_{2.5}$ are usually combined into PM$_{2.5}$ for discussion (Yang et al., 2018a; Wang et al., 2020). Since CPM exists in gaseous state before being discharged, it is difficult for traditional particulate removal equipment to effectively remove CPM. In many previous studies, CPM has been proven as an important source contributing to the total PM$_{2.5}$ emission (Qi et al., 2017; Yang et al., 2018a). In general, FPM emitted from oil-fired boiler is very fine (< 1 µm), has a low electrical resistivity compared to most fly ash, and is often viscous and hygroscopic (Dean, 1978). In addition, the flue gas generated from oil-fired boiler has a high concentration of sulfur oxides, which easily leads to the formation of CPM.

Polycyclic aromatic hydrocarbons (PAHs) refer to the hydrocarbons formed by the bonding of two or more benzene rings, and belong to semi-volatile organic compounds (SVOC). The most important sources of atmospheric PAHs are incomplete combustion and pyrolysis of hydrocarbons. There are two main mechanisms for the formation of PAHs in combustion processes, namely "cracking or incomplete combustion" and "thermal synthesis" (Mastral and Callén, 2000). Depending on the molecular weight, PAHs can exist in the gas or particle phase, depending primarily on their vapor pressure (Keller and Bidleman, 1984). Generally speaking, PAHs of higher molecular weights are more likely to distribute in the particle phase. PAHs have received great public attention due to their carcinogenicity, teratogenicity and genotoxicity (Yang et al., 2010). The U.S. EPA has listed 16 PAHs as priority pollutants, while the European Food Safety Authority has designated 24 PAHs for control and monitoring.

Few investigations are available regarding the emissions and control of PM and PAHs from oil-fired power plants. Moreover, some previous studies on the emission from oil-fired boilers only investigated a single pollutant, such as Yang et al. (2018a) merely studied the PM emissions, while Li et al. (1999) merely studied PAHs. Therefore, no study has investigated both PM and PAH emissions from oil-fired boilers. The purposes of this study are to (1) investigate the concentrations of air pollutants emitted from oil-fired process and understand the emission characteristics of PM and PM$_{2.5}$, (2) evaluate congeners distribution of PAHs, and (3) calculate the emission factors of relevant air pollutants emitted from this oil-fired power plant.

2 MATERIALS AND METHODS

2.1 Description of the Oil-fired Power Plant

In this study, an oil-fired power plant located in northern Taiwan was selected to measure the concentrations of FPM, FPM$_{2.5}$, CPM, and PAHs at the stack to understand the characteristics of air pollutants emitted from this plant. The oil-fired power plant has two units with a total installed capacity of 1,000 MW. In addition, the oil-fired boiler was operated at different loading (30% and 80%) to elucidate the influence of loading capacity on pollutant emissions. For 30% loading scenario, measurement was conducted in triplicate but only one measurement was conducted for the 80% loading scenario. The air pollution control devices (APCDs) adopted and important operating parameters of the oil-fired boiler investigated are shown in Fig. 1. Specifically, the gas flow rates were measured as 543,900 Nm$^3$ h$^{-1}$ and 1,272,600 Nm$^3$ h$^{-1}$ for 30% and 80% loading, respectively, and heavy oil with sulfur content less than 0.3% was applied as fuel. In order to improve the collection efficiency of electrostatic precipitator (ESP), NH$_3$ is injected into the gas stream just before the ESP to adjust the resistivity of the particulate matter and facilitate the agglomeration of fine particles. The injection rates of NH$_3$ were maintained at 6.4 kg h$^{-1}$ and 14 kg h$^{-1}$ for 30% and 80% loading, respectively, corresponding to the NH$_3$ concentration of 14 ppm in the flue gas.
As shown in Fig. 1, the exhaust gas generated from low NOx burner, firstly passes through the economizer to reduce the temperature of the flue gas and flows through ESP for reducing PM emission. Pollutants including FPM, FPM$_{2.5}$, CPM, NOx, SOx, and PAHs were sampled and measured at the stack. The concentrations of air pollutants reported in this study are corrected to 6% oxygen content for comparison.

2.2 Sampling and Analysis of FPM$_{2.5}$ and CPM

In this study, FPM$_{2.5}$ and CPM were sampled simultaneously following the U.S. EPA Method 201A (U.S. EPA, 2020b) and the U.S. EPA Method 202 (U.S. EPA, 2016), respectively. The sampling was conducted by an automatic isokinetic sampler. After flue gas entered the suction nozzle, the particles with an aerodynamic diameter greater than 2.5 µm were removed by a cyclone separator, and FPM$_{2.5}$ was collected with a 47 mm quartz filter. The gaseous substance penetrating through the quartz filter was condensed, and CPM was captured by impingers and Teflon filter. After sampling, the impingers and Teflon filter were purged by N$_2$ (99.99%) for 1 hour to remove the dissolved SO$_2$ to reduce the interference. CPM deposited on other sampling apparatus including sampling tube, condenser, impingers, and filter holder were rinsed with deionized water, acetone and n-hexane. The samples were then sent back to the laboratory for drying, conditioning and weighing. The results of PM concentration obtained in this study are reported in mg Nm$^{-3}$ (dry basis standard gas volume).

2.3 Sampling and Analysis of FPM and PAHs

Simultaneous sampling of FPM and polycyclic aromatic hydrocarbons (PAHs) in flue gas were carried out followed the U.S. EPA Method 5 (U.S. EPA, 2020a) and the U.S. EPA Method 23A (U.S. EPA, 2016), respectively. The flue gas first passed through a 90 mm quartz filter to collect FPM and particle-phase PAHs, and the gas stream was cooled by a condenser to capture gas-phase PAHs with XAD-2 adsorbent. The FPM samples were taken back to the laboratory for conditioning and weighing, and the PAHs samples were extracted and purified for analysis. The internal standard of PAHs was added to the sample prior to Soxhlet extraction with dichloromethane for at least 20 hours. The extracted solution was evaporated to less than 5 mL by rotary evaporation. The sample was then passed through a cleanup column packed with activated silica gel. The PAHs analysis was conducted by gas chromatography/mass spectrometry (GC/MS) in ion monitoring (SIM) mode using a fused silica capillary column DB-5 MS (60 m × 0.25 mm × 0.25 µm). Totally, 27 PAHs were measured including 16 U.S. EPA PAHs and 15 EU PAHs and three other PAHs (2-methylnaphthalene, benzo[e]pyrene and perylene). Detailed information regarding these PAHs including ring number and TEF values are presented in Table S1 of the Supporting Information. The toxic equivalency factors (TEFs) are used to calculate the toxic equivalent concentration of PAHs based on the toxicity of BaP (BaP$_{eq}$) as shown in Eq. (1).
\[
\text{BaP}_{eq} = \sum_{1}^{\text{PAH}} \text{PAH}_i \times \text{TEF}_i
\]

where PAH\(_i\) is the concentration of the individual PAH in the sample and TEF\(_i\) is the TEF of individual PAH.

The QC and QA for analysis of PAHs were carried out. Field blanks and method blanks were extracted and analyzed simultaneously with field samples. Low concentration of Nap, Ant, FL, and Pyr were detected in the field blank samples (< 3 \(\mu\)g, < 0.3 \(\mu\)g, < 0.1 \(\mu\)g, and < 0.2 \(\mu\)g per sample, respectively) and the recoveries of internal standards ranged from 75 to 110\%. Detailed of recoveries and method detection limits of PAHs congeners were presented in Table S2.

### 3 RESULTS AND DISCUSSION

#### 3.1 Characteristics of Gaseous Pollutants

Table S1 shows the moisture content, oxygen content, and the concentration of CO, CO\(_2\), NO\(_x\), SO\(_2\), and HCl measured for the flue gas emitted from the oil-fired boiler with different capacity loading. The results indicate that the moisture content and the concentrations of SO\(_2\) and HCl in exhaust gas from the oil-fired boiler with different loads are not significantly different but the concentrations of CO and NO\(_x\) with 80\% loading are significantly higher than that of 30\% loading. Differences in the concentrations of these pollutants are likely to impact PM\(_{2.5}\) and PAHs concentration, which will be discussed in Sections 3.2 and 3.3.

#### 3.2 Emission Characteristics of Particulate Matter

##### 3.2.1 Emissions of FPM, FPM\(_{2.5}\), and CPM

Fig. 2 shows the concentrations of FPM, FPM\(_{2.5}\), and CPM emitted from the oil-fired boiler investigated with two different loadings. The concentrations of FPM, FPM\(_{2.5}\), and CPM at 30\% loading were 0.2, 0.1, and 51.2 mg Nm\(^{-3}\), respectively, while those measured at 80\% load of the boiler were 1.1, 0.6, and 64.9 mg Nm\(^{-3}\), respectively. The FPM\(_{2.5}\) emitted from the oil-fired boiler accounts for 50\% of the total FPM concentration for both loading capacities (30\% and 80\%). In addition, the FPM and FPM\(_{2.5}\) concentrations measured at 80\% loading are 6.9 and 5.5 times higher than those of 30\% loading, respectively. The main reason is that higher loading results in higher oil consumption and higher gas flow rate. The specific collection area (SCA) is an important parameter.
2.5 and CPM emitted from different sources.

<table>
<thead>
<tr>
<th>Fuel type</th>
<th>APCD</th>
<th>Temp. (°C)</th>
<th>FPM$_{2.5}$ (mg Nm$^{-3}$)</th>
<th>CPM (mg Nm$^{-3}$)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Heavy oil</td>
<td>ESP (30% load)</td>
<td>118</td>
<td>0.1</td>
<td>51.2</td>
<td>This study</td>
</tr>
<tr>
<td></td>
<td>ESP (80% load)</td>
<td>155</td>
<td>0.6</td>
<td>64.9</td>
<td>This study</td>
</tr>
<tr>
<td></td>
<td>None</td>
<td>159</td>
<td>28.0 ± 5.6</td>
<td>163.0 ± 62.8</td>
<td>Yang et al., 2018b</td>
</tr>
<tr>
<td></td>
<td>Cyclone</td>
<td>195 ± 129</td>
<td>26.2 ± 5.3</td>
<td>84.2 ± 38.1</td>
<td>Yang et al., 2018a</td>
</tr>
<tr>
<td></td>
<td>Baghouse</td>
<td>125</td>
<td>2.3</td>
<td>3.2</td>
<td>Yang et al., 2018a</td>
</tr>
<tr>
<td>Coal</td>
<td>Cyclone</td>
<td>65 ± 5</td>
<td>18.6 ± 13.7</td>
<td>22.7 ± 5.6</td>
<td>Yang et al., 2018a</td>
</tr>
<tr>
<td></td>
<td>ESP</td>
<td>45 ± 6</td>
<td>3.8 ± 1.1</td>
<td>3.9 ± 1.1</td>
<td>Yang et al., 2018a</td>
</tr>
<tr>
<td></td>
<td>Baghouse</td>
<td>83 ± 17</td>
<td>3.5 ± 3.2</td>
<td>8.6 ± 4.0</td>
<td>Yang et al., 2018a</td>
</tr>
<tr>
<td></td>
<td>Cyclone + Baghouse</td>
<td>77</td>
<td>19.3 ± 2.9</td>
<td>27.2 ± 3.5</td>
<td>Yang et al., 2018b</td>
</tr>
<tr>
<td></td>
<td>SCR + ESP + WFGD + WESP</td>
<td>76</td>
<td>&lt; 0.1</td>
<td>37.4</td>
<td>Chen et al., 2022</td>
</tr>
</tbody>
</table>

On the other hand, the CPM concentration measured at 80% loading is not significantly higher than that of 30% loading (1.3 times higher). Various factors may affect CPM concentrations, such as the type of APCDs and temperature of the stack gas. The main factor causing the difference in CPM concentration in this study is the different flue gas temperature caused by different loadings. Storm Technologies, Inc. (2015) mentioned that as the loading of boiler increases, the combustion temperature also increases. The temperature of the stack gas measured at 80% loading is 37°C higher than that measured at 30% loading, resulting in slightly higher CPM concentration measured at 80% loading compared to 30% loading.

Another factor for insignificant CPM concentration changes with different loading scenarios is due to the lack of gaseous air pollutant control devices (APCDs) such as selective catalytic reduction (SCR) and wet flue-gas desulfurization (WFGD) in this oil-fired power plant. As mentioned earlier, CPM exists mainly in the gaseous state (mostly in SO$_2$ or SO$_3$) in the flue gas before being emitted from the stack, and various gaseous pollutants are its precursors. Specifically, the study conducted in seven ultra-low emission coal-fired power plants in China indicated that CPM emission was reduced by 76% via WFGD installation and the average CPM concentration was 5.1 mg Nm$^{-3}$ (Tao et al., 2020). In addition, the study conducted by Wang et al. (2020) in a coal-fired power plant which adopted WFGD as APCDs indicates that CPM emission could be reduced 61.9%–65.4%.

This study shows that the current APCDs adopted by the oil-fired boiler investigated has a good control efficiency for FPM and FPM$_{2.5}$, and the concentrations are lower than those reported by previous studies. The PM emission from this oil-fired power plant is mainly CPM, and how to effectively reduce CPM emission remains a big challenge. Overall, there are various causes for the formation of CPM, and the sources are complex. In order to effectively control CPM emission, it is necessary to further understand the composition of CPM in oil-fired process.

### 3.2.2 CPM composition

Since CPM is formed by the condensation of gaseous pollutants, understanding the composition of CPM is important to apply the suitable technique to reduce its emission. Fig. 3 shows the organic and inorganic compositions of the CPM emitted from this oil-fired boiler. The results show that inorganic CPM fraction is significantly higher than that of organic fraction. The organic and inorganic
Fig. 3. Distribution of organic and inorganic portions of CPM at two loadings.

CPMs emitted from the oil-fired boiler operated under 30% loading are 1.2 and 49.9 mg Nm⁻³, respectively, and operating under 80% loading are 2.3 and 62.7 mg Nm⁻³, respectively. Inorganic matter is the major component of CPM emitted from this oil-fired boiler, accounting for more than 96% of total CPM. Previous study also points out that CPM emissions from stationary sources are dominated by inorganic substances (Yang et al., 2014). However, Yang et al. (2018b) reported that the proportion of inorganic CPM in oil-fired boilers was between 19.5% and 79.6%. The big variation may be attributed to the different operating temperature and combustion condition of the boiler investigated. Generally speaking, more complete combustion results in lower emission of organic CPM.

Since inorganic CPM is the most important component of total CPM, this study also analyzed the major components of inorganic CPM. Contributions of major water-soluble ions including sulfate, nitrate, and chloride to the CPM are analyzed as shown in Fig. 4. Interestingly, gaseous HCl concentration is lower than NOₓ, but the contribution of Cl⁻ is higher than that of NO₃⁻ possibly due to the higher water solubility of HCl compared with NO₃⁻. Overall, SO₄²⁻ accounts for 41%–45% of CPM, indicating that SO₄²⁻ is the main component of CPM emitted from this oil-fired power plant. Tao et al. (2020) mentioned that SO₄²⁻ is the main component of CPM, accounting for more than 60% of CPM. Yang et al. (2018b) analyzed the CPM composition of oil-fired boilers, and the results indicate that SO₄²⁻ is of the highest proportion. In addition to SO₄²⁻, Cl⁻, NO₃⁻, inorganic CPM may also contain F⁻, NH₄⁺, Na, Ca, Fe, Mg, Al, K, and trace heavy metals (Zhang et al., 2021). Due to the complex composition of CPM, only sulfur component has been determined to significantly increase the concentration of CPM. In order to effectively control CPM emissions from oil-fired process, it is necessary to further study the composition of CPM in the future.

3.3 Emission Characteristics and Distribution of PAHs

3.3.1 Mass concentration and distribution of PAHs

Table 2 shows the gas-phase and particle-phase concentrations of 27 PAHs measured in the flue gas emitted from this oil-fired boiler. The total concentration of PAHs emitted at 30% loading was 2.8 µg Nm⁻³, while 2.5 µg Nm⁻³ was measured at 80% loading. It indicates that the boiler loading has no significant effect on the total mass concentration of PAHs emitted from this oil-fired power plant. Li et al. (1999) analyzed the PAHs emissions from 21 oil-fired boilers for 21 PAH congeners, and the average concentration was 566 µg Nm⁻³, which was much higher than the results obtained in this study. The possible reasons are related to fuel composition, combustion conditions, installed capacity of boilers and types of APCDs adopted.
Fig. 4. Contributions of Cl, NO₃, SO₄²⁻ to inorganic CPM.

Table 2. Concentrations of gas-phase and particulate phase PAHs measured in the oil-fired boiler investigated (ng Nm⁻³).

<table>
<thead>
<tr>
<th></th>
<th>P phase</th>
<th>G phase</th>
<th>P phase</th>
<th>G phase</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nap</td>
<td>46.2</td>
<td>2,176.0</td>
<td>8.3</td>
<td>2,213.1</td>
</tr>
<tr>
<td>2-MN</td>
<td>4.7</td>
<td>139.7</td>
<td>4.0</td>
<td>43.9</td>
</tr>
<tr>
<td>AcPy</td>
<td>0.7</td>
<td>5.6</td>
<td>0.3</td>
<td>1.0</td>
</tr>
<tr>
<td>Acp</td>
<td>1.0</td>
<td>3.2</td>
<td>0.7</td>
<td>5.6</td>
</tr>
<tr>
<td>Flu</td>
<td>0.5</td>
<td>1.5</td>
<td>1.8</td>
<td>5.1</td>
</tr>
<tr>
<td>PA</td>
<td>6.0</td>
<td>30.4</td>
<td>8.7</td>
<td>32.7</td>
</tr>
<tr>
<td>Ant</td>
<td>0.5</td>
<td>1.3</td>
<td>ND</td>
<td>1.5</td>
</tr>
<tr>
<td>FL</td>
<td>21.9</td>
<td>51.5</td>
<td>2.3</td>
<td>19.6</td>
</tr>
<tr>
<td>Pyr</td>
<td>60.0</td>
<td>132.8</td>
<td>2.3</td>
<td>44.0</td>
</tr>
<tr>
<td>BcFE</td>
<td>0.3</td>
<td>0.4</td>
<td>ND</td>
<td>0.4</td>
</tr>
<tr>
<td>CYC</td>
<td>1.3</td>
<td>0.7</td>
<td>ND</td>
<td>0.7</td>
</tr>
<tr>
<td>BaA</td>
<td>1.3</td>
<td>0.6</td>
<td>ND</td>
<td>0.7</td>
</tr>
<tr>
<td>CHR</td>
<td>2.0</td>
<td>1.3</td>
<td>0.3</td>
<td>1.5</td>
</tr>
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<td>5-MC</td>
<td>0.2</td>
<td>0.1</td>
<td>ND</td>
<td>ND</td>
</tr>
<tr>
<td>BbF</td>
<td>2.3</td>
<td>1.0</td>
<td>0.1</td>
<td>0.9</td>
</tr>
<tr>
<td>BkF</td>
<td>1.0</td>
<td>0.5</td>
<td>0.1</td>
<td>0.5</td>
</tr>
<tr>
<td>BjF</td>
<td>0.8</td>
<td>0.3</td>
<td>ND</td>
<td>0.2</td>
</tr>
<tr>
<td>BeP</td>
<td>30.5</td>
<td>6.3</td>
<td>ND</td>
<td>11.3</td>
</tr>
<tr>
<td>BaP</td>
<td>4.1</td>
<td>1.2</td>
<td>ND</td>
<td>2.5</td>
</tr>
<tr>
<td>PER</td>
<td>0.3</td>
<td>0.3</td>
<td>ND</td>
<td>0.3</td>
</tr>
<tr>
<td>IND</td>
<td>9.0</td>
<td>2.4</td>
<td>ND</td>
<td>3.8</td>
</tr>
<tr>
<td>DBA</td>
<td>ND</td>
<td>0.099</td>
<td>ND</td>
<td>ND</td>
</tr>
<tr>
<td>BghiP</td>
<td>60.5</td>
<td>15.0</td>
<td>0.1</td>
<td>23.9</td>
</tr>
<tr>
<td>DBaI P</td>
<td>0.6</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
</tr>
<tr>
<td>DBP</td>
<td>3.4</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
</tr>
<tr>
<td>DBaIP</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
</tr>
<tr>
<td>DBahP</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
</tr>
<tr>
<td>∑27 PAHs</td>
<td>258.9</td>
<td>2,572</td>
<td>29.06</td>
<td>2,413</td>
</tr>
<tr>
<td>Total PAHs</td>
<td>2,831</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Total BaP_{eq}</td>
<td>33.9</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Fig. 5. Distribution of PAHs in gas and particle phase in terms of mass concentrations.

Gas-phase PAHs emitted from the oil-fired boiler at 30% and 80% loadings accounted for 90% and 99% of the total PAHs concentration, respectively, which is consistent with those reported by Li et al. (2018a), Lu et al. (2019), and Lu et al. (2020). It is attributed to the fact that existing APCD has a good removal effect on particle-phase PAHs, but the removal efficiency on gas-phase PAHs is limited. In addition, the phase distributions of PAHs with different loadings are slightly different, which is related to the distribution of the number of rings. Fig. 5 shows the distribution of PAHs in mass concentration by groups of benzene rings. At 80% loading, the gas-phase and particle-phase PAHs are dominated by 2 rings, but the proportion of 3 rings and 4 rings in the particle-phase is significantly higher than that of the gas-phase PAHs. At 30% loading, the medium and high molecular weight (MMW and HMW) PAHs which contain 4–5 rings and ≥6 rings congeners, respectively, are the main contributors. More than 70% of the particle-phase PAHs are contributed by 4 to 6 rings congeners. This indicates that the increase in loading reduces the MMW and HMW congener distribution of the particle-phase PAHs.

3.3.2 TEQ concentration and distribution of PAHs

Fig. S2 shows the TEQ distribution of 27 PAHs emitted from the oil-fired boiler. The results indicate that the TEQ of total PAHs at 30% and 80% loadings are 33.9 and 13.5 ng-BaP eq Nm\(^{-3}\), respectively. Among the 27 PAHs investigated, BcFE (13 and 7.5 ng-BaP eq Nm\(^{-3}\), respectively), BaP (5.3 and 2.5 ng-BaP eq Nm\(^{-3}\)), and NaP (2.2 and 2.2 ng-BaP eq Nm\(^{-3}\)) contribute the most to TEQ value. The high contributions of BcFE and BaP are mainly attributed to their high TEFs (20 and 1,
respectively. In terms of mass concentration, the contributions of MMW and HMW PAHs are much lower than those of low ring number PAHs, but the overall toxicity contributions are much higher than that of low molecular weight (LMW) PAHs. As mentioned earlier, MMW and HMW PAHs are mainly formed by incomplete combustion and pyrolysis of fuel oil. Operating the boiler at a higher boiler load results in higher combustion temperatures and is more likely to oxidize high-ring PAHs in fuel oil. Therefore, operating the boiler at higher loading tends to reduce the formation of MMW and HMW PAHs. This result also indicates that the increase in boiler loading may help reduce the TEQ of PAHs emitted from oil-fired boiler.

3.4 Emission Factors of Pollutants

Emission factor (EF) is calculated based on pollutant concentrations, gas flow rates and fuel oil combustion rate. The fuel density is assumed as 0.98 ton m$^{-3}$. Emission factor (g ton$^{-1}$) can be used to calculate the total amount of air pollutants emitted by stationary sources in the area, thereby suggesting appropriate control and improvement measures to achieve the goal of maintaining air quality. EF is calculated with Eq. (2):

$$
EF \ (g \ ton^{-1}) = C \times Q \times 10^{-3} \ (g \ mg^{-1}) \times \text{oil feeding rate} \ (m^3 \ h^{-1}) \div 0.98 \ (ton \ m^3)
$$

where C is the concentration of pollutant emitted during testing (mg Nm$^{-3}$), Q is the gas flow rate (Nm$^3$ h$^{-1}$).

Table S3 lists the emission factors of various air pollutants based on pollutants concentrations measured and operating parameters. Emission factors of various pollutants from different boilers are also compiled and compared. The results show that the emission factors of FPM, FPM$_{2.5}$ and CPM at 30% loading are $2.1 \pm 0.1$, $1.5 \pm 0.1$, and $677 \pm 5$ g ton$^{-1}$, and are $14.3 \pm 0.1$, $7.8 \pm 0.1$, and $847 \pm 5$ g ton$^{-1}$ at 80% loading, respectively. It indicates that the emission factor of CPM is much higher than that of FPM, which is consistent with those reported by Chen et al. (2022). Emission factors of NO$_x$ and SO$_x$ for 30% loading are 1,590 and 4,610 g ton$^{-1}$, respectively, and for 80% loading are 3,070 and 4,920 g ton$^{-1}$, respectively. Compared with previous studies, the emission factors of NO$_x$ and SO$_x$ of this study are relatively higher, due to the lack of appropriate APCDs for reducing their emissions. The emission factors of PAHs at 30% and 80% loadings are 0.04 and 0.03 g ton$^{-1}$, respectively, which are lower than the values reported for other oil-fired boilers. The first possible reason could be the higher combustion efficiency of the boiler in this study compared with previous studies, resulting in lower PAHs formation. The second reason is that the oil-fired boiler investigated in this study is equipped with ESP, which can effectively remove solid-phase PAHs. Overall, the differences between the emission factors reported by various studies can be attributed to a number of factors, such as boiler operation conditions, fuel type and composition, and APCD configuration and performance.

4 CONCLUSIONS

The characteristics of FPM, FPM$_{2.5}$, CPM, PAHs, and gaseous pollutants including SO$_2$, NO$_x$ and HCl emitted from an oil-fired boiler operated at 30% loading and 80% loading, respectively, are investigated via intensive sampling/analysis. The results show that the concentrations of SO$_2$ and NO$_x$ were measured as 90 ppm and 122 ppm at 30% loading while 176 ppm and 132 ppm were measured at 80% loading, respectively. The FPM concentration increased from 0.16 mg Nm$^{-3}$ to 1.10 mg Nm$^{-3}$ as the loading was increased from 30% to 80%. It indicates that increasing boiler loading reduced the removal efficiency of FPM achieved with ESP. The effect of boiler loading on CPM was less significant than that of FPM, and the concentration of CPM was much higher than that of FPM. In addition, the main component of CPM was SO$_4^{2-}$, implying that SO$_x$ could be the main precursor of CPM emitted from this oil-fired boiler. The PAHs in the flue gas were dominated by 2-ring LMW PAHs, and the contribution of gas-phase PAHs was much higher than that of particle-phase PAHs. In terms of mass concentration, Nap was the dominant congener, while BcFE contributed the most to the toxic equivalent concentration (TEQ$_{BAP}$).
LIST OF ABBREVIATIONS

FPM: filterable particulate matter.
FPM$_{2.5}$: filterable particulate matter with a diameter of 2.5 microns or less.
CPM: condensable particulate matter.
PAHs: polycyclic aromatic hydrocarbons.
APCDs: air pollution control devices.
ESP: electrostatic precipitator.
SCR: selective catalytic reduction.
WFGD: wet flue-gas desulfurization.
TEFs: toxic equivalency factors.
EPA: Environmental Protection Agency.

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ADDITIONAL INFORMATION AND DECLARATIONS

Competing Interests
The authors have no relevant financial or non-financial interests to disclose.

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