Comparative investigation of coal- and oil-fired boilers based on emission factors, ozone and secondary organic aerosol formation potentials of VOCs

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ABSTRACT
Volatile organic compounds (VOCs) are the important precursors of the tropospheric ozone (O₃) and secondary organic aerosols (SOA), both of which are known to harm human health and disrupt the earth’s climate system. In this study, VOC emission factors, O₃ and SOA formation potentials were estimated for two types of industrial boilers: coal-fired boilers (n = 3) and oil-fired boilers (n = 3). Results showed that VOCs concentrations were more than nine times higher for oil-fired boilers compared to those for coal-fired boilers. Emission factors of VOCs were found to be higher for oil-fired boilers (9.26–32.83 mg-VOC/kg) than for coal-fired boilers (1.57–4.13 mg-VOC/kg). Alkanes and aromatics were obtained as the most abundant groups in coal-fired boilers, while oxygenated organics and aromatics were the most contributing groups in oil-fired boilers. Benzene, n-hexane and o-ethyl toluene were the abundant VOC species in coal-fired boiler emissions, whereas toluene was the most abundant VOC species emitted from oil-fired boilers. Benzene, n-hexane and o-ethyl toluene were found 12 and 18 times, respectively, higher for oil-fired than for coal-fired boilers. Total OFP ranged from 3.99 to 11.39 mg-O₃/kg for coal-fired boilers. For oil-fired boilers, total OFP ranged from 36.16 to 131.93 mg-O₃/kg. Moreover, total secondary organic aerosol potential (SOAP) ranged from 65.4 to 122.5 mg-SOA/kg and 779.9 to 2252.5 mg-SOA/kg for the coal-fired and oil-fired boilers, respectively.

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Introduction

It is hard to overstate the importance of industrial development for economic growth. However, industries are also an important source of air pollutants around the globe (Liu et al., 2019; Yang et al., 2018; Zhang et al., 2018, 2012). Industrial emissions consist of varieties of air pollutants such as particulate matter, oxides of carbon, oxides of nitrogen, volatile organic compounds (VOCs) and persistent organic pollutants. These pollutants pose threats to human health and the environment (Geng et al., 2019; Liang et al., 2019; Tsai et al., 2019). VOCs form a major group of air pollutants that play important roles in tropospheric chemistry (Wu et al., 2017; Zong et al., 2018). VOCs can react with oxides of nitrogen and hydroxyl radicals with the aid of sunlight to form photochemical oxidants (Shi et al., 2015). VOCs, after going through oxidation reactions in the atmosphere, may lead to the formation of low vapor pressure oxidation products. These oxidation products may get absorbed into the atmospheric aerosols (Derwent et al., 2010). VOCs have been gaining increasing concerns due to their important roles in the formation of tropospheric ozone ($O_3$), secondary organic aerosols (SOA), and their potential threats to human health (Shao et al., 2009; Wu et al., 2017). Some of the VOCs participate in the photochemical reactions and help in the formation of tropospheric $O_3$ (Li et al., 2018). However, different VOC species have different chemical reactivity, ozone and SOA formation potentials. Thus, it is crucial to analyze the speciated VOCs to evaluate the overall impacts of an emission source on air quality.

Industrial sectors make one of the major anthropogenic emission sources of VOCs in the atmosphere (Gariazzo et al., 2005; Ribeiro et al., 2012). Several studies have been conducted for VOC emissions from vehicles (Dhital et al., 2019; Liu et al., 2008), biomass burning (Jumpponen et al., 2013; Li et al., 2018), solvent usage (Geng et al., 2019; Zheng et al., 2013), refineries (Lin et al., 2004; Zhang et al., 2017) and petrochemical industries (Liu et al., 2008; Mo et al., 2017). Wang et al. (2009) studied biomass burning emissions in cooking stoves and observed a high percentage of alkenes, alkynes and aromatic VOCs (24.3%–25.2% alkenes and alkynes, 39.1%–49.9% aromatics). Lin et al. (2004) reported that benzene and toluene were the most abundant VOCs around Kaohsiung petroleum refinery in Taiwan. Tsai et al. (2008) reported toluene, 1,2,4-trimethyl benzene, $m/p$-xylene, 1-butene, ethylbenzene and benzene as the major VOCs in the emission from an integrated iron and steel plant in southern Taiwan.

There are only a limited number of studies available for VOC emissions from coal-fired and oil-fired boilers (Bo et al., 2008; Fernández-Martínez et al., 2001; Geng et al., 2019; Shi et al., 2015; Yen and Horng, 2009). Coal combustion in industrial boilers has been found to be an important source of aromatic VOCs (Fernández-Martínez et al., 2001; García et al., 1992). Toluene, xylene, ethylbenzene and benzene have been found to be the important VOCs in the emissions from a coal-fired power plant in Poland (Chmielewski et al., 2003). In Spain, a large amount of aromatic VOCs, namely, benzene, toluene, ethylbenzene, xylene and trimethyl benzenes was emitted from the coal-fired power plant (Fernández-Martínez et al. 2001). dos Santos Siqueira et al. (2017) sampled 36 VOCs from coal-fired boilers in Brazil, and benzene was reported to have the highest concentrations. Toluene and $n$-hexane were the major species in coal-fired boiler emissions, with a mass fraction of 38.6% (Shi et al., 2015). A better understanding of the industrial emissions of VOCs would be required to evaluate the impacts of emission sources on the air quality and to devise strategies for the effective control of industrial emissions (Shin et al., 2013).

In this study, VOC emission concentrations, emission factors and chemical profiles, ozone formation potentials and secondary organic aerosol potentials were analyzed for two types of industrial boilers: coal-fired boilers and oil-fired boilers. The results of this study would enhance the understanding of the VOC emission characteristics of the aforementioned industrial boilers. This study might also help policy-makers to formulate and update policies for VOCs emission control from industrial boilers.

1. Materials and methods

1.1. Description of industrial boilers

Two types of industrial boilers, namely coal-fired ($n = 3$) and oil-fired ($n = 3$) boilers, were selected in the present study for the collection of VOC emission samples. The boilers were operated intermittently as per the necessity of heat or hot water for industrial processes. All emission sources were sampled in triplicates. Table 1 provides detailed information about the industrial boilers tested in the present study.

1.2. VOCs sampling and analysis

Emission samples were collected using 6 L Silonite™ coated stainless steel canisters (Entech Instruments, Catalog# 29-10622) that had been pre-cleaned with high-purity nitrogen and evacuated. VOC sampling system included a sampling probe, a flow regulation system (Entech Instruments, CS1200E Passive Canister Sampler) and a canister. The flow regulation system consisted of a particulate filter, a vacuum gauge and a flow restrictor (code# 1, flow range: 50–150 cc/min). The flow regulation system was used to spread the sample flow over a specific time period to ensure an average composite or time-weighted average sample.

There are wide variations in the conditions in most industrial stacks which may produce different compositions and concentrations of VOC emissions. The selection of the sampling location in the stack is critical for obtaining representative samples. To minimize the effects of process variables, monitoring was conducted when there was nearly a constant flow through the stack. The VOC sampling system was placed on a platform at half the height of the stack, and it was ensured that there were no flow disturbances from any fan, bend constructions at least 0.5 stack diameter upstream (US EPA, 2017). The sample probe was inserted horizontally into the stack-holes perpendicular to the direction of exhaust flow. The probe was made up of stainless steel and was connected with a probe tube and VOC sampling system. The probe tube was thermally insulated to avoid cooling and condensation of the exhaust gases. Stack-holes were set by the local environment-
tal protection department for routine sampling. Moreover, the sampling point was located after the flue gas treatment system (for the stacks with treatment systems) to ensure that the samples would reflect the better picture of the pollutants emitted into the ambient atmosphere.

The collected samples were analyzed using gas chromatography and mass spectrometry (GC/MS). The analytical system consisted of a pre-concentrator (Entech 7100A), an autosampler (Entech 7032AB), a gas chromatograph (Agilent 6890 N GC) and a mass spectrometer (Agilent 5973 MSD). The VOC samples were cryogenically concentrated at -150 °C, and were thermally desorbed. After that, the sample was transferred to the GC equipped with a DB-5 MS column (60 m × 0.25 mm × 1.00 μm, Agilent Technologies). The carrier gas was helium with a flow rate of 1.0 L/min. The initial GC oven temperature was held at 32 °C for 8 min and then heated to 200 °C with the ramp of 8 °C/min. The oven temperature was held at this temperature for 2 min. Detailed information on the GC/MS analysis can be referred to several previous studies (Dhital et al., 2019; Wang et al., 2013). GC/MS was calibrated with PAMS and TO-15 standard mixture of gases (1.00 ppm, Linde SPECTRA Environmental gases). The target VOC species were identified with the help of retention times and mass spectra. The identified VOCs were quantified using the internal calibration method. Based on the functional groups, the target VOCs were classified as alkanes (27 species), alkenes (9 species), aromatics (18 species), oxygenated VOCs (8 species) and halocarbons (32 species) (Table 2).

1.3. Quality assurance and quality control (QA/QC)

The canisters were cleaned with nitrogen (99.999%) using a canister cleaning system (Entech Model 3100 A) for 12 cycles of filling (30 psia) and evacuation (100 mTorr) before each sampling. Blank analyses were performed to ensure that the canisters were not significantly contaminated. The target VOC species were quantified by the internal calibration method. Calibration was performed with 5 different concentrations of external standards from 0.5 to 50 ppbv. Bromochloromethane, 1,4-difluorobenzene, chlorobenzene-d5 and 4-bromofluorobenzene (BFB) were used as internal standards. Three replicate measurements were done for each experimental condition.

### Table 1 – Basic information of the test coal- and oil-fired industrial boilers.

<table>
<thead>
<tr>
<th>Boiler type</th>
<th>Abbreviation</th>
<th>Temp (°C)</th>
<th>Fuel consumption</th>
<th>Fuel type</th>
<th>Pollution control device</th>
<th>Industry type</th>
<th>Activity</th>
</tr>
</thead>
<tbody>
<tr>
<td>Coal-fired boiler</td>
<td>CL1</td>
<td>120.7</td>
<td>2.2 ton/h</td>
<td>Raw coal</td>
<td>Electrostatic precipitator</td>
<td>Pulp and paper products manufacturing</td>
<td></td>
</tr>
<tr>
<td></td>
<td>CL2</td>
<td>50.8</td>
<td>5.3 ton/h</td>
<td>Raw coal</td>
<td>Cyclone</td>
<td>Textile</td>
<td>Polyester and synthetic fiber</td>
</tr>
<tr>
<td></td>
<td>CL3</td>
<td>49.8</td>
<td>1.5 ton/h</td>
<td>Raw coal</td>
<td>Bag house</td>
<td>Textile</td>
<td>Polyester and synthetic fiber</td>
</tr>
<tr>
<td>Oil-fired boiler</td>
<td>HL1</td>
<td>127.6</td>
<td>0.35 kL/h</td>
<td>Heavy oil</td>
<td>No</td>
<td>Plastic</td>
<td>Plastic and plastic products</td>
</tr>
<tr>
<td></td>
<td>HL2</td>
<td>169.0</td>
<td>0.66 kL/h</td>
<td>Heavy oil</td>
<td>Cyclone</td>
<td>Chemical</td>
<td>Organic fertilizer, biological pesticides and chemicals</td>
</tr>
<tr>
<td></td>
<td>HL3</td>
<td>159.0</td>
<td>0.42 kL/h</td>
<td>Heavy oil</td>
<td>Bag house</td>
<td>Chemical</td>
<td>Chemicals manufacturing</td>
</tr>
</tbody>
</table>

1.4. Composite profile of VOC emissions

The composite source profiles are useful for the comparison of different emission sources based on the relative abundances of different VOC species. Since average profiles might not always be representative of the emission sources, a better approach would be a weighted-average calculation (Mo et al., 2015). We applied the weight-average calculation approach proposed by Mo et al. (2015) to develop the composite source profiles.

1.5. Estimation of OFP and SOAP

The ozone formation potentials (OFP) and the secondary organic aerosol potentials (SOAP) were estimated using the maximum incremental reactivity and SOA formation potential of the individual VOC species (Dhital et al., 2019; Mo et al., 2017). The OFP and SOAP were estimated using Eqs. (1) and (2).

\[
\text{OFP}_j = \sum_{i=1}^{n} f_{i,j} \times \text{MIR}_i \tag{1}
\]

where, \(\text{OFP}_j\) is the OFP of \(\Sigma\text{VOCs}\) of source \(j\) (mg-O3/kg), \(f_{i,j}\) is the weighted average of \(i\)th VOC species in source \(j\) (mg/kg), and \(\text{MIR}_i\) is the maximum incremental reactivity (MIR) of \(i\)th VOC species (g-O3/g VOCs) (Carter, 2009).

\[
\text{SOAP}_j = \sum_{j=1}^{n} f_{i,j} \times \text{SOAP}_i \tag{2}
\]

where \(\text{SOAP}_j\) is the total SOA formation potential of source \(j\) (mg-SOA/kg), \(\text{SOAP}_i\) is the SOA formation potential of \(i\)th VOC species, as cited by Derwent et al. (2010) and Geng et al. (2019). The secondary organic aerosol potential (SOAP) represents the tendency of a VOC to form SOA on an equal mass emitted basis relative to toluene.

2. Results and discussion

2.1. Emissions and mass distribution of VOC species

The sum of concentrations of the detected VOCs (ΣVOCs) emitted from coal-fired and oil-fired industrial boilers were
Table 2 – List of the target VOC species.

<table>
<thead>
<tr>
<th>No.</th>
<th>Species</th>
<th>No.</th>
<th>Species</th>
<th>No.</th>
<th>Species</th>
<th>No.</th>
<th>Species</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Isobutane</td>
<td>20</td>
<td>2,3,4-Trimethylpentane</td>
<td>38</td>
<td>Toluene</td>
<td>57</td>
<td>Acetone</td>
</tr>
<tr>
<td>2</td>
<td>n-Butane</td>
<td>21</td>
<td>2-Methylheptane</td>
<td>39</td>
<td>Ethylbenzene</td>
<td>58</td>
<td>Isopropyl alcohol</td>
</tr>
<tr>
<td></td>
<td></td>
<td>22</td>
<td>3-Methylheptane</td>
<td>40</td>
<td>m-Xylene</td>
<td>59</td>
<td>Methyl tert butyl ether</td>
</tr>
<tr>
<td>3</td>
<td>Isopentane</td>
<td>23</td>
<td>n-Octane</td>
<td>41</td>
<td>p-Xylene</td>
<td>60</td>
<td>Ethyl acetate</td>
</tr>
<tr>
<td></td>
<td></td>
<td>24</td>
<td>n-Nonane</td>
<td>42</td>
<td>Styrene</td>
<td>61</td>
<td>Methyl methacrylate</td>
</tr>
<tr>
<td>5</td>
<td>2,2-Dimethylbutane</td>
<td>25</td>
<td>n-Decane</td>
<td>43</td>
<td>o-Xylene</td>
<td>62</td>
<td>1,4-Dioxane</td>
</tr>
<tr>
<td>6</td>
<td>2,3-Dimethylbutane</td>
<td>26</td>
<td>n-Undecane</td>
<td>44</td>
<td>Isopropyl benzene</td>
<td></td>
<td></td>
</tr>
<tr>
<td>7</td>
<td>Cyclopentane</td>
<td>27</td>
<td>n-Dodecane</td>
<td>45</td>
<td>n-Propyl benzene</td>
<td>63</td>
<td></td>
</tr>
<tr>
<td></td>
<td>2-Methylpentane</td>
<td>46</td>
<td>m-Ethyl toluene</td>
<td>64</td>
<td></td>
<td>59</td>
<td>Methyl tert-butyl ether</td>
</tr>
<tr>
<td>9</td>
<td>3-Methylpentane</td>
<td>28</td>
<td>Propene</td>
<td>47</td>
<td>p-Ethyl toluene</td>
<td>65</td>
<td>Vinyl chloride</td>
</tr>
<tr>
<td>10</td>
<td>n-Hexane</td>
<td>29</td>
<td>1-Butene</td>
<td>48</td>
<td>1,3,5-Trimethylbenzene</td>
<td>66</td>
<td>Bromomethane</td>
</tr>
<tr>
<td>11</td>
<td>2,4-Dimethylpentane</td>
<td>30</td>
<td>Trans-2-butenene</td>
<td>49</td>
<td>o-Ethyl toluene</td>
<td>67</td>
<td>Feron-11</td>
</tr>
<tr>
<td>12</td>
<td>Methylcyclopentane</td>
<td>31</td>
<td>Cis-2-butenene</td>
<td>50</td>
<td>1,2,4-Trimethylbenzene</td>
<td>68</td>
<td>Cis-1,2-dichloroethene</td>
</tr>
<tr>
<td>13</td>
<td>2-Methylhexane</td>
<td>32</td>
<td>1-Pentene</td>
<td>51</td>
<td>1,2,3-Trimethylbenzene</td>
<td>69</td>
<td>Methylene chloride</td>
</tr>
<tr>
<td>14</td>
<td>Cyclohexane</td>
<td>33</td>
<td>Trans-2-pentene</td>
<td>52</td>
<td>m-Diethyl benzene</td>
<td>70</td>
<td>Trans-1,2-dichloroethene</td>
</tr>
<tr>
<td>15</td>
<td>2,3-Dimethylpentane</td>
<td>34</td>
<td>Isoprene</td>
<td>53</td>
<td>p-Diethyl benzene</td>
<td>71</td>
<td>1,1-Dichloroethene</td>
</tr>
<tr>
<td>16</td>
<td>3-Methylhexane</td>
<td>35</td>
<td>Cis-2-pentene</td>
<td>54</td>
<td>Naphthalene</td>
<td>72</td>
<td>1,1-Dichloroethene</td>
</tr>
<tr>
<td>17</td>
<td>2,2,4-Trimethylpentane</td>
<td>36</td>
<td>1-Hexene</td>
<td>55</td>
<td>Oxygenated VOC</td>
<td>73</td>
<td>Chloroform</td>
</tr>
<tr>
<td>18</td>
<td>n-Heptane</td>
<td>37</td>
<td>Methylcyclohexane</td>
<td>56</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>19</td>
<td></td>
<td></td>
<td>Methylcyclohexane</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

calculated. ΣVOCs of oil-fired boilers were > 9 times higher than those of coal-fired boilers. The ΣVOCs concentrations in the emissions from coal-fired (CL1 – CL3) and oil-fired (HL1 – HL3) boilers ranged from 0.11–0.30 mg/m³ and 1.90–2.61 mg/m³, respectively (Table 3). The differences in concentrations could have been caused by different emission strengths of each unit, which could be influenced by fuel types and consumptions, operating conditions, and control devices used during the sampling period (Mo et al., 2015). The VOC species resulting from coal and oil burning have been reported to be mainly aromatics, alkanes, alkenes and oxygenated organics (Li et al., 2018; Wang et al., 2018), which were also detected in all samples in the present study. The ΣVOCs concentrations obtained in the present study were relatively lower compared with those reported in the literature (Table 3).

The proportion of different VOC categories in VOC species in the emissions of coal-fired and oil-fired boilers are shown in Fig. 1. Alkanes (29.0%–47.8%) and aromatics (30.8%–39.6%) were obtained as the most abundant VOC groups in coal-fired boilers, while, in oil-fired boilers, oxygenated organics (1.8%–41.9%) and aromatics (56.0%–94.7%) were more contributing groups. High proportions of alkanes in the exhaust might be the result of incomplete combustion of volatile compounds present in fuel (Geng et al., 2019). The contributions of major VOCs measured in the present study were comparable to those reported in the literature. Geng et al. (2019) studied emissions from wood biomass burning in industrial boilers and found high proportions of alkanes (13.6%–20.2%) and aromatics (4.7%–10.6%). They also reported similar proportions of VOC categories for the coal-fired industrial boilers and the biomass boilers. Yan et al. (2016) found the contributions of aromatics and alkanes ranging from 1% to 10% of total VOCs in emissions from the coal-fired power plant. Wang et al. (2009) found that a high percentage of aromatics and alkanes (benzene, toluene and acetone) was emitted by different biofuel-based stoves. More variations were observed for coal-fired boilers due to temperature variations.

Higher concentrations of oxygenated VOCs such as ethyl acetate were observed in the oil-fired boiler HL3 compared to the HL1 and HL2. The reason for the differences may be related to the nature of industrial processes and the composition of heavy oil. Heavy oil contains varying amounts of sulfur, heavy metals, wax and carbon residues as contaminants. These contaminants make heavy oil unsuitable for uniform combustion which could affect emissions of different pollutants including VOCs. In Chinese Taipei, various heavy oil types are available such as IFO 380 and IFO 180 (IFO: intermediate fuel oil). IFO 380 is the representative of heavy residual oil (RO: 98%), whereas
Table 3 – Comparison of ΣVOCs obtained in this study with previous studies.

<table>
<thead>
<tr>
<th>Source type</th>
<th>Abbreviation of boiler</th>
<th>Fuel</th>
<th>ΣVOCs (mg/m³)</th>
<th>Emission factors (mg-VOC/kg)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Coal-fired boiler</td>
<td>CL1</td>
<td>Coal</td>
<td>0.11</td>
<td>1.57</td>
<td>This study</td>
</tr>
<tr>
<td></td>
<td>CL2</td>
<td>Coal</td>
<td>0.30</td>
<td>4.13</td>
<td>This study</td>
</tr>
<tr>
<td></td>
<td>CL3</td>
<td>Coal</td>
<td>0.16</td>
<td>2.26</td>
<td>This study</td>
</tr>
<tr>
<td>Oil-fired boiler</td>
<td>HL1</td>
<td>Heavy oil</td>
<td>1.90</td>
<td>23.94</td>
<td>This study</td>
</tr>
<tr>
<td></td>
<td>HL2</td>
<td>Heavy oil</td>
<td>0.74</td>
<td>9.29</td>
<td>This study</td>
</tr>
<tr>
<td></td>
<td>HL3</td>
<td>Heavy oil</td>
<td>2.61</td>
<td>32.83</td>
<td>This study</td>
</tr>
<tr>
<td>Coal-fired boiler</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Wei et al. (2008)</td>
</tr>
<tr>
<td>Coal-fired boiler</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>dos Santos et al. (2004)</td>
</tr>
<tr>
<td>Coal-fired boiler</td>
<td></td>
<td>Coal</td>
<td>0.50</td>
<td></td>
<td>Wei et al. (2008)</td>
</tr>
<tr>
<td>Coal-fired boiler</td>
<td></td>
<td>Coal</td>
<td></td>
<td>40.0</td>
<td>Yan et al. (2016)</td>
</tr>
<tr>
<td>Coal-fired boiler</td>
<td></td>
<td>Coal</td>
<td></td>
<td>23.0</td>
<td>Yan et al. (2016)</td>
</tr>
<tr>
<td>Coal-fired boiler</td>
<td></td>
<td>Coal gangue</td>
<td></td>
<td>5.0</td>
<td>Yan et al. (2016)</td>
</tr>
<tr>
<td>Coal-fired boiler</td>
<td></td>
<td>Biomass</td>
<td></td>
<td>57.0</td>
<td>Yan et al. (2016)</td>
</tr>
<tr>
<td>Oil-fired boiler</td>
<td>HL4</td>
<td>Fuel oil</td>
<td></td>
<td>143.3</td>
<td>Bo et al. (2008)</td>
</tr>
<tr>
<td>Oil-fired boiler</td>
<td>HL5</td>
<td>Oil</td>
<td></td>
<td>120.0</td>
<td>Wei et al. (2008)</td>
</tr>
<tr>
<td>Coal-fired boiler</td>
<td></td>
<td>Coal</td>
<td></td>
<td>180.0</td>
<td>Zheng et al. (2009)</td>
</tr>
<tr>
<td>Heating</td>
<td>Coal</td>
<td></td>
<td></td>
<td>198.4</td>
<td>Bo et al. (2008)</td>
</tr>
<tr>
<td>Heating</td>
<td>Heavy oil</td>
<td></td>
<td></td>
<td>209.4</td>
<td>Bo et al. (2008)</td>
</tr>
<tr>
<td>Biomass boiler</td>
<td>Wood pellets</td>
<td>24.58</td>
<td>128.59</td>
<td></td>
<td>Geng et al. (2019)</td>
</tr>
<tr>
<td>Biomass boiler</td>
<td>Straw pellets</td>
<td>13.09</td>
<td>146.16</td>
<td></td>
<td>Geng et al. (2019)</td>
</tr>
</tbody>
</table>

Fig. 1. – Mass proportions of VOCs emitted from coal- and oil-fired boilers.

IFO 180 is the representative of a lighter residual oil (RO: 88%). Thus, the nature of manufacturing and the type of fuels could account for the observed differences in the VOC compositions and concentrations. However, further studies might be required to fully understand the influences of fuels and the nature of industrial processes on VOCs.

2.2. Emission factors and species composition

The emission factors have been expressed as milligrams of VOC emitted per kilogram of fuel burned (mg-VOC/kg). The ΣVOCs emission factors of oil-fired boilers (9.26–32.83 mg-VOC/kg) were much higher than those of coal-fired boilers (1.57–4.13 mg-VOC/kg) (Table 3). The average emission factor for oil-fired boilers was 8 times that of the coal-fired boilers. Wei et al. (2008) also reported that the emission factor of the oil-fired boiler was 3 times the emission factor of the coal-fired boiler. Most of the previous works show that the emission factors of VOCs were relatively higher for oil combustion than for coal combustion (Bo et al., 2008; Wei et al., 2008). Among 94 VOC species, benzene, toluene, n-hexane, acetone, propene, ethyl acetate, 1-butene and methyl ethyl ketone were obtained as the most abundant species. The major VOCs species detected in this study were similar to those found in earlier studies (Liu et al., 2008; Wang et al., 2009).

2.2.1. Coal-fired boilers

The VOC composition in the coal-fired boiler emissions depends largely on the coal types, types of industries. Table 4 lists the emission factors and weight contributions to ΣVOCs...
Table 4 – Top 10 VOC species emission factors and composition for coal-fired boilers.

<table>
<thead>
<tr>
<th>Species</th>
<th>CL1 Emission factor (mg-VOC/kg)</th>
<th>wt., %</th>
<th>Species</th>
<th>CL2 Emission factor (mg-VOC/kg)</th>
<th>wt., %</th>
<th>Species</th>
<th>CL3 Emission factor (mg-VOC/kg)</th>
<th>wt., %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Benzene</td>
<td>0.34</td>
<td>21.5</td>
<td>n-Hexane</td>
<td>1.18</td>
<td>28.6</td>
<td>o-Ethyl toluene</td>
<td>0.36</td>
<td>16.1</td>
</tr>
<tr>
<td>o-Ethyl toluene</td>
<td>0.19</td>
<td>11.9</td>
<td>Toluene</td>
<td>0.78</td>
<td>18.9</td>
<td>n-Dodecane</td>
<td>0.32</td>
<td>14.1</td>
</tr>
<tr>
<td>n-Dodecane</td>
<td>0.18</td>
<td>11.7</td>
<td>n-Undecane</td>
<td>0.46</td>
<td>11.0</td>
<td>Benzene</td>
<td>0.19</td>
<td>8.4</td>
</tr>
<tr>
<td>Acetone</td>
<td>0.16</td>
<td>10.1</td>
<td>Ethyl acetate</td>
<td>0.44</td>
<td>10.7</td>
<td>Propene</td>
<td>0.16</td>
<td>7.2</td>
</tr>
<tr>
<td>n-Undecane</td>
<td>0.10</td>
<td>6.4</td>
<td>1,3,5-Trimethylbenzene</td>
<td>0.18</td>
<td>4.4</td>
<td>Methyl methacrylate</td>
<td>0.15</td>
<td>6.7</td>
</tr>
<tr>
<td>1-Butene</td>
<td>0.09</td>
<td>5.5</td>
<td>Ethyl acetate</td>
<td>0.09</td>
<td>2.3</td>
<td>2-Methylpentane</td>
<td>0.11</td>
<td>5.0</td>
</tr>
<tr>
<td>2-Methylpentane</td>
<td>0.08</td>
<td>5.0</td>
<td>Ethanol</td>
<td>0.13</td>
<td>3.1</td>
<td>n-Hexane</td>
<td>0.14</td>
<td>6.2</td>
</tr>
<tr>
<td>Methylene chloride</td>
<td>0.05</td>
<td>3.5</td>
<td>2-Methylpentane</td>
<td>0.12</td>
<td>3.0</td>
<td>Acetone</td>
<td>0.12</td>
<td>5.1</td>
</tr>
<tr>
<td>3-Methylhexane</td>
<td>0.04</td>
<td>2.7</td>
<td>Benzene</td>
<td>0.09</td>
<td>2.3</td>
<td>2-Methylpentane</td>
<td>0.11</td>
<td>5.0</td>
</tr>
<tr>
<td>Ethyl acetate</td>
<td>0.04</td>
<td>2.7</td>
<td>p-Xylene</td>
<td>0.08</td>
<td>1.9</td>
<td>n-Undecane</td>
<td>0.09</td>
<td>4.0</td>
</tr>
<tr>
<td>Total</td>
<td>1.27</td>
<td>80.8</td>
<td></td>
<td>3.64</td>
<td>88.0</td>
<td></td>
<td>1.80</td>
<td>79.5</td>
</tr>
</tbody>
</table>

Table 5 – Top 10 VOC species emission factors and composition for oil-fired boilers.

<table>
<thead>
<tr>
<th>Species</th>
<th>HL1 Emission factor (mg-VOC/kg)</th>
<th>wt., %</th>
<th>Species</th>
<th>HL2 Emission factor (mg-VOC/kg)</th>
<th>wt., %</th>
<th>Species</th>
<th>HL3 Emission factor (mg-VOC/kg)</th>
<th>wt., %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Toluene</td>
<td>21.57</td>
<td>90.1</td>
<td>Toluene</td>
<td>7.42</td>
<td>80.1</td>
<td>Toluene</td>
<td>17.43</td>
<td>53.1</td>
</tr>
<tr>
<td>Benzene</td>
<td>0.80</td>
<td>3.3</td>
<td>3-Methylpentane</td>
<td>0.27</td>
<td>2.9</td>
<td>Ethyl acetate</td>
<td>9.17</td>
<td>27.9</td>
</tr>
<tr>
<td>n-Undecane</td>
<td>0.30</td>
<td>1.3</td>
<td>1,3,5-Trimethylbenzene</td>
<td>0.18</td>
<td>1.9</td>
<td>Benzene</td>
<td>4.52</td>
<td>13.8</td>
</tr>
<tr>
<td>Ethyl acetate</td>
<td>0.25</td>
<td>1.0</td>
<td>2,2-Dimethylbutane</td>
<td>0.18</td>
<td>1.9</td>
<td>Benzene</td>
<td>0.29</td>
<td>0.9</td>
</tr>
<tr>
<td>n-Hexane</td>
<td>0.14</td>
<td>0.6</td>
<td>Ethyl acetate</td>
<td>0.16</td>
<td>1.7</td>
<td>n-Propyl benzene</td>
<td>0.14</td>
<td>0.4</td>
</tr>
<tr>
<td>1,3,5-Trimethylbenzene</td>
<td>0.13</td>
<td>0.6</td>
<td>Benzene</td>
<td>0.15</td>
<td>1.6</td>
<td>2,2-Dimethylbutane</td>
<td>0.12</td>
<td>0.4</td>
</tr>
<tr>
<td>o-Xylene</td>
<td>0.12</td>
<td>0.5</td>
<td>1,2,4-Trimethylbenzene</td>
<td>0.15</td>
<td>1.6</td>
<td>1,3,5-Trimethylbenzene</td>
<td>0.11</td>
<td>0.3</td>
</tr>
<tr>
<td>Acetone</td>
<td>0.11</td>
<td>0.5</td>
<td>n-Undecane</td>
<td>0.14</td>
<td>1.5</td>
<td>1,2,4-Trimethylbenzene</td>
<td>0.11</td>
<td>0.3</td>
</tr>
<tr>
<td>Methylcyclopentane</td>
<td>0.09</td>
<td>0.4</td>
<td>n-Propyl benzene</td>
<td>0.10</td>
<td>1.1</td>
<td>n-Undecane</td>
<td>0.10</td>
<td>0.3</td>
</tr>
<tr>
<td>2,3-Dimethylbutane</td>
<td>0.09</td>
<td>0.4</td>
<td>Acrolein</td>
<td>0.10</td>
<td>1.1</td>
<td>m-Xylene</td>
<td>0.08</td>
<td>0.2</td>
</tr>
<tr>
<td>Total</td>
<td>23.61</td>
<td>98.6</td>
<td></td>
<td>8.86</td>
<td>95.6</td>
<td></td>
<td>32.06</td>
<td>97.6</td>
</tr>
</tbody>
</table>

of 10 most abundant species emitted from the coal-fired boilers types. It was found that benzene (0.34 mg-VOC/kg and 21.5%), n-hexane (1.18 mg-VOC/kg and 28.6%) and o-ethyl toluene (0.36 mg-VOC/kg and 16.1%) had the highest emission factors and weight percentages for CL1, CL2 and CL3, respectively. Other major VOC species in the coal-fired boilers were n-dodecane, acetone, toluene, ethyl acetate, and propane. These top 10 species accounted for more than 79% of the VOCs. The variations might have been caused by the differences in the quality of coals (Li et al., 2018). Liu et al. (2008) reported that propane, benzene and toluene were major contributors of the VOCs emitted from coal combustion. Fernández-Martínez et al. (2001) observed higher percentages of benzene, toluene, ethyl benzene, xylenes and trimethylbenzenes in VOCs for coal-fired boilers. Toluene and n-hexane have been found to be the most abundant species in coal-fired boilers, with the mass contributions of 38.6% (Shi et al., 2015). Li et al. (2018) reported n-decane (18.3% of ΣVOCs) and benzene (16.5% of ΣVOCs) were the most abundant VOCs emitted from coal-fired boilers. They also reported that alkanes, alkenes and aromatics accounted for 42.9%, 22.1% and 35%, respectively, of VOCs for the coal-fired power plants. The results of the present study were mostly comparable to those of the above literature.

2.2.2. Oil-fired boilers

Table 5 presents the top 10 VOC species in terms of their emission factors and weight percentages in the VOCs in the emissions of oil-fired boilers. Toluene was the most abundant VOC species with its mass contribution ranging from 53% to 90% for all oil-fired boilers. Other major species from the oil-fired boilers were ethyl acetate and acrolein accounting for 27.9% (9.17 mg-VOC/kg) and 13.8% (4.52 mg-VOC/kg) of the VOCs, respectively. Some other species were 3-methylpentane, n-undecane, 2,2-dimethylbutane, ethyl acetate, benzene and
### Table 6 – Top 10 VOC species in terms of the contribution to OFP.

<table>
<thead>
<tr>
<th></th>
<th>OFP from top 10 VOC species (mg-O3/kg)</th>
<th>OFP from ΣVOCs (mg-O3/kg)</th>
<th>Sum (top 10)/ΣVOCs</th>
</tr>
</thead>
<tbody>
<tr>
<td>Coal-fired boilers</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CL1 o-Ethyltoluene</td>
<td>1.04 1-Butene 0.83 p-Xylene 0.15</td>
<td>3.99 65.7%</td>
<td></td>
</tr>
<tr>
<td>CL2 Toluene</td>
<td>3.12 1,3,5-Trimethylbenzene 2.14 1,4-Butene 0.46</td>
<td>11.39 76.2%</td>
<td></td>
</tr>
<tr>
<td>CL3 o-Ethyltoluene</td>
<td>2.04 Propene 1.90 2-Methylpentane 0.17</td>
<td>6.31 60.9%</td>
<td></td>
</tr>
<tr>
<td>Oil-fired boilers</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>HL1 Toluene</td>
<td>86.28 1,3,5-Trimethylbenzene 1,4-Butene 1.57</td>
<td>91.31 98.1%</td>
<td></td>
</tr>
<tr>
<td>HL2 Toluene</td>
<td>29.67 1,3,5-Trimethylbenzene 2.35 1,2,4-Trimethylbenzene 0.21</td>
<td>29.67 94.2%</td>
<td></td>
</tr>
<tr>
<td>HL3 Toluene</td>
<td>69.72 Acrolein 33.68 1,2,3-Trimethylbenzene 0.56</td>
<td>131.93 96.6%</td>
<td></td>
</tr>
<tr>
<td>Avg. (coal-fired boilers)</td>
<td></td>
<td>7.2</td>
<td></td>
</tr>
<tr>
<td>Avg. (oil-fired boilers)</td>
<td></td>
<td>86.5</td>
<td></td>
</tr>
<tr>
<td>Coal-fired boilers</td>
<td>CL1</td>
<td>Benzene</td>
<td>31.26</td>
</tr>
<tr>
<td>-------------------</td>
<td>-----</td>
<td>---------</td>
<td>-------</td>
</tr>
<tr>
<td></td>
<td></td>
<td>p-Xylene</td>
<td>1.74</td>
</tr>
<tr>
<td></td>
<td>CL2</td>
<td>Toluene</td>
<td>77.91</td>
</tr>
<tr>
<td></td>
<td></td>
<td>o-Xylene</td>
<td>5.81</td>
</tr>
<tr>
<td></td>
<td></td>
<td>o-Ethyltoluene</td>
<td>34.56</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Ethylbenzene</td>
<td>1.55</td>
</tr>
<tr>
<td></td>
<td></td>
<td>n-Propylbenzene</td>
<td>198.5</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1,3,5-Trimethylbenzene</td>
<td>1.17</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1,2,3-Trimethylbenzene</td>
<td>3.70</td>
</tr>
<tr>
<td></td>
<td>Oil-fired boilers</td>
<td>HL1</td>
<td>Toluene</td>
</tr>
<tr>
<td></td>
<td></td>
<td>n-Propylbenzene</td>
<td>1.17</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1,3,5-Trimethylbenzene</td>
<td>2.70</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1,2,3-Trimethylbenzene</td>
<td>1.17</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1,2,3-Trimethylbenzene</td>
<td>3.70</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1,2,3-Trimethylbenzene</td>
<td>1.17</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1,2,3-Trimethylbenzene</td>
<td>3.70</td>
</tr>
</tbody>
</table>
other compounds accounting for more than 1% of the ΣVOCs. In total, the top 10 VOC species accounted for 98.6%, 95.6% and 97.6% of ΣVOCs for HL1, HL2 and HL3, respectively. Kansal (2009) reported that benzene was the most abundant aromatic compound emitted from motor vehicles. The major species in the gasoline vehicle emissions were n-butane, trans-2-butene, n-pentane, benzene and toluene (Liu et al., 2008). They also reported that toluene and benzene showed higher contributions in diesel vehicle exhausts. The highest contributions of aromatic compounds were observed in the ambient air of Kaohsiung petroleum refinery, Taiwan ranging from 28.6% to 34.2% of the ΣVOCs (Liu et al., 2008). Acetone was a major VOC in ambient air around a petrochemical complex and an oil refinery in Izmir, Turkey (Cetin et al., 2003).

The emission factors of ΣVOCs were notably different for the aforementioned coal-fired and oil-fired boilers. The highest emission factors were observed for oil-fired boilers (8.86–32.06 mg-VOC/kg) compared to coal-fired boilers (1.27–3.64 mg-VOC/kg). It shows that oil-fired boilers could contribute more to the ambient VOCs than the coal-fired boilers.

2.3. OFP and SOAP for coal- and oil-fired boilers

OFP and SOAP were estimated for the coal- and oil-fired boilers. Tables 6 and 7 list the top 10 VOCs with the highest contributions to O3 and SOA formation. Those VOCs accounted for more than 60% of total OFP and more than 45% of SOAP. The total OFP ranged from 3.99 to 11.39 mg-O3/kg for coal-fired boilers. Moreover, total OFPs were obtained between 36.16 and 131.93 mg-O3/kg for oil-fired boilers (Table 6). Alkenes and alkanes were the major components for coal-fired and oil-fired boilers, respectively. Moreover, aromatic species such as o-ethyl toluene and toluene were the major VOCs for both types of boilers. Toluene and o-ethyl toluene contributed most to the OFP, accounting for more than 25% for coal-fired boilers, while toluene accounted for more than 50% of the total OFP for oil-fired boilers. The top 10 species accounted for more than 60% and 90% of total OFP for coal-fired and oil-fired boilers, respectively. Coal-burning emits significant amounts of aromatics and alkenes from O3 and SOA formation.

The SOAP of individual VOCs ranged from 65.4 to 122.5 mg-SOA/kg for the coal-fired boilers. Aromatics, alkenes and alkanes were the major components for all three boilers. The total SOAP for the tested oil-fired boilers ranged from 779.9 to 2252.5 mg-SOA/kg for all three oil-boilers (Table 7). Moreover, for oil-fired boilers, aromatics and alkenes were the major contributors to total SOAP. Benzene, toluene and o-ethyl toluene contributed most to SOAP, accounting for more than 40% for coal-fired boilers, while, in oil-fired boilers, toluene accounted for more than 90% of total SOAP. The VOC species with the highest contributions to SOAP were benzene, toluene, o-ethyl toluene, n-dodecane and n-undecane for coal-fired boilers. For oil-fired boilers, toluene, benzene, o-xylene and n-propyl benzene showed relatively higher SOAP contributions. Benzene, toluene and o-ethyl toluene were the VOC species that contributed the most to both OFP and SOAP.

In terms of total OFP and SOAP of both types of boilers, oil-fired boilers had a higher contribution of O3 (92%) and SOA (95%). Wu et al. (2017) reported that 18.7% and 80.8% of OFP were contributed by coal-fired boilers/stove and domestic biomass sectors, respectively for domestic combustion. Moreover, they also reported SOA for mechanical coking to be 30.5% of total SOAP for industrial processes. However, the individual sectors of boilers that have the highest OFP per unit VOC emissions are different from those with the highest SOAP per unit VOCs. For unit OFP, oil-fired boilers are significant contributors. Oil-fired boilers should be paid attention in the regions with severe ozone pollution. Oil-fired boilers also showed high contributions to SOAP, and it would be required to control oil-fired boiler emissions in the regions with high haze pollution. These results may help identify severe emission sectors. However, oil- and oil-fired boilers covered in the present study are not enough to represent all emission sources, and further studies are needed.

3. Conclusion

In this study, VOC emissions from two types of emission sources: coal- and oil-fired industrial boilers were investigated. Emission factors, OFP and SOAP of VOCs were estimated. Results showed that average ΣVOCs concentrations were > 9 times higher for oil-fired boilers (1.90–2.61 mg/m3) than for coal-fired boilers (0.11–0.30 mg/m3). Similarly, higher ΣVOCs emission factors were obtained for oil-fired boilers (9.26–32.83 mg-VOC/kg) than for coal-fired boilers (1.57–4.13 mg-VOC/kg). Alkanes (29.0%–47.8%) and aromatics (30.8%–39.6%) were the most abundant groups of VOCs for coal-fired boilers, while, oxygenated organics (1.8%–41.9%) and aromatics (56.0%–94.7%) were the most contributing groups for oil-fired boilers. Benzene, n-hexane and o-ethyl toluene were the abundant species for coal-fired boilers, while, toluene was the most abundant species emitted from oil-fired boilers. Moreover, OFP and SOAP were estimated 12 and 18 times, respectively, higher for oil-fired boilers than for coal-fired boilers. These results provide a supplement to the VOCs emission factors, O3 and SOA potentials for different fuel-based industrial boilers which would be valuable for a better understanding of VOCs emission characteristics of coal and oil-fired boilers.

Declaration of Competing Interest

The authors declare no competing financial interest.

REFERENCES


