Chemical Characteristics of Particulate Matter Emission from a Heavy-Duty Diesel Engine Using ETC Cycle Dynamometer Test

Taosheng Jin1*, Kaibo Lu1, Shuangxi Liu2, Shuai Zhao1, Liang Qu1, Xiaohong Xu3

1 State Environmental Protection Key Laboratory of Urban Ambient Air Particulate Matter Pollution Prevention and Control, College of Environmental Science and Engineering, Nankai University, Tianjin 300071, China
2 China Automotive Technology and Research Center, Tianjin 300030, China
3 Department of Civil and Environmental Engineering, University of Windsor, Windsor, Ontario N9B 3P4, Canada

ABSTRACT

This paper presents chemical characteristics of diesel particulate matter (DPM). A heavy-duty diesel engine was tested in ETC cycle with an engine dynamometer. The DPM was sampled with quartz fiber membrane and organic membrane filter. Quartz fiber membrane was used for total carbon (TC) and particle-phase PAHs (p-PAHs) measurement, while the organic membrane was used for inorganic elements measurement. On the quartz fiber membrane, the total of 15 elements detected were 11% of DPM mass. Ca, Si, Na and Al were the major components, accounted for 79% of the 15 elements mass. On the organic membrane, total carbon (elemental carbon + organic carbon) was 90% of total DPM mass. Three-ring p-PAHs were the major components (66%) of total p-PAHs mass followed by four-ring (18%) and two-ring (16%). The FLT/(FLT + PYR) ratio was 0.62, indicative of diesel vehicle emissions.

Keywords: Diesel particulate matter (DPM); Inorganic elements; Total carbon (TC); Polycyclic aromatic hydrocarbons (PAHs).

INTRODUCTION

With a rapid growth of vehicle population in Asian developing countries, traffic emission has become one of the major contributors to the ambient particulate matter (PM) (Kim et al., 2006; Hai and Kim, 2013; Li et al., 2013; Liang et al., 2013). PM emitted from diesel engines (DPM, Diesel Particulate Matter) accounts for 35–76% of vehicular PM emissions (Tsai and Chen, 2006; Shen et al., 2010; Goyal et al., 2013). Human health effects of DPM are associated with its chemical composition (Maricq, 2007). Some metals in DPM such as Pb (Lead), Cr (Chromium) and Cd (Cadmium) have been classified by USEPA as toxic air pollutants (USEPA, 2013). Polycyclic aromatic hydrocarbons (PAHs), although a very small portion of total DPM mass (e.g., Jin et al., 2014), are carcinogenic (ATSDR, 1995).

Chemical composition of DPM is affected by numerous factors, such as engine model year, operating conditions, fuel characteristics, and emission control technology. Many studies have explored the relationships between DPM chemical composition and these factors. Compared with their newer counterparts (model year 1992–1999), relative abundances of PAHs in DPM emitted from older vehicle (model year 1985) were significantly higher (Riddle et al., 2007). With advanced emission control technology, DPM PAHs and inorganic elements emissions have been reduced significantly (Pakbin et al., 2009; Khalek et al., 2011; Hu et al., 2013). Positive relations between diesel sulfur content and inorganic elements emissions, as well as between diesel sulfur content and particle-phase PAHs emissions have been found (Lim et al., 2007; Lu et al., 2012). Significant differences in PAHs emissions were observed under different engine operation conditions (Shah et al., 2005; Riddle et al., 2007). Our previous study (Jin et al., 2014) analyzed total carbon, 15 inorganic elements, and 12 particle-phase PAHs in DPM in 6 sets of speed–load conditions. Strong positive correlations (r > 0.99, p < 0.05) between phenanthrene and anthracene, as well as among benzo[a]pyrene, benzo[b]fluoranthene and benzo[k]fluoranthene were found.

More experimental data will help us to further explore the emission mechanism and health effects of DPM. In this paper, a heavy-duty diesel engine was tested in ETC cycle with an engine dynamometer. DPM was sampled and inorganic elements, total carbon as well as PAHs in the DPM were analyzed.

EXPERIMENTAL METHODS

Bench Test

The test engine was mounted on a bench testing system...
(AVL, Graz, Austria) which could perform both stationary and transient testing for engine emission measurement. Detailed description of the testing system can be found in Jin et al. (2014). A Yuchai YC6J200-30 engine (model year 2007) was tested on an engine dynamometer. This engine model was installed on many urban buses in Tianjin, China in 2008 when the study was carried out. Table 1 lists the properties of the engine. Fuel used in this study was China III#20 diesel (equivalent to Euro III standards).

**Driving Cycle**

The Yuchai YC6J200-30 engine was tested in ETC cycle (DieselNet, 2000). The ETC cycle included three modes, namely, urban driving, rural driving, and motorway driving. The duration of each mode was 600 s. Urban driving, with a maximum speed of 50 km h–1, had frequent start, stop and idling. Rural driving started with a steep acceleration segment. The average speed of rural driving was 72 km h–1. Motorway driving had an average speed of 88 km h–1. These three modes can be found in real-world driving conditions in China. More details of ETC cycle are available online (DieselNet, 2000). Due to the use of a single filter in each test, the integrated result of all modes was reported in this paper.

**DPM Sampling and Analysis**

In the engine dynamometer test, the sampling process was repeated twice, once with quartz fiber membrane and then with organic membrane filter respectively. Quartz fiber membrane was used for total carbon (TC) and particle-phase PAHs (p-PAHs) measurement. Organic membrane was used for inorganic elements. The diameter and porosity of membranes were 47 mm and 0.3 µm respectively. The filters were weighed before and after sampling. Before weighing, the filters were stored in a room with a temperature of 25 ± 5°C and humidity of 45 ± 5% for 72 hours. Then the filters were dark stored in a freezer with a set temperature of −19°C before extraction. For each filter, the total PM mass was calculated as the difference between the weights of that filter after and before sampling.

Nineteen inorganic elements (Ca, Si, Na, Al, Mg, Fe, K, Cr, Zn, Ti, Mn, Ni, As, V, Cd, Cu Co, Pb and Hg) were measured with Inductively Coupled Plasma-Atomic Emission Spectrometry (ICP-9000, Thermo Jarrell-Ash, US). TC was measured with thermal optical reflectance (TOR) carbon analyzer (DRI, US). Thirty-one PAHs were measured (ten of them were detected, refer to results and discussion) with Gas Chromatography-mass Spectrometry (GC8000Top-Voyager, Finnigan, US). Sample analysis procedure and quality assurance/quality control were provided in Jin et al. (2014).

**RESULTS AND DISCUSSION**

**Inorganic Elements and TC**

For inorganic elements and TC on the organic membrane filter, weight percentage in total DPM mass was calculated, as listed in Table 2 along with results from other studies. Total DPM mass on the organic membrane was 8.09 mg. Cu, Co, Pb and Hg were not detected. The remaining 15 inorganic elements accounted for 11.1% of the total DPM mass, higher than those in other studies (1.3–6.3%) (Khalek et al., 2011; USEPA, 2014; Jin et al., 2014). Proportions of Ca, Si, Na and Al each was higher than 1% of total DPM. These four elements combined accounted for 79% of the 15 inorganic elements. Inorganic elements in DPM are from three sources, lubricating oil, fuel, and engine wear (Lyyränen et al., 2002; Lim et al., 2007). Lyyränen et al. (2002) pointed out that Ca in DPM mainly originated from lubricating oil. Compared with the SPECIATE3.2 profile which was based on a study by Hildemann et al. (1991), proportions of Ca and Al in this study were significantly higher (> a factor of 20, 4.4% vs. 0.16% for Ca and 1.3% vs. 0.052% for Al). Proportions of Si (1.8%) and Al (1.3%) in this study were much higher (> a factor of 10) than those in Khalek et al. (2011) (0.1%).

Total DPM mass on the Quartz fiber membrane was 8.19 mg. TC, as the sum of elemental carbon and organic carbon, was 89.7%. It was in the upper range of 70–92% reported by Jin et al. (2014), but higher than the percentage of 73.1% in SPECIATE 3.2 (Hildemann et al., 1991). Other studies also reported that carbonaceous components are the dominant constituents of DPM (Kim et al., 2010; Lu et al., 2012). The total proportions of inorganic elements and TC in DPM mass were slightly above 100%, because these two components were analyzed using two different filters.

**Particle-Phase PAHs**

Based on tunnel testing, Ho et al. (2009) analyzed the distribution of PAHs in vehicle emissions and found that two- and three-ring PAHs accounted for 98% of gas-phase PAH concentrations while four-, five- and six- ring PAHs for less than 2% of gas-phase PAHs due to low vapor pressure. They also pointed out that in particle-phase PAHs, the proportion of four-, five- and six- ring PAHs was 60%, 17%, and 10% respectively, the total of which was much higher than that of two- and three-ring PAHs (< 9%).

<table>
<thead>
<tr>
<th>Item</th>
<th>Specification</th>
</tr>
</thead>
<tbody>
<tr>
<td>Structure</td>
<td>Turbocharged 6 cylinder in line</td>
</tr>
<tr>
<td>Displacement</td>
<td>6.5 L</td>
</tr>
<tr>
<td>Maximum power</td>
<td>147 kW@ 2500 rpm</td>
</tr>
<tr>
<td>Maximum torque</td>
<td>780 Nm@ 1200 rpm</td>
</tr>
<tr>
<td>Minimum fuel consumption at full load</td>
<td>≤ 196 g kW⁻¹ h⁻¹</td>
</tr>
<tr>
<td>Emission regulation</td>
<td>China III*</td>
</tr>
</tbody>
</table>

*Ministry of Environmental Protection China (2001).
Table 2. Weight percentage of inorganic elements and TC in total DPM mass in this study and other studies.

<table>
<thead>
<tr>
<th>Element</th>
<th>This study</th>
<th>Jin et al. (2014)</th>
<th>SPECIATE 3.2 No.32208</th>
<th>Khalek et al. (2011)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>mean ± standard deviation</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ca</td>
<td>4.4</td>
<td>2.3 ± 0.8</td>
<td>0.16</td>
<td>0.5</td>
</tr>
<tr>
<td>Si</td>
<td>1.8</td>
<td>0.67 ± 0.58</td>
<td>0.59</td>
<td>0.1</td>
</tr>
<tr>
<td>Na</td>
<td>1.3</td>
<td>0.49 ± 0.18</td>
<td>0.17</td>
<td>1.1</td>
</tr>
<tr>
<td>Al</td>
<td>1.3</td>
<td>0.24 ± 0.13</td>
<td>0.052</td>
<td>0.13</td>
</tr>
<tr>
<td>Mg</td>
<td>0.99</td>
<td>0.28 ± 0.15</td>
<td>0</td>
<td>0.2</td>
</tr>
<tr>
<td>Fe</td>
<td>0.95</td>
<td>0.48 ± 0.17</td>
<td>0.13</td>
<td>0.7</td>
</tr>
<tr>
<td>K</td>
<td>0.12</td>
<td>0.29 ± 0.19</td>
<td>0.056</td>
<td>0.1</td>
</tr>
<tr>
<td>Cr</td>
<td>0.099</td>
<td></td>
<td>0.018</td>
<td>&lt;0.1</td>
</tr>
<tr>
<td>Zn</td>
<td>0.067</td>
<td>0.22 ± 0.13</td>
<td>0</td>
<td>0.1</td>
</tr>
<tr>
<td>Ti</td>
<td>0.066</td>
<td></td>
<td>0.03</td>
<td>&lt;0.1</td>
</tr>
<tr>
<td>Mn</td>
<td>0.022</td>
<td>0.0060 ± 0.0023</td>
<td>0.009</td>
<td>&lt;0.1</td>
</tr>
<tr>
<td>Ni</td>
<td>0.0094</td>
<td>0.027 ± 0.024</td>
<td>0.027</td>
<td>&lt;0.1</td>
</tr>
<tr>
<td>As</td>
<td>0.0017</td>
<td></td>
<td>0.015</td>
<td>&lt;0.1</td>
</tr>
<tr>
<td>V</td>
<td>0.0017</td>
<td>0.0014 ± 0.0009</td>
<td>0.007</td>
<td>&lt;0.1</td>
</tr>
<tr>
<td>Cd</td>
<td>0.0016</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cu</td>
<td>N.D.</td>
<td>0.017 ± 0.007</td>
<td>0</td>
<td>&lt;0.1</td>
</tr>
<tr>
<td>Co</td>
<td>N.D.</td>
<td>0.015 ± 0.005</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Pb</td>
<td>N.D.</td>
<td>0.012 ± 0.024</td>
<td>0</td>
<td></td>
</tr>
<tr>
<td>Hg</td>
<td>N.D.</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Total elements</td>
<td>11.1</td>
<td>6.3</td>
<td>1.3</td>
<td>2.9</td>
</tr>
<tr>
<td>TC</td>
<td>89.7</td>
<td>82 ± 9</td>
<td>73.1</td>
<td></td>
</tr>
</tbody>
</table>

\(^a\) YC4G180-20 engine, the same model as the engine tested in this study.

\(^b\) Heavy-duty diesel trucks source profile No. 32208 in SPECIATE 3.2 is a composite profile representing two 1987 low-mileage (2920 miles and 5581 miles) heavy-duty trucks without control device reported by Hildemann et al. (1991). Version SPECIATE 4.4 can be found in USEPA (2014).

\(^c\) 2007-technology heavy-duty diesel engines in US with commercial refinery ultralow sulfur diesel fuel.

N.D.: not detected.

To further analyze components of particle-phase PAHs, 10 p-PAHs were detected in this study, including two rings (naphthalene, methylnaphthalene and biphenyl), three rings (phenantherene, anthracene, methylphenantherene and fluoranthenone) and four rings (pyrene, benzo[b]fluoranthenone and benzo[k]fluoranthenone). Weight percentages of different rings in total p-PAHs mass in this and other studies are summarized in Fig. 1. In this study, three-ring p-PAHs were the major components of p-PAHs (66%), while the proportions of two-ring and four-ring p-PAHs were similar (16% and 18%, respectively).

Volatility of PAHs increases with the decrease their molecular weight or number of rings and lighter PAHs are found mostly in gas phase (Ravindra et al., 2008a; Hu et al., 2013). However, the proportions of p-PAHs with different rings vary significantly among studies as shown in Fig. 1. Proportions of two-ring, three-ring and four-ring p-PAHs in this study were similar to those in Jin et al. (2014) and Lu et al. (2012), studies in China. However, the two-ring percentage was higher than that in Hu et al. (2013), but lower than that in Shah et al. (2005). For three-ring p-PAHs, result in this study was higher than that in Hu et al. (2013) and Shah et al. (2005). Proportion of four-ring p-PAHs was lower than that in Hu et al. (2013), but higher than that in Shah et al. (2005). In this study p-PAHs with more than four-ring were not detected, which was different from previous studies shown in Fig. 1.

**Diagnostic Ratios**

The ratios of individual PAHs in ambient samples, such as BeP/(BeP + BaP) ratio, BaP/(BaA + CHR) ratio, and IND/(IND + BghiP) ratio, have been employed as diagnostic tools to identify the origin of PAHs (e.g., diesel engine, gasoline engine, wood combustion, oil burning) by comparing with the ratios in source emissions (Guo et al., 2003; Manoli et al., 2004; Mantis et al., 2005). However, benzo[a]anthracene, chrysene, benzo[e]pyrene, benzo[a]pyrene, indeno[1,2,3-cd]pyrene, and benzo[ghi]perylene were not detected in our study. Therefore, the only diagnostic ratios can be used in this study were fluoranthenone/(fluoranthenone + pyrene) ratio and benzo[b]fluoranthenone/benzo[k]fluoranthenone ratio, expressed as FLT/(FLT + PYR) and BbF/BkF, respectively. To distinguish diesel engine and gasoline engine emissions, diagnostic ratios should be in the range of or at least close to those for one source and different from those for another source, as established in the literature.

Table 3 lists FLT/(FLT + PYR) ratios and BbF/BkF ratios in our study and other studies. FLT/(FLT + PYR) ratio in this study was 0.62, in the range for diesel vehicles (0.60–0.70) (Sicre et al., 1987, calculated by Kavouras et al., 2001) but higher than those in all other diesel vehicles (0.25–0.50) (Manoli et al., 2004; Jin et al., 2014). Our value was higher than those in gasoline vehicles (0.14–0.40) (Rogge et al., 1993; Manoli et al., 2004). The result indicated that...
Fig. 1. Weight percentage of p-PAHs with different rings in total p-PAHs mass in this study and related studies.

1 YC4G180-20 engine, the same model as the engine in Test 1 in this study, without emission control device.
2 ISUZU 4HF1 engine, a pre-Euro standard naturally-aspirated, water cooled, 4-cylinder direct-injection diesel engine, without emission control device.
3 1998 Cummins M11 diesel engine, mounted in a class 8 tractor, without emission control device. UDDS: Urban Dynamometer Driving Schedule, a transient cycle.
4 1996 Detroit Diesel Series 60 diesel engine, mounted in a heavy-duty diesel truck, without emission control device.
5 1999 Caterpillar C-12 diesel engine, mounted in a heavy-duty diesel truck, without emission control device.

Table 3. Diagnostic ratios in this study and other studies.

<table>
<thead>
<tr>
<th>Source of PAHs</th>
<th>FLT/(FLT + PYR)</th>
<th>BbF/BkF</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Diesel engines</td>
<td>0.62</td>
<td>1</td>
<td>This study</td>
</tr>
<tr>
<td></td>
<td>0.25–0.50</td>
<td>1</td>
<td>Jin et al. (2014)</td>
</tr>
<tr>
<td></td>
<td>0.60–0.70</td>
<td>2.18–2.46</td>
<td>Ravindra et al. (2008b)</td>
</tr>
<tr>
<td></td>
<td>0.38&lt;sup&gt;a&lt;/sup&gt;, 0.43&lt;sup&gt;b&lt;/sup&gt;</td>
<td>3.4&lt;sup&gt;b&lt;/sup&gt;, 3.8&lt;sup&gt;a&lt;/sup&gt;</td>
<td>Sicre et al. (1987); Kavouras et al. (2001)</td>
</tr>
<tr>
<td>Gasoline engines</td>
<td>0.40</td>
<td>5.2&lt;sup&gt;c&lt;/sup&gt;, 5.8&lt;sup&gt;e&lt;/sup&gt;</td>
<td>Manoli et al. (2004)</td>
</tr>
<tr>
<td></td>
<td>0.14&lt;sup&gt;c&lt;/sup&gt;, 0.17&lt;sup&gt;d&lt;/sup&gt;</td>
<td>1.07–1.45</td>
<td>Dickhut et al. (2000)</td>
</tr>
</tbody>
</table>

<sup>a</sup> Diesel bus.
<sup>b</sup> Diesel taxi.
<sup>c</sup> Catalyst equipped car.
<sup>d</sup> Car without catalyst.

FLT/(FLT + PYR) ratio is indicative of diesel vehicle emissions.

BbF/BkF ratio in this study was 1, the same as that in our previous study (Jin et al., 2014), but lower than all other diesel vehicle studies in Table 3 (2.18–3.8) (Manoli et al., 2004; Ravindra et al., 2008b). Our value was also lower than the ones for gasoline vehicles in Manoli et al. (2004) (5.2 and 5.8), but similar to the ones for gasoline vehicles in Dickhut et al. (2000) (1.07–1.45). The result implied that in this study BbF/BkF ratio failed to differentiate diesel vehicle from gasoline vehicle emissions.

Isomer ratios have been used as diagnostic ratios to identify the source of PAHs because isomer pairs are diluted to a similar extent by ambient air and distribute similarly to other phases due to similar physicochemical properties (Dickhut et al., 2000). However, diagnostic ratios varied greatly among different studies as shown in Table 3, partially because of the reactions of PAH with other compounds (Manoli et al., 2004; Mantis et al., 2005). Diagnostic ratios should be used with caution especially when only one diagnostic ratio is employed. Further studies are necessary to evaluate whether these ratios can be regarded as diagnostic tools to identify PAHs sources.

CONCLUSIONS

This paper provides chemical characteristics of DPM from experimental study of a heavy-duty diesel engine (Yuchai YC6J200–30) tested in ETC cycle. The major inorganic elements were Ca, Si, Na and Al, accounted for 79% of the total mass of 15 detected inorganic elements. TC was 90% of total DPM mass. The major components of
total p-PAHs mass were three-ring p-PAHs (66%) followed by four-ring (18%) and two-ring (16%). FLT/(FLT + PYR) ratio and BbF/BkF ratio were 0.62 and 1, respectively, the former is indicative of diesel emission while the latter is not.

Due to resources limitation, this study tested only one heavy-duty engine. Systematic investigations are needed in future studies to explore the factors that affect the chemical characteristics of DPM emissions. These factors include model year by emission standards, operating conditions, and diesel fuel property including biodiesel. Only p-PAHs were monitored in this study. Previous studies indicated that low molecular PAHs were mostly in the gas phase. Although P-PAHs were usually more harmful to human health, toxicity evaluation of vehicle emission must include both gas- and particle-phase (Ho et al., 2009; Hu et al., 2013).

ACKNOWLEDGMENT

This study was funded by National Natural Science Foundation of China (Grants No.21477057).

REFERENCES


Received for review, June 26, 2016
Revised, September 16, 2016
Accepted, October 17, 2016