



Chemical characteristics of particulate matter emitted from a heavy duty diesel engine and correlation among inorganic and PAH components



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HIGHLIGHTS

- DPM chemical composition is influenced by engine speed and load.
- The proportions of TC, inorganic elements and p-PAHs are $82 \pm 9\%$, $6.3 \pm 1.4\%$ and $0.034 \pm 0.013\%$.
- Three-ring and four-ring PAHs are the main constituents of the total p-PAHs mass.
- Significant correlations are found between some p-PAHs and between some inorganic elements and p-PAHs.

ARTICLE INFO

Article history:

Received 16 September 2012

Received in revised form 25 August 2013

Accepted 27 August 2013

Available online 5 September 2013

Keywords:

Diesel Particulate Matter (DPM)

Polycyclic Aromatic Hydrocarbons (PAHs)

Inorganic elements

Dynamometer test

Pearson correlation analysis

ABSTRACT

This study investigated the chemical characteristics of the particulate matter emitted from a diesel engine (Diesel Particulate Matter, DPM) and the correlations between polycyclic aromatic hydrocarbons (PAHs) species as well as between PAHs and inorganic elements in DPM through dynamometer testing. There were six sets of speed–load conditions. Engine speeds varied from 1000 to 1600 rpm, while engine loadings were 60% and 100% of engine load. Total carbon accounted for $82 \pm 9\%$ of the total DPM mass, followed by 15 inorganic elements ($6.3 \pm 1.4\%$), and 12 particle-phase PAHs (p-PAHs) ($0.034 \pm 0.013\%$). The three-ring and four-ring p-PAHs constituted $54 \pm 25\%$ and $27 \pm 19\%$ of the total p-PAHs mass, respectively, much higher than that of two-ring p-PAHs ($11 \pm 10\%$) and five-ring ($9 \pm 5\%$). The fluoranthene/(fluoranthene + pyrene) and benzo[a]anthracene/(benzo[a]anthracene + chrysene) ratios were below or in the lower range of ambient ratios indicative of diesel vehicle emissions observed in previous studies with on-board testing system. Strong positive correlation ($r > 0.99$, $p < 0.05$) among isomeric p-PAHs (between phenanthrene and anthracene, as well as among benzo[a]pyrene, benzo[b]fluoranthene and benzo[k]fluoranthene) were observed. Furthermore, the weight percentages of some inorganic elements and p-PAHs in total DPM were correlated.

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1. Introduction

Vehicle emissions are one of the major sources of air pollution in urban areas worldwide [1]. Of special concerns are diesel-powered vehicles that emit a complex mixture of toxic gaseous pollutants and particulate matter (PM) [2]. Diesel vehicles contribute significantly to the particulate air pollution burden, especially in metropolitan areas of Asian developing countries [3,4].

Diesel Particulate Matter (DPM), defined as particulate matter emitted from diesel engines, has significant health, atmospheric and climate implications. Toxic species in DPM include arsenic,

nickel and polycyclic aromatic hydrocarbons (PAHs), all of which are known to cause cancer [5,6]. Epidemiological studies have demonstrated the correlations between exposure to roadway PM and increasing risk of respiratory illnesses [7,8]. Therefore, the chemical composition of DPM is important for the assessment of the human health effects from exposure to diesel vehicles exhaust [9].

DPM has been extensively investigated since the 1990s, including emission factors [10,11], size distributions [12,13], and source profiles [14,15]. Chassis dynamometer tests [16], tunnel experiments [14,17], and on-board monitoring [18] have been widely used to measure various pollutants emitted from diesel vehicles. These studies offered original data of emission factors, size distribution as well as PAHs proportion of vehicle particulate matter,

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Table 1
Design of dynamometer tests using a YC4G 180–200 Engine.

| Test | Engine rotational speed(rpm) | Engine load(%) | Engine torque(Nm) | Sampling flow rate(L/min) | Mass of DPM(mg) |
|------|------------------------------|----------------|-------------------|---------------------------|-----------------|
| 1 | 1000 | 100 | 773.0 | 100 | 1.55 |
| 2 | 1000 | 60 | 463.0 | 100 | 1.61 |
| 3 | 1200 | 100 | 781.3 | 100 | 1.84 |
| 4 | 1200 | 60 | 469.0 | 100 | 1.75 |
| 5 | 1600 | 100 | 757.0 | 100 | 1.29 |
| 6 | 1600 | 60 | 454.2 | 100 | 1.39 |

which contributed to the development of strategies and techniques for DPM control.

Previous studies have shown that the concentration and speciation of DPM depend on various factors such as engine operating conditions. Di et al. [19] used an ultra-low sulfur diesel blended with ethanol as the fuel to analyze total DPM emissions under five engine loads and two engine speeds. Ho et al. [20] quantified 17 PAHs in ShingMun Tunnel, Hong Kong during summer and winter in 2003. They found that there were significant correlations among PAHs. In addition, the correlations between the particle-phase PAHs (p-PAHs, the PAHs existed in particle-phase [20]) were higher than those for gas-phase PAHs. For identifying the origin of PAHs in ambient air, diagnostic ratios of individual PAHs species, such as indeno [1, 2, 3-cd]pyrene/(indeno [1, 2, 3-cd]pyrene + benzo[g,h,i]perylene), benzo[a]anthracene/(benzo[a]anthracene + chrysene), fluoranthene/(fluoranthene + pyrene), and benzo[a]anthracene/benzo[g,h,i]perylene, have been considered effective tools [21–24].

The objective of this study is to investigate the effects of engine speed and load on chemical characteristics of the total carbon, inorganic and PAH components of DPM as well as the correlations between different species in DPM. The exhaust samples were collected from an urban bus diesel engine mounted on a bench testing system. This research will further our knowledge about the emission characteristics of DPM.

2. Experimental methods

2.1. Drive cycles

The driving cycles used in this study were ‘point’ cycles [25] as listed in Table 1. The ‘point’ cycles were based on operational data collected from previous studies of actual driving cycles of buses in

Table 2
Characteristics of the Yuchai YC4G180-200 engine.

| Parameter | Value |
|---------------------------------------|---|
| Structure | Turbocharged 4 cylinder in line |
| Displacement | 5.2 L |
| Maximum power | 148 kW@2200 rpm |
| Maximum torque | 781 Nm@1200 rpm |
| Minimum fuel consumption at full load | ≤196 g/kW h |
| Emission regulation | China III ^a (equivalent to Euro III) |

^a Chemical composition of China III: total insoluble ≤ 2.5 mg/mL, sulfur content ≤ 350 ppm, 10% carbon residue on residuum ≤ 0.3%, ash content ≤ 0.01.

Table 3
Proportion of inorganic elements located in DPM in each test listed in Table 1, mean wt% of DPM mass.

| Elements | Test | | | | | |
|----------------|----------------|----------------|----------------|-------------------|----------------|-------------------|
| | 1 ^a | 2 ^b | 3 ^a | 4 ^b | 5 ^a | 6 ^b |
| Na | 0.68 | 0.64 | 0.40 | 0.35 | 0.65 | 0.25 |
| Mg | 0.56 | 0.25 | 0.34 | 0.14 | 0.25 | 0.17 |
| Al | 0.37 | 0.28 | 0.40 | 0.12 | 0.14 | 0.12 |
| Si | 0.92 | 0.75 | 1.7 | 0.12 | 0.46 | 0.12 |
| S | 1.1 | 0.97 | 1.3 | 1.6 | 1.5 | 1.4 |
| K | 0.31 | 0.17 | 0.17 | N.D. [*] | 0.61 | 0.19 |
| Ca | 3.7 | 1.8 | 2.7 | 1.4 | 2.2 | 1.8 |
| V | 0.0033 | 0.0010 | 0.0010 | 0.0010 | 0.0010 | 0.0010 |
| Mn | 0.0089 | 0.0060 | 0.0080 | 0.0040 | 0.0060 | 0.0030 |
| Fe | 0.55 | 0.47 | 0.64 | 0.64 | 0.34 | 0.24 |
| Co | 0.022 | 0.015 | 0.0070 | 0.020 | 0.013 | 0.015 |
| Ni | 0.065 | 0.0070 | 0.014 | 0.024 | 0.046 | 0.0030 |
| Cu | 0.020 | 0.018 | 0.017 | 0.0060 | 0.0230 | N.D. [*] |
| Zn | 0.052 | 0.22 | 0.14 | 0.34 | 0.21 | 0.39 |
| Pb | 0.0026 | 0.061 | 0.0020 | 0.0020 | 0.0020 | 0.0030 |
| Total elements | 8.3 | 5.6 | 7.7 | 4.8 | 6.5 | 4.7 |

^{*} Not detected.

^a 100% engine load.

^b 60% engine load.

some Chinese cities [26]. The engine speeds were set at 1000 rpm, 1200 rpm, 1600 rpm, and the engine loads were 60% and 100% of engine load.

2.2. Bench testing system

The test engine was mounted on a bench testing system (AVL, Graz, Austria) shown in Fig. 1. The system could perform both

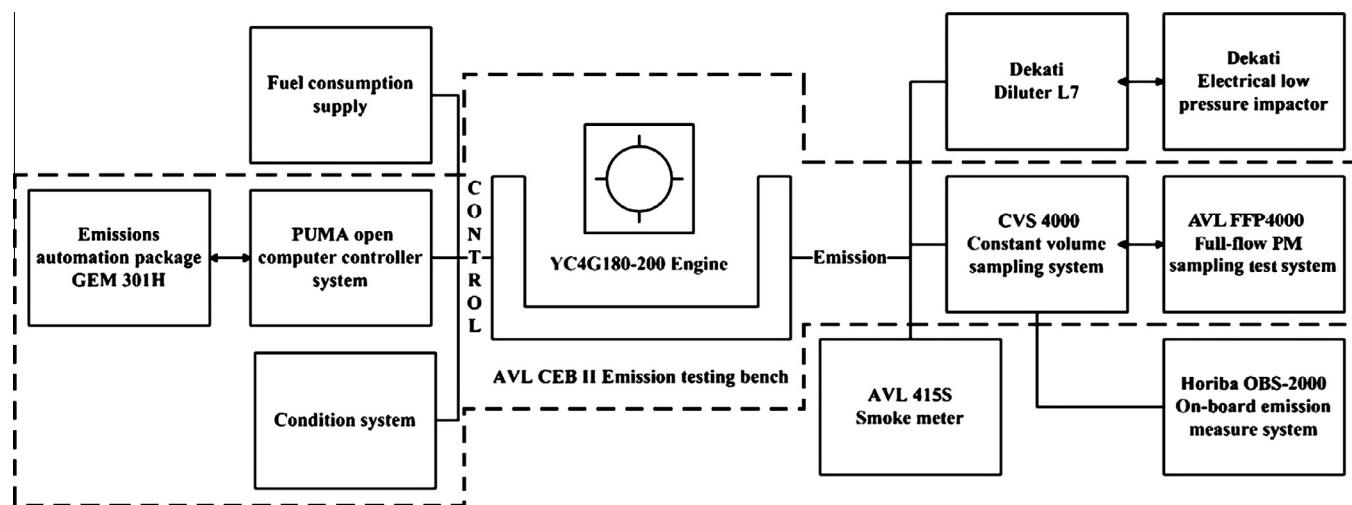


Fig. 1. Experiments settings of the bench testing system (dotted portion was used in this study).

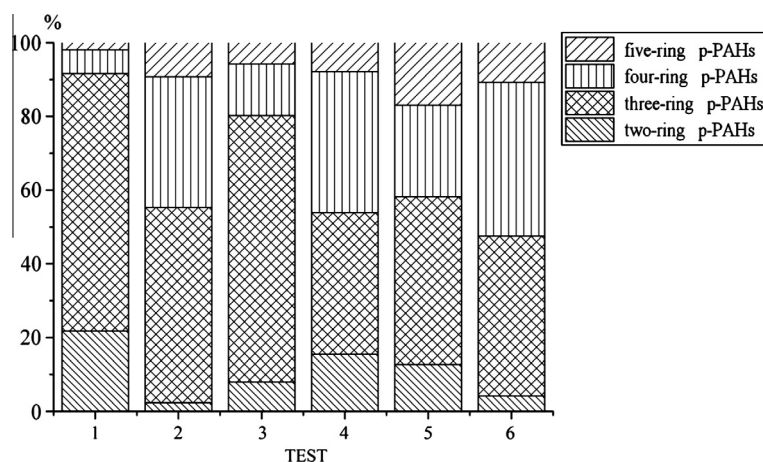


Fig. 2. Proportion of p-PAHs (wt% of total p-PAHs). Tests 1, 3, 5 were 100% engine load and Tests 2, 4, 6 were 60% engine load.

Table 4

Proportion of p-PAHs (wt% of total p-PAHs) in this study and in other studies, mean values (\pm standard deviation).

| PAHs | This study | Ho et al. [20] | Shah et al. [34] |
|---------------------------|---------------|----------------|------------------|
| Naphthalene | 7.4 \pm 4.3 | 9 \pm 10 | 25 \pm 21 |
| Acenaphthylene | 1.3 \pm 2.8 | 2.0 \pm 6.0 | 1.2 \pm 0.7 |
| Fluorene | 2.2 \pm 2.6 | 1.3 \pm 0.9 | 6.2 \pm 3.0 |
| Phenanthrene | 22 \pm 11 | 9.3 \pm 1.1 | 16.3 \pm 7.4 |
| Anthracene | 22 \pm 7 | 1.9 \pm 1.1 | 0.5 \pm 0.3 |
| Fluoranthene | 9.5 \pm 7.1 | 17 \pm 10 | 8.7 \pm 4.1 |
| Pyrene | 17 \pm 10 | 24 \pm 15 | 25 \pm 12 |
| Benzo[a]anthracene | 1.0 \pm 2.0 | 5.8 \pm 5.8 | 1.2 \pm 0.8 |
| Chrysene | 1.8 \pm 2.5 | 11 \pm 11 | 1.1 \pm 0.9 |
| Benzo[b]fluoranthene | 3.7 \pm 2.0 | 5.5 \pm 9.2 | 0.9 \pm 0.9 |
| Benzo[k]fluoranthene | 3.7 \pm 2.0 | 2.5 \pm 4.3 | 1.1 \pm 1.2 |
| Benzo[a]pyrene | 8.8 \pm 5.0 | 2.3 \pm 3.8 | 1.1 \pm 1.0 |
| Acenaphthene | N.D.* | 6.0 \pm 2.3 | 2.3 \pm 1.1 |
| Indeno [1, 2, 3-cd]pyrene | N.D.* | 0.1 \pm 0.2 | 2.8 \pm 3.9 |
| Dibenzo[a,h]anthracene | N.D.* | 3.9 \pm 6.6 | 3.3 \pm 4.5 |
| Benzo[g,h,i]perylene | N.D.* | 2.5 \pm 4.2 | 3.7 \pm 4.7 |

* Not detected.

point cycle (this study) and driving cycle for engine emission measurements. Before sampling, the engine was warmed up to full power for 30 min. The exhaust samples were diluted and collected from an urban bus diesel engine by CVS (constant volume sampling system) and FFP4000 particle sampler mounted on a bench testing system.

2.3. Test engine and fuel

A Yuchai YC4G180-200 diesel engine was used in this research. It is a popular engine installed on many heavy-duty urban buses in Tianjin, China. Table 2 lists specifications of this engine. China III

(equivalent to Euro III) diesel was used in this study [27]. All fuels came from the same batch of the same supplier, and were mixed well before each use.

2.4. PM sampling and analysis

Each sampling process was repeated twice, one with quartz fiber membranes (PALL, Washington, US) for organic compound (PAHs) and total carbon (TC is the sum of elemental carbon and organic carbon in this paper), and the other with organic membrane filters (PALL, Washington, US) for inorganic elements. The diameter and porosity of the membranes were 47 mm and 0.3 μ m, respectively. The filters were weighed before and after sampling, and the used filters were stored in darkness at -18°C until extraction. To avoid contamination, the filters were handled by wearing one-time gloves or using tweezers [28].

Concentrations of 15 inorganic elements (Na, Mg, Al, Si, S, K, Ca, V, Mn, Fe, Co, Ni, Cu, Zn and Pb) in the extracts were measured by Inductively Coupled Plasma-Atomic Emission Spectrometry (ICP-9000, Thermo Jarrell-Ash, US). The pretreatment and setup of test were referred to Saitoh et al. [29]. Calibration of the element concentration was performed with coal fly ash (GBW 08401) provided by the National Institute of Metrology P.R. China as a standard reference material. The results of DPM compositions were considered acceptable when the deviation was within $\pm 15\%$ of the certified/reference values for major elements (concentrations $> 1 \text{ mg g}^{-1}$) and within 2-fold for minor elements. Concentrations of total carbon in the extracts were analyzed by a thermal optical reflectance carbon analyzer (DRI, US), referring to the method described in Fung et al. [30].

Concentrations of 16 p-PAHs (Naphthalene, acenaphthylene, acenaphthene, fluorene, phenanthrene, anthracene, fluoranthene, pyrene, benzo[a]anthracene, chrysene, benzo[b]fluoranthene,

Table 5

Diagnostic ratios of fluoranthene/(fluoranthene + pyrene) and benzo[a]anthracene/(benzo[a]anthracene + chrysene) in this and other studies.

| Source of PAHs | Fluoranthene/(fluoranthene + pyrene) | Benzo[a]anthracene/(benzo[a]anthracene + chrysene) | Reference |
|------------------|--------------------------------------|--|---------------|
| Gasoline vehicle | 0.40 | 0.22–0.55 | [38] |
| | | 0.49 | [39] |
| | | | [40] |
| Diesel vehicle | 0.25–0.5 | 0.5 | This research |
| | 0.60–0.70 | 0.38–0.64 | [39] |
| | 0.43 | 0.92 | [22] |
| | | 0.73 | [40] |

Table 6
Correlation coefficients among the concentrations of p-PAHs in DPM (bold numbers indicate $p \leq 0.05$).

| Group of isomers | PAHs | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 | 11 | 12 |
|---|---------------------------|-----------------|-------------|-------------|-------|-------|-------------|-------------|-------|-----------------|-----------------|-----------------|
| Group(phenanthrene, anthracene) | Naphthalene (1) | 0.44 | 0.44 | 0.50 | 0.53 | 0.03 | 0.46 | -0.29 | 0.51 | 0.35 | 0.35 | 0.35 |
| | Acenaphthylene (2) | 0.74 | 0.85 | 0.87 | -0.36 | -0.31 | -0.05 | -0.25 | -0.42 | -0.43 | -0.41 | |
| | Fluorene (3) | 0.95 | 0.95 | -0.41 | -0.54 | -0.23 | -0.41 | 0.15 | 0.14 | 0.16 | | |
| | Phenanthrene (4) | >0.99 | -0.57 | -0.52 | -0.35 | -0.43 | -0.10 | -0.11 | -0.08 | | | |
| | Anthracene (5) | | | | | -0.51 | -0.47 | -0.30 | -0.37 | -0.08 | -0.09 | -0.07 |
| Group(fluoranthene, pyrene) | Fluoranthene (6) | | | | | 0.62 | 0.80 | 0.77 | 0.39 | 0.40 | 0.39 | |
| | Pyrene (7) | | | | | | 0.14 | 0.93 | 0.30 | 0.31 | 0.29 | |
| Group(benzo[a]anthracene, chrysene) | Benzo[a]anthracene (8) | | | | | | | 0.36 | -0.06 | -0.06 | -0.06 | |
| | Chrysene (9) | | | | | | | | 0.37 | 0.38 | 0.36 | |
| | Benzo[b]fluoranthene (10) | | | | | | | | | >0.99 | >0.99 | |
| Group(benzo[b]fluoranthene, benzo[k]fluoranthene, benzo[a]pyrene) | Benzo[k]fluoranthene (11) | | | | | | | | | | | >0.99 |
| | Benzo[a]pyrene (12) | | | | | | | | | | | |

benzo[k]fluoranthene, benzo[a]pyrene, indeno[1, 2, 3-cd]pyrene, dibenzo[a,h]anthracene and benzo[g,h,i]perylene) in the extracts were measured by Gas Chromatography–Mass Spectrometry (GC8000Top-Voyager, Finnigan, US) following USEPA Method TO-13A [31]. GC (gas chromatography) inject port were keeping 280 °C. GC oven was programmed with an initial temperature of 70 °C, held for 2 min, elevated at rate of 10 °C/min to 260 °C, and then to 300 °C at 5 °C/min and held for 8 min. The transfer line between GC and MSD (mass spectrometer detector) were held 300 °C. The MSD was operated under the following condition: electron impact mode with energy of 70 eV, mass range: 50–300 μm . Selected Ion Mode (SIM) was used for quantitative analysis. When the concentrations of internal standards (Supelco, US) were 0.5 mg L^{-1} , the recovery for each PAH species varied between 86% and 95%, and the relative standard deviation was less than 10%.

2.5. Quality assurance (QA)/quality control (QC)

The QA/QC protocol of the monitoring sequence was followed at all stages from sample preparation to chemical analysis. Blank field filters were placed unopened next to the samplers for the duration of sampling, after which they were returned to the laboratory and treated as regular samples to ensure there was no significant background interference. A blank sample was run for each chemical analysis. Results showed that all analyte concentrations in the blank quartz fiber membranes and blank organic membrane filters were less than the method detection limits (MDL).

2.6. Data analysis

Species with lab reported concentrations under the MDL in all six tests were excluded from further analysis. Lab reported extract concentrations were used to calculate weight percentage (wt%) of TC, inorganic elements and PAHs in total DPM mass, as well as wt% of PAHs in total p-PAHs mass. The concentration ratios of fluoranthene/(fluoranthene + pyrene) and benzo[a]anthracene/(benzo[a]anthracene + chrysene) were also calculated using the wt% of those species in DPM.

Pearson correlation analysis among p-PAHs as well as between p-PAHs and inorganic elements was conducted. The p-PAHs were classified into several groups on the basis of their chemical formulas.

3. Results and discussion

3.1. Effects of engine speed and engine load on components in DPM

TC was the main content and contributed 70–92% of the DPM mass. The wt% of TC was higher at 100% engine load than at 60%

engine load (92% vs. 78% at 1000 rpm, 87% vs. 70% at 1200 rpm, 90% vs. 76% at 1600 rpm).

Table 3 summarizes the wt% of the 15 elements in total DPM mass from the six tests. The wt% of inorganic elements was higher at 100% engine load ($7.5 \pm 1\%$) than at 60% engine load ($5.1 \pm 0.5\%$). Ca, S, Na, and Si combined accounted for $75 \pm 2\%$ of inorganic elements. The dominant elements in DPM observed in this study were similar with that reported by Ntziachristos et al. [32]. Their study, conducted next to a busy Southern California freeway with heavy diesel vehicle emissions, showed that S was the most abundant element in ambient PM, followed by Na, Fe and Ca [32].

Mixed results were observed for the effect of the engine load on p-PAHs. The proportion of p-PAHs in DPM (Table 3) were higher at 100% engine load with high and low speeds (1000 rpm, 1600 rpm), but lower at medina speed (1200 rpm).

3.2. Characteristics of p-PAHs in DPM

Among the sixteen p-PAH detected, the concentrations of the following four (acenaphthene, indeno[1, 2, 3-cd]pyrene, dibenzo[a,h]anthracene and benzo[g,h,i]perylene) were below the MDL. The remaining 12 p-PAHs contributed a small fraction ($0.034 \pm 0.013\%$) of the DPM mass, which is consistent with previous studies (e.g. 0.046% in He et al. [33]). Fig. 2 illustrates the wt% of the p-PAHs in the six tests. The two-ring, three-ring, four-ring, and five-ring p-PAHs accounted for $11 \pm 10\%$, $54 \pm 25\%$, $27 \pm 19\%$, $9 \pm 5\%$ of the total p-PAHs mass, respectively. The proportions of four-ring and five-ring p-PAHs were consistent with those obtained by Shah et al. [34] (four-ring p-PAHs: $29 \pm 16\%$, five-ring p-PAHs: $11 \pm 9\%$). The proportion of two-ring p-PAHs was lower and three-rings p-PAHs was higher than those obtained by Shah et al. [34] (two-ring p-PAHs: $35 \pm 26\%$, three-ring p-PAHs: $26 \pm 12\%$). Ho et al. [20] showed the proportions of two-ring and four-ring PAHs were $18 \pm 20\%$ and $48 \pm 46\%$, higher than these in our research. The three-ring PAHs was $29 \pm 12\%$, lower than in our research, and five-ring PAHs was $9 \pm 15\%$, similar with our research. The difference of these PAHs proportions might be resulted from the diversity of testing methods, engine type and driving mode.

The proportion of three-ring p-PAHs was higher ($63 \pm 15\%$) at 100% engine load than those at 60% engine load ($45 \pm 7\%$). The opposite trend was observed for four-ring p-PAHs, $15 \pm 9\%$ at 100% engine load and $38 \pm 1\%$ at 60% engine load. However, the relationships of proportions of two-ring and five-ring p-PAHs and engine load were not obvious.

Table 4 compares wt% of p-PAHs in total PAHs observed in this and in other studies. The proportions of naphthalene, acenaphthylene, fluorene, fluoranthene, pyrene, benzo[b]fluoranthene and benzo[k]fluoranthene in our study were similar to those by Ho et al. [20]. The proportions of acenaphthylene, phenanthrene,

Table 7
Correlation coefficients between the weight% of inorganic elements and p-PAHs in DPM (bold numbers indicate $p \leq 0.05$).

| Element | Naphthalene | Acenaphthylene | Fluorene | Phenanthrene | Anthracene | Fluoranthene | Pyrene | Benzo[a]anthracene | Chrysene | Benzo[b]fluoranthene | Benzo[k]fluoranthene | Benzo[a]pyrene |
|---------|-------------|----------------|--------------|--------------|--------------|--------------|--------------|--------------------|--------------|----------------------|----------------------|----------------|
| Na | 0.54 | -0.35 | -0.15 | -0.23 | -0.18 | 0.62 | 0.63 | 0.21 | 0.83 | 0.64 | 0.65 | 0.63 |
| Mg | -0.41 | 0.13 | 0.22 | 0.34 | 0.29 | -0.81 | -0.81 | 0.43 | -0.81 | -0.49 | -0.50 | -0.49 |
| Al | -0.36 | 0.41 | 0.31 | 0.41 | 0.43 | -0.84 | -0.81 | 0.37 | -0.85 | -0.70 | -0.71 | -0.70 |
| Si | -0.06 | 0.57 | 0.71 | 0.78 | 0.74 | 0.88 | -0.86 | 0.52 | -0.88 | -0.33 | -0.35 | -0.32 |
| S | 0.04 | 0.82 | 0.82 | 0.87 | 0.85 | -0.67 | 0.78 | 0.20 | -0.72 | -0.47 | -0.48 | -0.46 |
| K | 0.04 | 0.76 | 0.82 | 0.87 | 0.86 | -0.58 | -0.82 | 0.11 | -0.68 | -0.36 | -0.37 | -0.35 |
| Ca | 0.08 | 0.44 | 0.69 | 0.64 | 0.59 | -0.65 | -0.53 | 0.56 | -0.68 | 0.09 | 0.08 | 0.10 |
| V | 0.06 | 0.04 | 0.67 | 0.43 | 0.41 | -0.47 | -0.47 | 0.10 | -0.36 | 0.66 | 0.65 | 0.67 |
| Mn | 0.03 | 0.28 | 0.68 | 0.65 | 0.59 | -0.80 | -0.69 | 0.70 | -0.78 | 0.12 | 0.10 | 0.13 |
| Fe | 0.01 | -0.60 | -0.74 | -0.81 | -0.77 | 0.87 | 0.84 | 0.52 | 0.86 | 0.31 | 0.33 | 0.30 |
| Co | -0.56 | -0.24 | -0.38 | -0.37 | -0.42 | -0.25 | -0.06 | 0.23 | -0.39 | -0.25 | -0.25 | -0.26 |
| Ni | 0.64 | 0.78 | 0.97 | 0.96 | 0.96 | -0.40 | -0.34 | 0.32 | -0.25 | 0.16 | 0.15 | 0.17 |
| Cu | 0.61 | 0.70 | 0.30 | 0.37 | 0.41 | 0.14 | 0.40 | 0.10 | 0.34 | 0.14 | -0.14 | -0.14 |
| Zn | 0.31 | 0.31 | 0.05 | 0.34 | 0.32 | -0.71 | -0.04 | 0.69 | -0.16 | -0.50 | -0.50 | -0.51 |
| Pb | 0.25 | 0.95 | 0.67 | 0.82 | 0.81 | -0.58 | -0.45 | 0.20 | -0.47 | -0.58 | -0.58 | -0.57 |

fluoranthene, pyrene, benzo[a]anthracene, chrysene were also similar to that reported by Shah et al. [34]. However, anthracene and benzo[a]pyrene were higher than those by Ho et al. [20] and Shah et al. [34]. Acenaphthene, indeno[1, 2, 3-cd]pyrene, dibenzo[a,h]anthracene and benzo[g,h,i]perylene were not detected in our research, these four PAHs were accounted for 13% and 12% in researches conducted by Ho et al. [20] and Shah et al. [34].

Due to limitations of the samplers, only p-PAHs were monitored. Although 2- and 3-ring PAHs (e.g. naphthalene, acenaphthylene and acenaphthene) were predominant in the gas-phase, 4- to 6-ring PAHs (e.g. benzo[a]anthracene, chrysene, benzo[b]fluoranthene and benzo[g,h,i]perylene) mainly existed in the particulate-phase [20,35]. Previous studies indicated that many low molecular PAHs were in the gas phase, however most carcinogenic PAHs were found in the particulate phase, especially in fine particulate matter [5,34,36].

Diagnostic ratios obtained in this and previous studies are presented in Table 5. The fluoranthene/(fluoranthene + pyrene) ratios ranged from 0.25 to 0.5 in the six tests, with a mean value of 0.37. It is below the ratio found in Manoli et al. [22] (0.43). The benzo[a]anthracene/(benzo[a]anthracene + chrysene) ratio (0.5 and only measured in test #6) found in this study is in the range of Nelson [36] but well below values found in Manoli et al. [22] and Geller et al. [37].

3.3. Correlation among PAHs in DPM

Correlation coefficients of wt% of PAHs in DPM are presented in Table 6. Because PAH isomers (i.e. having the same chemical formula) have similar properties and origins, correlations between isomers having the same number of rings or not were found. The weight percentages of 3-ring isomers (phenanthrene and anthracene) and 4- 5-rings isomers (benzo[a]pyrene, benzo[b]fluoranthene, benzo[k]fluoranthene) were strongly correlated ($r > 0.99$, $p < 0.05$) with each other. Ho et al. [20] also reported strong correlation among p-PAH emission factors in group (benzo[a]pyrene, benzo[b]fluoranthene, benzo[k]fluoranthene) ($r \geq 0.97$). In Geller et al.'s [37] study, correlation of p-PAH concentrations were very strong ($r = 0.99$) in group (benzo[a]anthracene, chrysene), and relatively strong in group (phenanthrene, anthracene) ($r = 0.68$), while weak correlation was observed in group (fluoranthene, pyrene).

There were other strong correlations (ranging from 0.74 to 0.95) between wt% of p-PAHs. Acenaphthylene was correlated with fluorene, phenanthrene and anthracene, fluoranthene with benzo[a]anthracene and chrysene, pyrene with chrysene.

3.4. Correlation between the contents of inorganic elements and PAHs in DPM

Correlation between wt% of inorganic elements and p-PAHs in total DPM are listed in Table 7. PAH group (phenanthrene, anthracene) had strong positive correlation with Si, S, K, Ni and Pb ($r \geq 0.74$, $p < 0.05$) and negative correlation with Fe ($r \leq -0.77$, $p < 0.05$). Similarly, Fe had significant positive correlation with PAH group (fluoranthene, pyrene) ($r \geq 0.84$, $p < 0.05$), and Mg, Al, Si had significant negative correlation with this PAH group ($r \leq -0.81$, $p < 0.05$). The PAH group (benzo[a]pyrene, benzo[b]fluoranthene, benzo[k]fluoranthene) had no significant correlation with any of the 15 inorganic elements. Acenaphthylene and fluorene had strong positive correlation between S, K and Ni ($r > 0.76$, $p < 0.05$), while acenaphthylene was also positively correlated with Pb ($r = 0.95$, $p < 0.05$), and fluorene was negatively correlated with Fe ($r = -0.74$, $p < 0.05$). Geller et al. [37] had also observed strong correlations between concentrations of some

inorganic elements (Li, Be, Ti, Ni, Zn) and some organic species (element carbon, light PAHs: naphthalene, pyrene and phenanthrene).

4. Conclusions

This paper presents the results of the chemical characteristics of the inorganic and organic components of DPM using dynamometer testing. It provides original data on the correlation between p-PAHs and inorganic elements determined from diesel engine emissions. The data and analysis contribute in the completion of the knowledge concerning the composition of particles emitted by diesel engines.

It was found that TC was the major constituent and that it accounted for $82 \pm 9\%$ of the total DPM mass, much higher than the 15 inorganic elements ($6.3 \pm 1.4\%$), and 12 PAHs ($0.034 \pm 0.013\%$). Ca, Na, S and Si accounted for $75 \pm 2\%$ of total inorganic element mass. Weight percentage of TC and total inorganic elements increased with engine load (60% vs. 100%). The weight percentages of the 12 p-PAHs in total p-PAHs were in agreement with previous studies. The three-ring and four-ring p-PAHs constituted $54 \pm 25\%$ and $27 \pm 19\%$ of the total p-PAHs mass, respectively, followed by two-ring p-PAHs ($11 \pm 10\%$) and five-ring ($9 \pm 5\%$). The concentration ratios of fluoranthene/(fluoranthene + pyrene) and benzo[a]anthracene/(benzo[a]anthracene + chrysene) were below or at the lower range considered indicative of diesel vehicle emissions in previous ambient studies.

In some group of isomers, including PAH group (phenanthrene, anthracene), and group (benzo[a]pyrene, benzo[b]fluoranthene, benzo[k]fluoranthene), the weight percentages (in DPM) were highly positively correlated with each other, but not in all isomer p-PAHs groups. Some p-PAHs correlated with those had the same number of rings or differed by one ring. Some inorganic elements had strong correlation with some PAH groups, including Si, S, K, Ni, Pb and Fe with PAH group (phenanthrene, anthracene), as well as Mg, Al, Si and Fe with PAH group (fluoranthene, pyrene).

Future studies should sample gas-phase PAHs (g-PAHs, PAHs existed in gas phase) and analyze the correlation between g-PAHs and inorganic elements. Furthermore, on-board testing system could be used to fully characterize pollutant emissions from vehicles. The test results should be expressed as emission factors (i.e. emissions per km travelled or emissions per amount of fuel consumed). Differences and similarities of these correlations also should be analyzed between on-board testing and dynamometer testing.

Acknowledgements

This study was supported by the National Natural Science Foundation of China (Grant #21177064) and China's National Basic Research Program (Grant #2011CB503801). The authors would like to thank Mr. Chuck Freed and Mr. David Vance Wagner for their editorial assistance.

References

- Colville RN, Hutchinson EJ, Mindell JS, Warren RF. The transport sector as a source of air pollution. *Atmos Environ* 2001;35:1537–65.
- Kerminen VM, Makela TE, Ojanen CH, Hillamo RE, Vilhunen JK, Rantanen L, et al. Characterization of the particulate phase in the exhaust from a diesel car. *Environ Sci Technol* 1997;31:1883–9.
- Gupta I, Kumar R. Trends of particulate matter in four cities in India. *Atmos Environ* 2006;40:2552–66.
- Chiang HL, Huang YS. Particulate matter emissions from on-road vehicles in a freeway tunnel study. *Atmos Environ* 2009;43:4014–22.
- Ravindra K, Sokhi R, Grieken RV. Atmospheric polycyclic aromatic hydrocarbons: source attribution, emission factors and regulation. *Atmos Environ* 2008;42:2895–921.
- Nelson PF, Tibbett AR, Stuart J, Day SJ. Effects of vehicle type and fuel quality on real world toxic emissions from diesel vehicles. *Atmos Environ* 2008;42:5291–303.
- Lin S, Munsie JP, Hwang SA, Fitzgerald E, Cayo MR. Childhood asthma hospitalization and residential exposure to state route traffic. *Environ Res* 2002;88:73–81.
- Ye SH, Zhou W, Peng BC, Yuan D, Lu YM, Qi PP. Toxicity and health effects of vehicle emissions in Shanghai. *Atmos Environ* 1999;34:419–29.
- Adonis MI, Riquelme RM, Gil L, Rios C, Rodriguez L, Rodriguez EM. PAHs and mutagenicity of inhalable and respirable diesel particulate matter in Santiago, Chile. *Polycyclic Aromat Compd* 2003;23:495–514.
- Weingartner E, Keller C, Stahel WA, Burtscher H, Baltensperger U. Aerosol emission in a road tunnel. *Atmos Environ* 1997;31:451–62.
- Abu-Allaban M, Gillies JA, Gertler AW, Clayton R, Proffitt D. Tailpipe, resuspended road dust, and brake-wear emission factors from on-road vehicles. *Atmos Environ* 2003;37:5283–93.
- Kleeman MJ, Schauer JJ, Cass GR. Size and composition distribution of fine particulate matter emitted from motor vehicles. *Environ Sci Technol* 2000;34:1132–42.
- Sturm PJ, Baltensperger U, Bacher M, Lechner B, Hausberger S, Heiden B, et al. Roadside measurements of particulate matter size distribution. *Atmos Environ* 2003;37:5273–81.
- Fraser MP, Cass GR, Simoneit BRT. Gas-phase and particle-phase organic compounds emitted from motor vehicle traffic in a Los Angeles roadway tunnel. *Environ Sci Technol* 1998;32:2051–60.
- Schauer JJ, Kleeman MJ, Cass GR, Simoneit BRT. Measurement of emissions from air pollution sources. 2. C₁ through C₃₀ organic compounds from medium duty diesel trucks. *Environ Sci Technol* 1999;33:1578–87.
- Zhang J, He KB, Ge YS, Shi XY. Influence of fuel sulfur on the characterization of PM₁₀ from a diesel engine. *Fuel* 2009;88:504–10.
- He LY, Hu M, Zhang YH, Yu BD, Liu DQ. Chemical characterization of fine particles from on-road vehicle in the Wutong tunnel in Shenzhen, China. *Chemosphere* 2006;62:1565–73.
- Liu H, He KB, Lents JM, Wang QD, Tolvett S. Characteristics of diesel truck emission in China based on portable emissions measurement system. *Environ Sci Technol* 2009;43:9507–11.
- Di YG, Cheung CS, Huang ZH. Experimental study on particulate emission of a diesel engine fueled with blended ethanol-dodecanol-diesel. *J Aerosol Sci* 2009;40:101–12.
- Ho KF, Ho SH, Lee SC, Cheng Y, Chow JC, Watson JG, et al. Emissions of gas- and particle-phase polycyclic aromatic hydrocarbons (PAHs) in the Shing Mun tunnel Hong Kong. *Atmos Environ* 2009;43:6343–51.
- Shi JW, Peng Y, Li WF, Qiu WG, Bai ZP, Kong SF, et al. Characterization and source identification of PM₁₀-bound polycyclic aromatic hydrocarbons in urban air of Tianjin China. *Aerosol Air Qual Res* 2010;10:507–18.
- Manoli E, Kouras A, Samara C. Profile analysis of ambient and source emitted particle-bound polycyclic aromatic hydrocarbons from three sites in northern Greece. *Chemosphere* 2004;56:867–78.
- Mantis J, Chaloulakou A, Samara C. PM₁₀-bound polycyclic aromatic hydrocarbons (PAHs) in the greater area of Athens Greece. *Chemosphere* 2005;59:593–604.
- Kavouras JG, Lawrence J, Koutrakis P, Stephanou EG, Oyola P. Measurement of particulate aliphatic and polynuclear aromatic hydrocarbons in Santiago de Chile: Source reconciliation and evaluation of sampling artifacts. *Atmos Environ* 1999;33:4977–86.
- Kim Oanh NT, Thiansathit W, Bond TC, Subramanian R, Winijkul E, Paw-armart I. Compositional characterization of PM_{2.5} emitted from in-use diesel vehicles. *Atmos Environ* 2010;44:15–22.
- Li ML, Zhang JW, Zhang FX, Zhao CM. A study on real driving cycle of passenger cars in typical cities of China. *Automotive Eng* 2006;6:554–7 [in Chinese].
- GB/T19147-2009. Automobile diesel fuels. Beijing, (China): Standards Press of China; 2009 [in Chinese].
- Han B, Bai ZP, Guo GH, Wang F, Li F, Liu QX, et al. Characterization of PM₁₀ fraction of road dust for polycyclic aromatic hydrocarbons (PAHs) from Anshan China. *J Hazard Mater* 2009;170:934–40.
- Saitoh K, Sera K, Gotoh T, Nakamura M. Comparison of elemental quantity by PIXE and ICP-MS and/or ICP-AES for NIST standards. *Nucl Instrum Meth Phys Res Sect B: Beam Inter Mater Atoms* 2002;189:86–93.
- Fung K, Chow JC, Watson JG. Evaluation of OC/EC speciation by thermal manganese dioxide oxidation and the IMPROVE method. *J Air Waste Manage* 2002;52:1333–41.
- USEPA. Compendium of methods for the determination of toxic organic compounds in ambient determination of polycyclic aromatic hydrocarbons (PAHs) in ambient air using gas chromatography/mass spectrometry (GC/MS), EPA/625/R-96/010b, In: Center for environmental research information office of research and development. 1999.
- Ntziachristos L, Ning Z, Geller MD, Sheesley RJ, Schauer JJ, Sioutas C. Fine, ultrafine and nanoparticle trace element compositions near a major freeway with a high heavy-duty diesel fraction. *Atmos Environ* 2007;41:5684–96.
- He LY, Hu M, Zhang YH, Huang XF, Yao TT. Fine particle emissions from on-road vehicles in the Zhujiang tunnel China. *Environ Sci Technol* 2008;42:4461–6.
- Shah SP, Ogunyoku TA, Miller IW, Cocker DR. On-road emission rates of PAH and n-alkane compounds from heavy-duty diesel vehicles. *Environ Sci Technol* 2005;39:5276–84.

- [35] Kim JY, Lee JY, Kim YP, Lee SB, Jin HC, Bae GN. Seasonal characteristics of the gaseous and particulate PAHs at a roadside station in Seoul Korea. *Environ Res* 2012;116:142–50.
- [36] Nelson PF. Effects of vehicle type and fuel quality on the exposure risk of toxic emissions from diesel vehicles. *Environ Chem* 2009;6:260–7.
- [37] Geller MD, Ntziachristos L, Mamakos A, Samaras Z, Schmitz DA, Froines JR, et al. Physicochemical and redox characteristic of particulate matter (PM) emitted from gasoline and diesel passenger cars. *Atmos Environ* 2006;40:6988–7004.
- [38] Rogge WF, Hildemann LM, Mazurek MA, Cass GR, Simoneit BRT. Sources of fine organic aerosol. 2. Road dust, non-catalyst and catalyst-equipped automobiles and heavy duty diesel trucks. *Environ Sci Technol* 1993;27:636–51.
- [39] Sicre MA, Marty JC, Saliot A, Aparicio X, Grimalt J, Albaiges J. Aliphatic and aromatic hydrocarbons in different sized aerosols over the Mediterranean Sea: occurrence and origin. *Atmos Environ* 1987;21:2247–59.
- [40] Khalili NR, Scheff PA, Holsen TM. PAH source fingerprints for coke ovens, diesel and gasoline engines, highway tunnels, and wood combustion emissions. *Atmos Environ* 1995;4:533–42.