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Characterizations of organic compounds in diesel exhaust particulates

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ABSTRACT

To characterize how the speed and load of a medium-duty diesel engine affected the organic compounds in diesel particle matter (PM) below 1 μm , four driving conditions were examined. At all four driving conditions, concentration of identifiable organic compounds in PM ultrafine (34–94 nm) and accumulation (94–1000 nm) modes ranged from 2.9 to 5.7 $\mu\text{g}/\text{m}^3$ and 9.5 to 16.4 $\mu\text{g}/\text{m}^3$, respectively. As a function of driving conditions, the non-oxygen-containing organics exhibited a reversed concentration trend to the oxygen-containing organics. The identified organic compounds were classified into eleven classes: alkanes, alkenes, alkynes, aromatic hydrocarbons, carboxylic acids, esters, ketones, alcohols, ethers, nitrogen-containing compounds, and sulfur-containing compounds. At all driving conditions, alkane class consistently showed the highest concentration (8.3 to 18.0 $\mu\text{g}/\text{m}^3$) followed by carboxylic acid, esters, ketones and alcohols. Twelve polycyclic aromatic hydrocarbons (PAHs) were identified with a total concentration ranging from 37.9 to 174.8 ng/m^3 . In addition, nine nitrogen-containing polycyclic aromatic compounds (NPACs) were identified with a total concentration ranging from 7.0 to 10.3 ng/m^3 . The most abundant PAH (phenanthrene) and NPACs (7,8-benzoquinoline and 3-nitrophenanthrene) comprise a similar molecular (3 aromatic-ring) structure under the highest engine speed and engine load.

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Introduction

Organics in diesel particle matter (PM) can cause higher cytotoxicity and oxidative stress than urban fine particles (Hirano et al., 2003; Li et al., 2003). Pan et al. (2004) reported that organics in PM that are resistant to extraction by organic solvents and acidic solutions were capable of catalyzing the generation of the reactive oxygen species (ROS), leading to the oxidative DNA damages, indicating an inherent toxicity of PM. Most published studies up to date mainly measured aliphatics and polycyclic aromatic hydrocarbons (PAHs) in PM (Shah et al., 2012), while identification of other organic compounds in detail is needed because the organics containing hydroxyl

and/or carbonyl substitutes in PM could cause more cytotoxicity, oxidative stress, and inflammatory response than aliphatics and PAHs (Kumagai and Taguchi, 2007; Shima et al., 2006; Xia et al., 2004). Up to date, two studies identified several carbonyl-containing organic compounds in PM (Schauer et al., 1999; Rogge et al., 1993a), including n-alkanoic acids, n-alkenoic acids, benzoic acids, substituted benzaldehydes, polycyclic aromatic ketones, aromatic acids, aromatic ketones, and quinines from heavy-duty and medium-duty diesel trucks using chassis dynamometers, which may partially represent the actual on-road conditions.

Okamura et al. (2004) observed that a higher engine load of diesel trucks emitted PM containing more polycyclic aromatic

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compounds and caused greater endocrine disruption. Relative to the cruise driving fashion, creeping conditions (heavily congested traffic condition) of heavy-duty diesel engines generated around 8–18 times more of n-alkanes and PAHs in PM (Shah et al., 2005). In addition, Riddle et al. (2007) reported that diesel engines under idle or creep operation generate more PAHs in PM of 100–320 nm. PM smaller than 320 nm at the driving conditions under low engine loads contained more PAHs of smaller molecular weight, while 100–530 nm PM under heavier engine loads tend to contain PAHs of larger molecular weight (Zielinska et al., 2004a). This demonstrates that the driving conditions can substantially affect the amounts, compositions and size distribution of the organics in PM. In addition, since Geller et al. (2006) reported that the aftertreatment devices unnecessarily decreased the chemical (redox) activity of PM, the toxicity and size distribution of the chemical species in PM require additional characterization to properly assess effectiveness of control devices.

Although the gasoline-vehicle exhausts contained higher proportions of PAHs of larger molecular weight, and emissions from diesel vehicles had more nitro-PAHs (Zielinska et al., 2004b), differentiating emissions from diesel- vs. gasoline-powered vehicles based on the identified aromatic compounds remains challenging (Kim et al., 2012), which suggests that more comprehensive characterization of the organics in PM may provide necessary insights on the representative fingerprints for either emission sources.

In this study, we quantified 11 classes of the organic compounds in PM from a medium-duty diesel engine to evaluate how the driving conditions that most frequently occur on roads affect the concentration, compositions, and size segregation of the identifiable organic species in PM. This study further characterizes the size segregation of alkanes, PAHs, nitro-PAHs and aza arenes. Based on the molecular structure and concentration profiles, additional attempts are given to discuss formation processes and toxicity of the organics in PM, as well as to explore the potential fingerprints differentiating particulates of diesel vs. gasoline emissions.

Nitrogen-containing polycyclic aromatic compounds (NPACs) were also examined since some of NPACs (e.g., nitro-PAHs) can be 100,000 times more mutagenic and 10 times more carcinogenic than PAHs (Bamford and Baker, 2003), and Zielinska et al. (2004b) identified nitro-PAHs in total particulate matter in diesel exhausts.

1. Experimental

1.1. Sampling and measurements

All procedures and setups of sampling and monitoring diesel particle matter (PM) in this study have been provided in detail elsewhere (Lim et al., 2008, 2009). In brief, a medium-duty diesel engine, which is equipped in most popular on-road diesel vehicles in Korea, was operated at four steady-state driving conditions using a dynamometer (APA DYNO, AVL Co., Graz, Austria). Four steady-state driving modes, which occurred on-road most frequently (or for longest duration), were selected for laboratory investigation; they comprised two engine speeds (1800 and 3000 rpm) under either medium

(60%) or full (100%) engine load. Detail basic information, such as a cetane number of 56 with a specific gravity of 830 kg/m³ (15°C), sulfur content of 0.02 wt.%, and 10% distillation residue of 0.01 wt.%, of the diesel fuel for this study also have been provided in elsewhere (Lim et al., 2008, 2009). In addition, previous study (Lim et al., 2008) showed satisfactory reproducibility with relative deviation of 0.4%–10% (engine experimental number for one set of duplicate test (*n*) = 4) by duplicate test.

For individual driving tests, exhaust stream was, in part, introduced through a mini dilution tunnel (MDT, SPC 472, AVL Co, Graz, Austria) before total particulate matter (TPM) was collected. An additional isokinetic sampling port directed exhaust through an ejector diluter (Dekati® Diluter, Dekati Ltd., Tampere, Finland) to monitor size distribution and number concentrations of PM using a scanning mobility particle sizer (SMPS, TSI 3936, TSI Inc., MN, USA). In parallel, PM were collected using a low pressure impactor (LPI, Hauke Aeras 25-4/0.015, Uusimaa, Finland), which segregated PM into 6 groups with 25 L/min flow rate and individual cut-off size of 34, 66, 94, 170, 330 and 550 nm for following gravimetric measurements and chemical speciation. A schematic experimental setup and sample monitoring in detail is given elsewhere (Lim et al., 2008, 2009) and in supplementary data (Fig. S1).

1.2. Analysis of organic compounds in PM

To monitor procedural loss of non-polar and polar compounds, two internal standards, perdeuterated tetracosane (C₂₄D₅₀, 31.25 µg) (Aldrich, MO, USA) and perdeuterated succinic acid (C₄D₆O₄, 26.25 µg) (Cambridge Isotope Lab. Inc., MA, USA) were spiked onto filter samples prior to solvent extraction. All filter samples were extracted successively using three types of solvents in the order of tetrahydrofuran (THF, 99.9%) (Merck, Darmstadt, Germany), dichloromethane (DCM, 99.8%) (Merck, Darmstadt, Germany), and hexane (98.5%) (Merck, Darmstadt, Germany). Each solvent ultrasonication lasted for 10 min. All solvent extracts were further filtered and concentrated down to 0.5 mL. All prepared extract samples were stored in a freezer (–25°C) in dark before following chemical analyses.

To successfully resolve polar compounds via a gas chromatograph coupled with mass spectrometer (GC–MS, Agilent Technologies, CA, USA), 10 µL of concentrated extracts was transferred into a 2-mL vial before 4 µL of N,O-bis(trimethylsilyl) trifluoroacetamide (1% of trimethylsilyl (TMS), BSTFA, Pierce, IL, USA) was added. After 20–30 min, 1–2 µL of derivatized extract was injected into GC–MS. 1-Phenyldodecane (1-PD, 51.4 µg/mL THF) (Aldrich, MO, USA) was used as a co-injection standard to correct injection loss and to account for deviating performance of GC–MS. A GC–MS HP-5MS column (5% phenylmethylpolysiloxane capillary column of 30 m × 0.25 mm i.d. × 0.25 µm, Agilent Technologies, USA) directed helium as carrier gas at a flow rate of 1 mL/min undergoing an initial temperature of 60°C for 3 min before an increase to 280°C at a rate of 8°C/min. Final oven temperature of 280°C was held for 15 min.

Individual compounds were identified based on spectrum reference provided by the National Institute of Standards and Technology (NIST) mass spectral library, or confirmed by comparing with the mass fragmentation patterns and the elution time of authentic standards. Identified compounds

were classified into two categories: (1) positive identification, when a compound was confirmed with authentic standards, or showed a mass spectrum matching against the library database for $\geq 70\%$, and (2) probable identification, when compounds showed a mass spectrum against library database between 50% and 70%. Identifiable compounds were quantified taking into account the response of co-injection standard (1-PD) and extraction recovery efficiencies as the procedure of quality assurance/quality control (QA/QC), resulting in propagated errors of 7%–13%. Blank analyses were conducted to examine background interference. To enhance detection sensitivity of polycyclic aromatic hydrocarbons (PAHs) in extracts, selected ion monitoring (SIM) was employed during separated GC–MS analyses, and PAHs in extract samples were identified against a suite of 16 priority standards (Supelco, PA, USA) recommended by US EPA.

1.3. Analysis of nitrogen containing compounds in particulate matter

Nitrogen-containing organic compounds were separated using a HP-5MS capillary column in a GC (GC-2010, Shimadzu, Kyoto, Japan) equipped with dual detectors, flame-ionization detector (GC-FID, Shimadzu, Kyoto, Japan) and chemiluminescence detector (Antek 7090, Antek Inc., TX, USA). While adopting a temperature program same as the GC–MS measurements, the carrier gas, helium, was set at a constant flow rate of 3 mL/min. At the end of a separation column, sample stream was introduced to a 10:1 split adaptor leading to flame-ionization detector (FID) and chemiluminescence detector. The chemiluminescence detector was operated at 950°C to pyrolyze samples, and to quantify amounts of nitrogen-containing compounds.

Similar to the above mentioned approach of quality assurance for GC–MS measurements, each sample was co-injected with 1-PD (51.4 $\mu\text{g/mL}$, Aldrich, MO, USA) and 50.0 $\mu\text{g/mL}$ of N-nitrosodiphenylamine- d_6 ($\text{C}_{12}\text{H}_4\text{D}_6\text{N}_2\text{O}$) (Cambridge Isotope Lab. Inc., MA, USA) to monitor the performance of FID and chemiluminescence detectors, respectively. To account for procedural loss, additional internal standards, 1,10-phenanthroline- d_8 ($\text{C}_{12}\text{D}_8\text{N}_2$, 50.0 μg , Aldrich, MO, USA), perdeuterated tetracosane and perdeuterated succinic acid were spiked onto filter samples prior to solvent extraction. Calibration curves of 20 standard nitrogen-containing compounds in five concentrations were established to quantify the detected nitrogen-containing compounds. The 20 standards were injected individually for five times (total 100 injections) and the injection of the standard mixtures composed of these 20 standards in five concentrations was repeated 8 times to assess reproducibility of elution behavior of these nitrogen-containing organic compounds. Each nitrogen-containing compound, whether injected individually or as a part of standard mixtures, exhibited a satisfactorily consistent elution time with a deviation of 0.004–0.021 sec. Among the standard compounds tested, since the shortest time between the elution of any two standard compounds is at least 0.1 sec, much longer than the deviation of elution time of a single compound, identification of individual NPAC based on their elution behaviors is well characterized and acceptable.

To take into account the influence of instrument performance on elution behavior, for each batch of injection, calibration curves (2.857–67.687 ng/mL) were established individually, and an injection of the standard mixture was conducted before and after the analysis of actual samples. Among the injections of 24 PM samples, the largest difference between the eluted compounds and its presumably corresponding standard compounds is 0.092 sec. In other words, any isomers or unknown NPAC eluted within 0.092 sec may be inaccurately identified. Based on the data resulting from the chemiluminescence detection, recovery efficiency of 1,10-phenanthroline- d_8 was $99.96\% \pm 20.43\%$ and R^2 for 20 standard calibration curves ranged from 0.93816 to 0.99956.

2. Results and discussion

2.1. Effects of driving conditions on identified organic compounds in PM

Based on previous study (Lim et al., 2008), the total particulate matter (TPM) were emitted from the individual driving conditions in a decreasing order of 3000 rpm/100% (engine speed and engine load) (69 mg/m^3) > 1800 rpm/100% (47 mg/m^3) > 3000 rpm/60% (28 mg/m^3) > 1800 rpm/60% (17 mg/m^3). However, Fig. 1a shows that the concentrations of identifiable organic compounds in PM ($< 1 \mu\text{m}$) ranged from 12.4 to around 19.7 $\mu\text{g/m}^3$ at individual driving conditions, with the corresponding concentrations of total organic compounds shown in the up X-axis. Note that it is reasonable to estimate concentrations of total organic compounds based on experimentally measured organic carbon (OC) in PM ($< 1 \mu\text{m}$) coupled with an organic-mass-to-organic carbon (OM-OC) ratio of 1.2 (up X-axis) because most organics in PM have alkane structure (Lim et al., 2008). When engine speeds and loads increased from 1800 rpm/60% to 3000 rpm/100%, the total organic in PM increased almost 4 times, changing from 0.12 up to 0.47 mg/m^3 (up X-axis, Fig. 1a), while no more than 10% of the organic compounds were identifiable (Fig. 1b). This indicates that more than 90 wt.% of organics in PM ($< 1 \mu\text{m}$) in this study could be under detection limit and/or unidentifiable by using the existing analytical techniques because they could be humic-like substances (Ghio et al., 1996). Although literature studies reporting organics in PM $< 1 \mu\text{m}$ in detail are unavailable for comparison, the small fraction of identifiable organics observed in this study can be supported by the measurements of Schauer et al. (1999) (particle diameter (d_p) $< 1.8 \mu\text{m}$) and Rogge et al. (1993a) ($d_p \leq 2 \mu\text{m}$), who identified around 4% and 6% of organics in total PM emitting from a medium-duty and a heavy-duty diesel engine, respectively. While the break specific fuel consumption (BSFC) can be employed as the emission factor to evaluate engine efficiency and emissions based on the fuel type, “organic concentration” (mass per unit of air volume in Fig. 1a) is applicable to examine the effects of the driving conditions on the identifiable organic compounds in PM. In addition, because the expression (unit) of the organic concentrations in diesel exhausts is similar to that in air (e.g., along roadside, road tunnel and urban atmosphere), using “organic concentration” in this study provides a common basis to evaluate the effects of diesel exhausts, among other primary emissions, on ambient air quality.

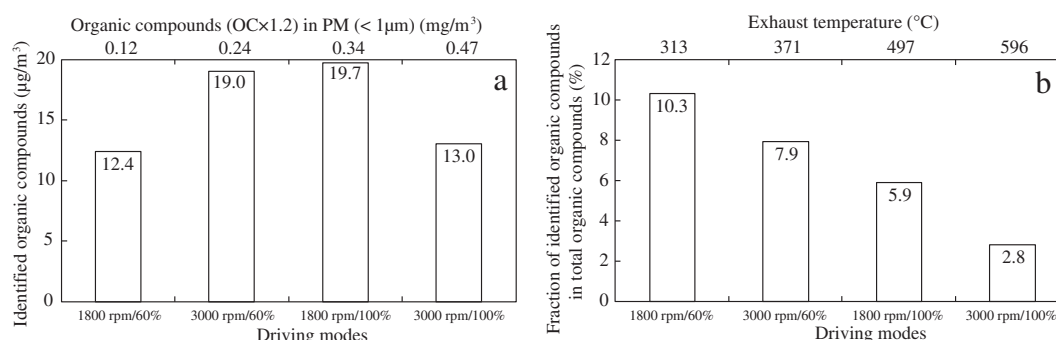


Fig. 1 – Effect of the driving conditions on (a) the concentrations of identified organic compounds in PM (< 1 μm) and (b) the fraction of identifiable organic compounds in total organic compounds at different exhaust temperatures. Total organic compounds (organic mass) = OC (organic carbon) × 1.2. Driving modes are engine speed and engine load.

When the driving conditions changed from 1800 rpm/60% to 3000 rpm/100%, Fig. 1b shows that the fraction of identifiable organics in PM (< 1 μm) reduced more than 3 times (range 10.3%–2.8%), indicating stronger formation of unresolved organics under more strenuous driving conditions, which were accompanied with more fuel injection and higher combustion temperature (as shown in the up X-axis of Fig. 1b) as well as larger pyrolysis zones in diesel engines. Such incomplete combustion could encourage formation of organics with large molecular weights, such as humic-like substances, or with complex mixture of branched and cyclic hydrocarbons, which are difficult to be resolved from analytical column (Ghio et al., 1996; Simoneit, 1984). It is worthwhile to note that the organics in PM, which are resistant to extraction by organic solvents and acidic solutions, can catalyze the generation of ROS, leading to the oxidative DNA damages, indicating an inherent toxicity of PM (Pan et al., 2004).

Table 1 shows that the concentration of the identifiable organic compounds in PM of ultrafine (34–94 nm) size and accumulation (94–1000 nm) modes ranged from 2.9 to 5.7 μg/m³ and 9.5 to 16.4 μg/m³, respectively; a large amount (70%–83%) of the identifiable organics in PM (< 1 μm) were allocated in the accumulation-mode PM, suggesting that the organic compounds in PM could have undergone prominent condensation. Although PM under the driving condition of 3000 rpm/60% and 1800 rpm/100% contained the largest concentration of identifiable organics in the ultrafine (5.7 μg/m³) and accumulation modes (16.4 μg/m³), respectively (Table 1), changes in combustion (or driving conditions) ambiguously correlated with the size distribution of the identified organic. Trends of the size distribution of the organics could be correlated with

combustion (or driving conditions) if more organics were successfully identified.

Since organics containing hydroxyl and/or carbonyl substitutes (O-containing organics) in PM could provoke different oxidative stress (Chio et al., 2007), and cytotoxic as well as inflammatory response from aliphatic compounds and PAHs (non O-containing organics) (Shima et al., 2006; Xia et al., 2004), the identified organics were grouped as oxygen (O)-containing organics vs. non-O-containing organics. The former consists of quantifiable carboxylic acids, ester, ketones, ethers, oxygenated S-containing and/or N-containing compounds, oxygenated PAHs, and the non-O-containing organics include alkanes, alkenes, alkynes, aromatic hydrocarbons and aza arenes. More than 80% of the O-containing organics (except PM of 1800 rpm/100%) and more than 60% of the non-O-containing organics were found in accumulation-mode PM (data not shown). The concentration of the identified non-O-containing organics in PM ranged from 8.4 to 17.9 μg/m³, two times more than the O-containing organics (0.9–4.5 μg/m³). Majority of both classes of the identified organics were in the accumulation-mode PM. Interestingly, the non-O-containing organic compounds generally showed a concentration trend opposite to the O-containing organic compounds in both ultrafine (34–94 nm) and accumulation-mode (94–1000 nm) PM (Fig. 2). In ultrafine PM, the non-O-containing organics peaked at the driving condition of 3000 rpm/60% (5.6 μg/m³), corresponding to the lowest concentration of the O-containing organics (Fig. 2a). Similarly, in the accumulation-mode PM, when the non-O-containing organics exhibited a pivotal concentration (15.2 μg/m³) under the driving condition of 1800 rpm/100%, the O-containing organics reversed a decreasing trend and peaked

Table 1 – Identifiable organic compounds in ultrafine and accumulation-mode particulate matter (PM).

Driving modes	Ultrafine PM (34–94 nm)		Accumulation-mode PM (94–1000 nm)	
	Concentration (μg/m³)	Fraction (%)	Concentration (μg/m³)	Fraction (%)
1800 rpm/60%	2.9	23	9.5	77
3000 rpm/60%	5.7	30	13.3	70
1800 rpm/100%	3.3	17	16.4	83
3000 rpm/100%	3.0	23	10.0	77

Driving modes are engine speed and engine load.

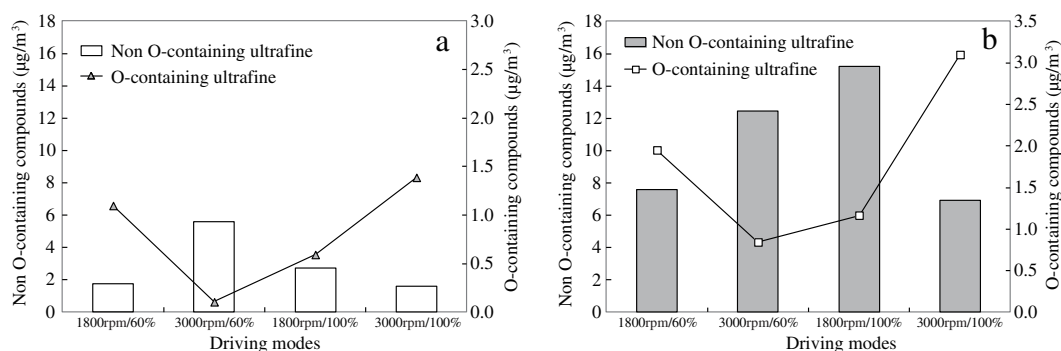


Fig. 2 – Oxygen-containing and non-oxygen-containing organic compounds in (a) the ultrafine PM and (b) the accumulation-mode PM.

at the driving condition of 3000 rpm/100% with the largest concentration of $3.1 \mu\text{g}/\text{m}^3$ (Fig. 2b). This is consistent with the observations of the organics during in-cylinder diesel engine measurements that the oxidative pyrolysis and the partial oxidation of aliphatic hydrocarbons could increase the amount of oxygenated organic compounds (Barbella et al., 1990). Since the toxicity of the O-containing compounds differs from that of the non-O-containing compounds (Walgraeve et al., 2010), elucidation of the molecular structure of the organic compounds can provide more specific assessment of the potential health problems imposed by PM.

According to molecular structure, the identified 101 organic compounds in PM (34 nm to $1 \mu\text{m}$) were further classified into eleven classes: alkanes, alkenes, alkynes, aromatic hydrocarbons, carboxylic acids, esters, ketones, alcohols, ethers, nitrogen (N)-containing compounds, and sulfur (S)-containing compounds. Among the identified organic classes, alkane consistently exhibited the highest concentration, followed by carboxylic acid, esters, ketones and alcohols (Fig. 3). Alkanes accounted for more than 60% (or up to 95%) of the identified organics in PM ($<1 \mu\text{m}$) with a concentration ranging from 8.3 to $18.0 \mu\text{g}/\text{m}^3$ (Fig. 3). For the ultrafine PM among the tested driving conditions, PM of 3000 rpm/60% contained the largest amount of alkanes ($5.6 \mu\text{g}/\text{m}^3$) (Fig. 3b), accounting for $>97\%$ of the quantified organics in this size range. On the other hand, most abundant alkanes in larger PM were emitted at the driving condition of 1800 rpm/100% (Fig. 3c), responsible for $\sim 88\%$ of the identifiable organics in the accumulation mode, agreeable with Rogge et al. (1993a) that alkanes contributed more than 60% of PM ($\leq 2 \mu\text{m}$). A large amount of alkanes in PM is expected because more than 98 wt.% of the diesel fuel used for this study consists of alkanes (ranging from C9 to C24) (Table 2); the unburned fuel could be involved in the resultant PM.

Consistent with the opposite trend between the oxygenated and the non-oxygenated organics (Fig. 2), alkanes show a reversed concentration trend to oxygenated compounds (including carboxylic acids, esters, ketones and alcohols) (Fig. 3). For example, a smaller concentration of alkanes (8.3 – $9.3 \mu\text{g}/\text{m}^3$) was accompanied by higher concentrations in the oxygenated organics (3.0 – $4.3 \mu\text{g}/\text{m}^3$) in PM under the driving conditions of 1800 rpm/60% and 3000 rpm/100% (Fig. 3a, d). In particular, the maximum engine speed and load (3000 rpm/100%) (Fig. 3d) emitted PM ($<1 \mu\text{m}$) containing the least amount of alkanes ($8.3 \mu\text{g}/\text{m}^3$) along with the largest amount of carboxylic acids

($2.2 \mu\text{g}/\text{m}^3$), alcohols ($0.9 \mu\text{g}/\text{m}^3$), N-containing compounds ($0.2 \mu\text{g}/\text{m}^3$) and aromatic hydrocarbons ($0.2 \mu\text{g}/\text{m}^3$). This could support the oxidation scheme given by Faravelli et al. (1998) that in expense of alkanes, the oxygenated compounds can be formed through the isomerization of the hydroperoxy radicals and the reactions of the peroxyalkyl hydroperoxy radicals. Among the generated oxygenated compounds, abundant carboxylic acid could be contributed by lubricant used in this study (Table 2) because under heavier engine loads and higher temperatures, larger amounts of lubricants used can enhance the evaporation of lubricant, leading to their presence in PM (Liang et al., 2005; Brandenberger et al., 2005).

2.2. Effects of driving conditions on alkanes in particulate matter

A closer examination of the concentration distribution among individual alkanes demonstrates that consistent with Fig. 3, most alkanes concentrated in the accumulation-mode PM of the four driving conditions (Fig. 4); while individual alkanes in the ultrafine PM contained a similar concentration, in accumulation-mode PM, C19–C25 alkanes had a larger concentration than other alkane species. Since diesel fuel mainly comprises C9–C24 (Table 2), the presence of C25–C31 alkanes indicated the polymerization during fuel combustion, which appeared to be more prominent under median engine loads (Fig. 4a, b). Interestingly, after an increase in the engine speed or engine load, larger alkanes (C25–C31) decreased in concentration for more than 2 times of low engine speed and load (Fig. 4), which could be due to more severe thermal decomposition (Yu and Eser, 1997) since an increase in the engine speed or load in this study could enhance the combustion (exhaust) temperatures for more than 200°C .

Fig. 4 shows that total alkanes quantified in PM ($<1 \mu\text{m}$) (dashed lines, Fig. 4) generally peaked between C19–C25 and exhibited a bi-modal distribution. Among the identified 17 alkane species in PM, C19 exhibited the highest concentration at all the driving conditions, except for the maximum engine speed and load (Fig. 4d). Since diesel fuel used in this study contained alkanes C9–C24 with a concentration peaking at C15, a shift from lighter alkanes in diesel fuel to larger alkanes in PM could result from the combustion synthesis, similar to the observations of other studies (Schauer et al., 1999; Liang et al., 2005). While concentration of alkanes in PM ($<1 \mu\text{m}$) varies

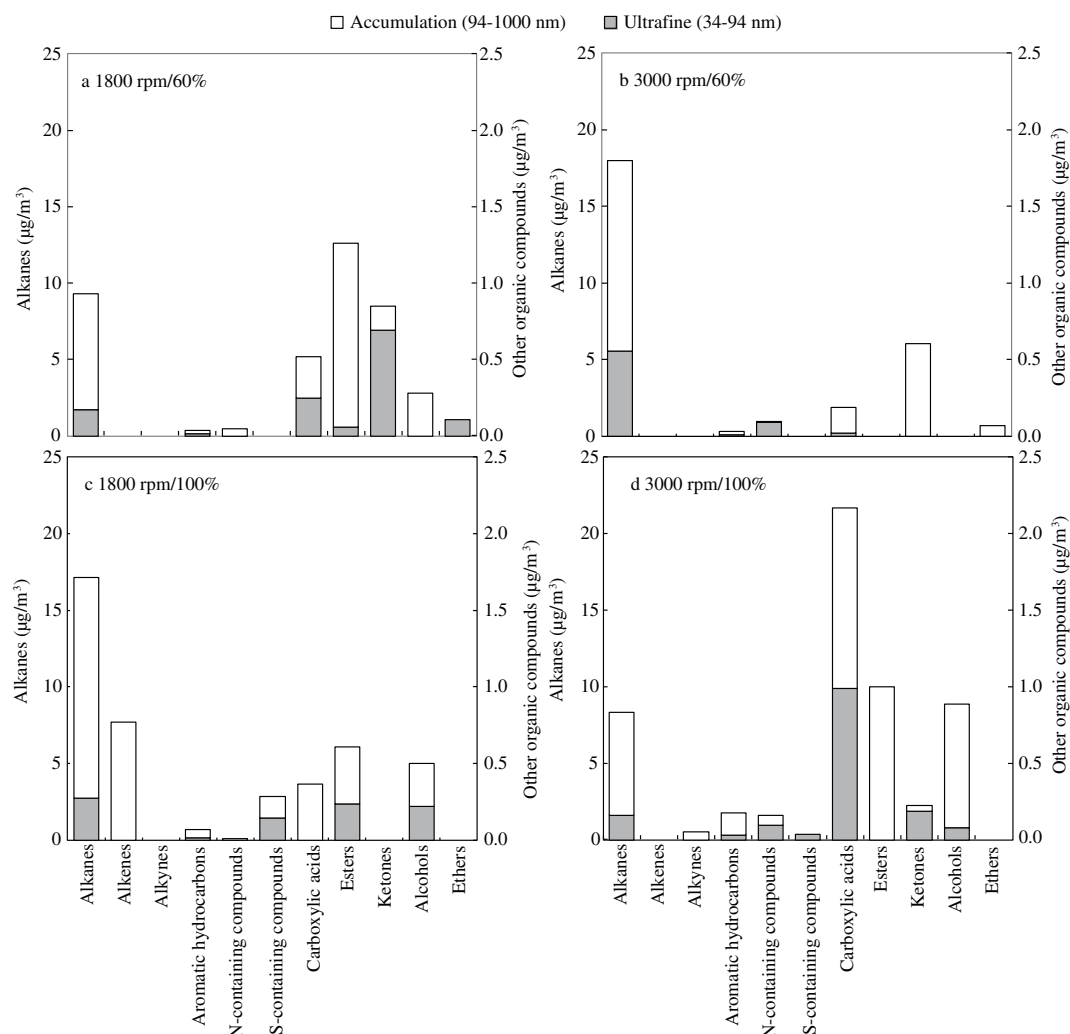


Fig. 3 – Identified organic compound classes in PM (<1 μm) under four driving conditions of 1800 rpm/60% (a), 3000 rpm/60% (b), 1800 rpm/100% (c) and 3000 rpm/100% (d). The concentration of non-alkane compound classes corresponds to the right Y-axis.

marginally with the driving conditions, a concentration ratio between two alkanes peaking individual modes may characterize the effects of the individual driving conditions. For example, the concentration ratios of the individual driving

conditions are: 1.7 (C19/C25) at 1800 rpm/60%, 2.9 (C19/C24) at 3000 rpm/60%, 1.8 (C19/C24) at 1800 rpm/100%, and 2.0 (C21/C25) at 3000 rpm/100%. This demonstrates that a ratio higher than 2 could represent PM of the maximum engine speed. According to the data of other studies following the Federal Test Procedure (FTP) (Rogge et al., 1993a; Schauer et al., 1999), we obtained concentration ratios of 3.0 (C20/C25) and 2.7 (C20/C26) for alkanes in PM from a heavy-duty and a medium-duty truck, respectively. This could demonstrate the difference of the combustion condition between 4 steady state driving conditions and the transient driving condition (FTP) which includes the idle and low speed. Since the testing conditions, engine types, and diesel fuel employed could affect the emitted alkane composition, the resultant alkane ratios should be employed conditionally and may not be generalized. Nevertheless, alkane ratios may characterize the contributions of the particulates from diesel- vs. gasoline-powered vehicles during the tailpipe measurements because the alkanes ratios in the exhaust particulates of gasoline-powered vehicles undergoing

Table 2 – Identifiable organic compounds in diesel fuel and lubricant employed in this study.

Compound classes	Diesel fuel	Lubricant
	Concentration (μg/mL)	
Alkanes (C9–C24)	11067.6	–
Carboxylic acids	–	482.8
Ketones	–	42.2
Oxygenated N containing compounds	–	18.8
Alcohols	–	8.3
Esters	–	6.3
PAHs	133.5	1.6
PAHs: polycyclic aromatic hydrocarbons.		

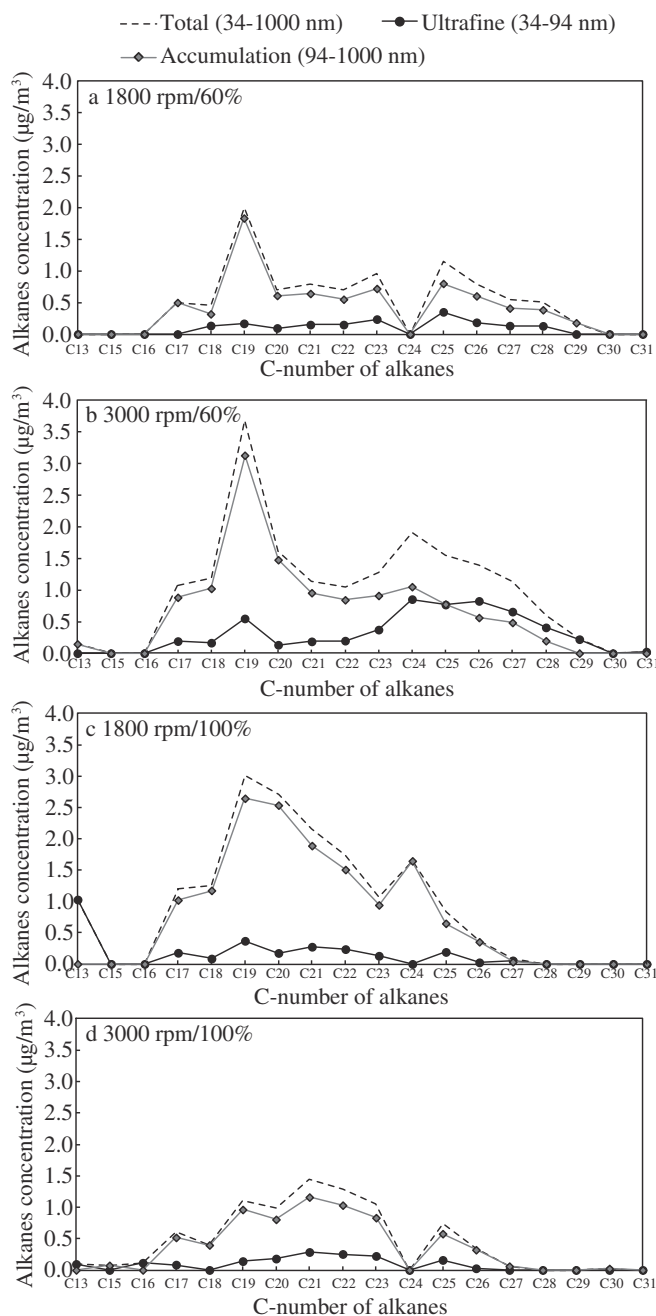


Fig. 4 – Identified alkanes species in the ultrafine and accumulation-mode PM under four driving conditions of 1800 rpm/60% (a), 3000 rpm/60% (b), 1800 rpm/100% (c) and 3000 rpm/100% (d).

the FTP tests were all smaller than 1.0; based on data of gasoline-powered vehicles without and with the catalytic converters (Rogge et al., 1993a; Schauer et al., 2002), we calculated the ratios ranging from 0.3 (C22/C26) to 0.9 (C20/C25) and 0.7 (C20/C25) to 0.8 (C18/C25), respectively.

2.3. Effects of driving conditions on polycyclic aromatic hydrocarbons (PAHs) in PM

Fig. 5 depicts twelve identified polycyclic aromatic hydrocarbons (PAHs) in PM (<1 µm), according to the molecular weight, namely acenaphthylene (Acy), acenaphthene (Ace), fluorene

(Flu), phenanthrene (Phe), anthracene (Ant), fluoranthene (Flt), pyrene (Pyr), chrysene (Cry), benzo(a)anthracene (BaA), benzo(b)fluoranthene (BbFt), benzo(k)fluoranthene (BkFt) and benzo(a)pyrene (BaP), with a total concentration ranging from 37.9 to 174.8 ng/m³. The engine at driving condition of 3000 rpm/100% emitted PM (<1 µm) containing the largest amount of PAHs, followed by 1800 rpm/100%, 1800 rpm/60% and 3000 rpm/60%. When the engine load increased from 60% to 100%, the amount of identifiable PAHs increased at least 2 times (under the engine speed of 1800 rpm) or more than 5 times (under the maximum engine speed). This is expected because a higher combustion temperature and a larger pyrolysis zone

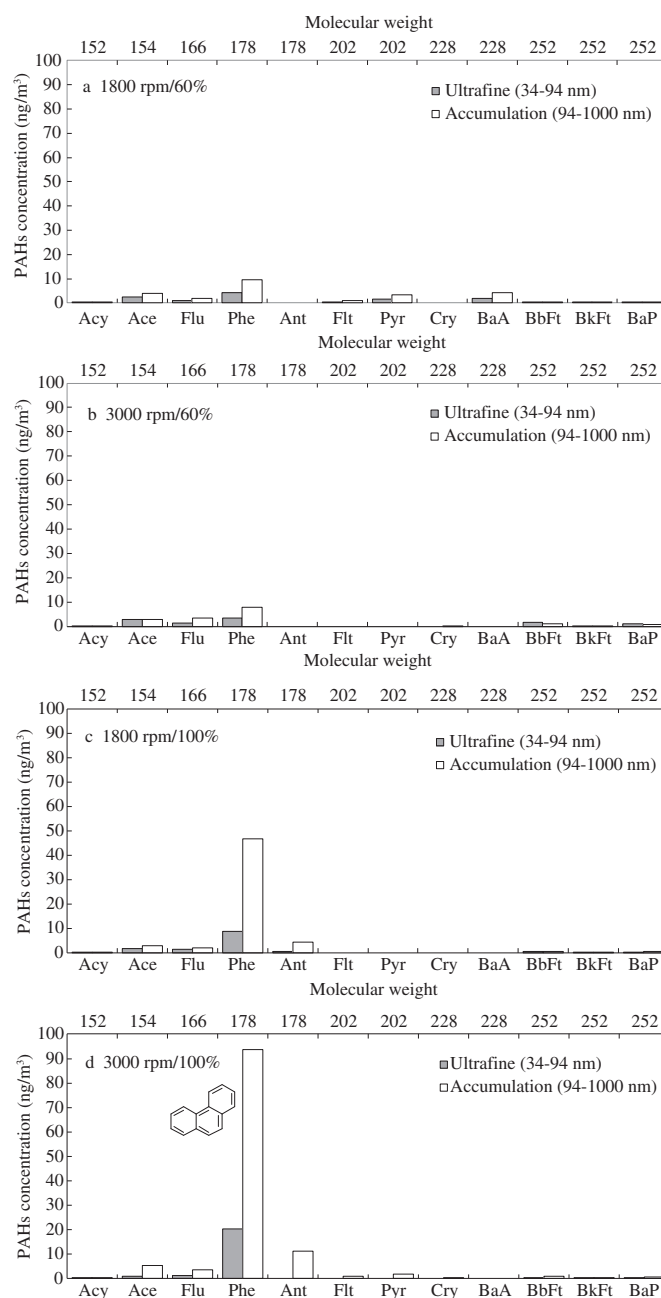
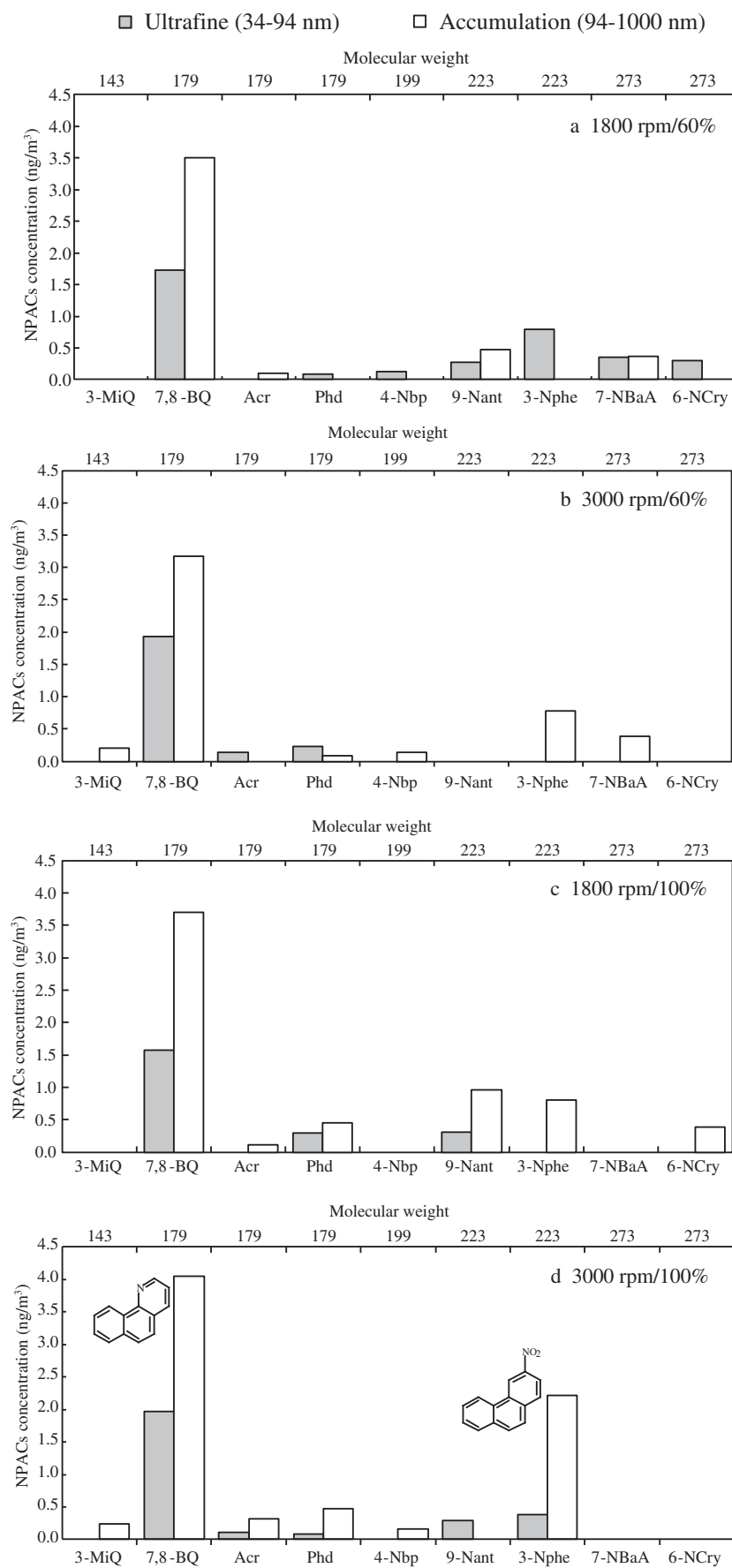


Fig. 5 – Identified polycyclic aromatic hydrocarbons (PAHs) in the ultrafine and accumulation-mode PM under four driving conditions of 1800 rpm/60% (a), 3000 rpm/60% (b), 1800 rpm/100% (c) and 3000 rpm/100% (d). Acy: acenaphthylene; Ace: acenaphthene; Flu: fluorene; Phe: phenanthrene; Ant: anthracene; Flt: fluoranthene; Pyr: pyrene; Cry: chrysene; BaA: benzo(a)anthracene; BbFt: benzo(b)fluoranthene; BkFt: benzo(k)fluoranthene; BaP: benzo(a)pyrene.

under the maximum engine load could encourage the highly reactive free radicals undergoing pyrosynthesis (fusion of smaller molecules under pyrolysis conditions) to form larger and more stable PAHs (Collier et al., 1995; Mastral and Callén,

2000). Similar to the size distribution of alkanes, Fig. 5 shows that relative to PAHs in ultrafine PM (10.8–23.2 ng/m³), the accumulation-mode PM contained more PAHs (16.3–119.0 ng/m³).

Fig. 6 – Identified nitrogen-containing polycyclic aromatic compounds (NPACs) in the ultrafine and accumulation-mode PM under four driving conditions of 1800 rpm/60% (a), 3000 rpm/60% (b), 1800 rpm/100% (c) and 3000 rpm/100% (d). 3-MiQ: 3-methylisoquinoline; 7,8-BQ: 7,8-benzoquinoline; Acr: acridine; Phd: phenanthridine; 4-Nbp: 4-nitrobiphenyl; 9-Nant: 9-nitroanthracene; 3-Nphe: 3-nitrophenanthrene; 7-NBaA: 7-nitrobenzo[a]anthracene; 6-NCry: 6-nitrochrysene.



Among the identified PAHs in PM ($<1\ \mu\text{m}$), the concentration of phenanthrene was the highest under all four driving conditions (Fig. 5). When the engine load increased to the maximum, the concentration of phenanthrene increased up to 10 times (from 11.4 to 114.0 ng/m^3) (Fig. 5). This is consistent with other studies examining PM from the light-duty diesel vehicles (chassis dynamometer tests) (Lu et al., 2012; Devos et al., 2006; de Abrantes et al., 2004) and from the heavy-duty diesel vehicles (Mobile Emission Laboratory tests) (Shah et al., 2005). At a bus station devoted to only diesel-powered vehicles, phenanthrene was also the most abundant PAH ($>40\%$ of identified PAHs) (Tavares et al., 2004). This indicates that phenanthrene could represent the diesel emissions if other emission sources of phenanthrene remained insignificant.

In this study, when the engine load increased from 60% to 100%, phenanthrene in the accumulation-mode PM increased from 7.9 up to 93.6 ng/m^3 (Fig. 5), accounting for 83% of the corresponding increase in PAHs (from 16.3–119.0 ng/m^3) in the accumulation-mode PM. The significant amount of phenanthrene in the accumulation mode under the most strenuous driving condition indicates the prominent condensation of PAHs onto PM. Because phenanthrene was postulated as one of the dominant intermediates during the PAH growth and the soot formation (Skj  th-Raamussen et al., 2004; Marinov et al., 1998), which can take place through the hydrogen abstraction acetylene addition (HACA) (Lombaert et al., 2006), polymerization involving the prominent condensation could be important to form PM in the accumulation mode. It is worth noting that the maximum engine speed and engine load (3000 rpm/100%) generated the most abundant phenanthrene (Fig. 5d), which could be due to the largest pyrolysis zone and highest combustion temperature, stimulating the formation of more resonantly stabilized radicals (e.g., cyclopentadienyl radical), and subsequently leading to the formation of phenanthrene (Richter and Howard, 2000). Since phenanthrene (22 $\mu\text{g}/\text{mL}$) was one of the dominant PAHs in the diesel fuel employed for this study, more injection of diesel fuel under the maximum engine load could also contribute to the abundant phenanthrene in PM. Uniquely, around 13% (23.2 ng/m^3) of fluorenone (oxygenated PAH) among the total identified aromatic hydrocarbons was emitted mainly at the most strenuous driving condition (maximum speed and load (3000 rpm/100%)) in this study. This could be resulted from the strongest oxidative pyrolysis under the maximum combustion temperature.

2.4. Effects of driving conditions on nitrogen-containing polycyclic aromatic compounds (NPACs) in PM

Nine NPACs were identified in PM ($<1\ \mu\text{m}$) with a total concentration ranging from 7.0 to 10.3 ng/m^3 . Similar to the trend in quantified PAHs, the identified NPACs were more abundant in accumulation-mode PM, in particular, under the full engine load. The identified 9 NPACs consist of four aza arenes (nitrogen-containing heterocyclic aromatic hydrocarbons) and five nitroarenes (nitro-PAHs) with a total concentration of 5.4–7.3 and 1.3–3.1 ng/m^3 , respectively. The four aza arenes are mainly composed of 2–3 aromatic rings, including 3-methylisoquinoline (3-MiQ), 7,8-benzoquinoline

(7,8-BQ), acridine (Acr), and phenanthridine (Phd). The identified five nitroarenes are 4-nitrobiphenyl (4-Nbp), 9-nitranthracene (9-Nant), and 3-nitrophenanthrene (3-Nphe), 7-nitrobenz[a]anthracene (7-NBaA), and 6-nitrochrysene (6-NCry), which consist of 1–3 aromatic rings. According to their molecular weight, Fig. 6 shows the concentration of the individual NPACs in PM ($<1\ \mu\text{m}$) at the individual driving conditions. Under all driving conditions, 7,8-benzoquinoline (7,8-BQ) showed the highest concentration, 5.1–6.0 ng/m^3 , or 59%–72% of the quantified NPACs. The concentration of 7,8-BQ increased with the increasing engine loads, and peaked in PM at the most demanding driving condition (3000 rpm/100%) (Fig. 6). 7,8-BQ was responsible for 66% and 63% of the quantified NPACs in the ultrafine and accumulation mode PM, respectively.

Similar to 7,8-BQ, the concentration of 3-nitrophenanthrene (3-Nphe) also peaked (2.6 ng/m^3) when the engine was operated at the maximum speed and load. Interestingly, while 3-Nphe was the most abundant in the accumulation-mode PM under 3000 rpm/100% (Fig. 6d), it only participated in the ultrafine PM under 1800 rpm/60% (Fig. 6a). This indicates that 3-Nphe could mainly undergo nucleation under the mild driving conditions, while condensation became more prominent along with an increase in the engine speed and/or engine load.

It is worth noting that the most abundant PAH (phenanthrene) and NPACs (7,8-benzoquinoline and 3-nitrophenanthrene) comprise a similar molecular (3 aromatic-ring) structure, in particular under the most strenuous driving condition (3000 rpm/100%) (Figs. 5 and 6). This could evidence the formation of aza arenes (7,8-benzoquinoline) and nitro-PAHs (3-nitrophenanthrene) through respective pyrosynthesis and nitration between PAH radicals and NO_x radicals. Forming aza arenes through pyrosynthesis seems to be consistent with Rogge et al. (1993b) reporting that aza arenes could be formed during the combustion of the fossil fuels, similar to the PAH formation, by incorporating N-atoms into their ring structures. Nitro-PAHs can be also formed through pyrosynthesis between the pyrolyzed PAH radicals and the NO_x radicals in a diesel engine with a stronger pyrolysis and higher combustion temperature as proposed by a few studies (Wiersum, 1996; Ghigo et al., 2006). Others (Williams et al., 1986, 1989; Murahashi et al., 2003) also considered that the reaction of NO_x with PAHs in the hot diesel exhausts or incomplete diesel combustion could generate NPACs. In addition to pyrosynthesis, Ghigo et al. (2006) suggested the direct nitration of NO_2 radicals followed by H abstraction to form nitroarenes under high-temperature (1200 K) combustion. It is worth noting that a bay-region like structure of the aromatic compounds can impose more genotoxicity and higher tumor-initiating potential compared with other types of PAHs (linear structure) (Upham et al., 1998; Rummel et al., 1999). Hence, larger amounts of phenanthrene, 7,8-benzoquinoline and 3-nitrophenanthrene, which contain the bay-region structure, suggest a higher toxic potential in PM generating under the largest engine speed and engine load.

In this study, three nitro-PAHs (9-Nant, 7-NBaA and 6-NCry) in PM from the medium-duty diesel engine tested were also found by Zielinska et al. (2004b), who measured 6 nitro-PAHs in PM by testing a light- and a medium-duty diesel vehicles using a transient chassis dynamometer. This indicates that the measured airborne NPACs could be mainly

contributed by diesel combustion because NPACs carried by particulates emitting from gasoline-powered vehicles are too low to be detected (Zielinska et al., 2004b). Chen and Preston (1998) also reported that the methylated quinoline isomers had the highest concentration (0.01–2.29 ng/m³) among the identified ambient NPAC and could mainly originate from the combustion of the fossil fuel. Chen and Preston (1998) observed strong seasonal variation of the atmospheric aza arenes having a total concentration fluctuating between 0.4 and 7.6 ng/m³ in urban atmosphere. They also reported that while aza arenes (benzoquinoline, phenanthridine and acridine) were measured in particulate samples collected from the exhausts of the natural gas combustion (Rogge et al., 1993b), four (3-methylisoquinoline, 7,8-benzoquinoline, acridine, and phenanthridine) of the nine NPACs identified in this study have been reported in the urban ambient environments, suggesting that PM could be one of the major primary emission sources contributing to the atmospheric NAPCs (Hayakawa et al., 2007).

3. Conclusions

The composition and size distribution of organics in PM at four driving conditions were characterized. When the engine speed and load increased from 1800 rpm/60% to 3000 rpm/100%, the fraction of the identifiable organic compounds in PM (<1 µm) reduced >3 times, indicating stronger formation of unresolved organics which could catalyze the generation of the reactive oxygen species (ROS), leading to the oxidative DNA damages under more strenuous driving condition. In addition, the highest engine load and speed (3000 rpm/100%) could encourage the oxidation of the non-oxygen-containing organics, resulting in a larger concentration of the oxygen-containing organics in PM. The concentration of alkanes accounted for more than 60% (or up to 95%) of the identified eleven classes' organics in PM, and generally shows a bimodal distribution among the 17 alkane species. A concentration ratio of the peak alkane species (>2.0) could characterize PM from particulates emitting from the gasoline-powered vehicles. When the engine load increased from 60% to 100%, polycyclic aromatic hydrocarbons (PAHs) in PM increased more than 2 times, which was mainly contributed by an ~10 times increase in phenanthrene among the twelve identified PAHs. Because phenanthrene was postulated as one of the dominant intermediates during PAH growth through hydrogen abstraction acetylene addition (HACA), polymerization involving the prominent condensation could be important to form PM in the accumulation mode. Similar to the alkane class, quantified PAHs and NPACs were mainly distributed in the accumulation-mode PM, with a concentration of 16.3–119.0 and 6.4–7.5 ng/m³, respectively. The most abundant PAH (phenanthrene) and NPACs (7,8-benzoquinoline and 3-nitrophenanthrene) comprise a similar molecular (3 aromatic-ring) structure, which could evidence the formation of aza arenes (7,8-benzoquinoline) and nitro-PAHs (3-nitrophenanthrene) through respective pyrosynthesis and nitration between PAH radicals and NO_x radicals under the highest engine speed and engine load (3000 rpm/100%). Because a bay-region like structure of aromatic compounds can impose more genotoxicity and

higher tumor-initiating potential compared with other types of PAHs (linear structure), larger amounts of phenanthrene, 7,8-benzoquinoline and 3-nitrophenanthrene, which contain the bay-region structure, suggest a higher toxic potential in the PM generating under the largest engine speed and engine load.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <http://dx.doi.org/10.1016/j.jes.2015.03.013>.

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