Pollutant Constituents of Exhaust Emitted from Light-Duty Diesel Vehicles

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ABSTRACT

Light-duty diesel exhaust particulate matter and its constituents, including elemental carbon, organic carbon, water-soluble ionic species, elements, and polyaromatic hydrocarbons (PAHs), were measured by a dynamometer study and following the driving pattern of federal test procedure-75 (FTP-75). Fuel consumption of these light-duty diesel vehicles was in the range of 0.106-0.132 l km^{-1}, and the average emission factors of NMHC (non-methane hydrocarbon), CO and NOx for light-duty vehicles were 0.158 (92% of total hydrocarbon), 1.395, and 1.735 g km^{-1}, respectively. The particulate emission factor of light-duty diesel vehicles was 0.172 g km^{-1}, and $PM_{2.5}$ contributed to 88% of particulate mass. Al, S, Ca, and Fe emission factors were about 0.83-1.24 mg km^{-1} for $PM_{2.5}$, and the particulate mass fractions of these elements ranged from 66-90% in $PM_{2.5}$. Nitrate, sulfate, ammonium and nitrite were the major ionic species in diesel PM, and their emission factor ranged from 0.22-0.82 mg km^{-1} for $PM_{2.5}$. The emission factor of total PAHs was 3.62 mg km^{-1} in this study, with about 40% in the gas phase and 60% in the particulate phase. Acenaphylene, naphthalene, fluoranthene, pyrene, and anthracene were the dominant PAHs, and their emission factors were more than 0.19 mg km^{-1}. The content of nitro-PAHs was low, with most less than

0.040 mg km^{-1}.

Keywords: diesel exhaust, particulate composition, emission factor,

1. INTRODUCTION

Chemical constituents are an important issue in the study of diesel exhaust emission. Exposure to air pollutants increases the risk of cardiovascular disease. Numerous epidemiological studies have shown that an increase in adverse cardio-pulmonary effects is associated with an increase in particulate matter level (HEI, 2003; Pope et al., 2004). Recent studies have revealed that diesel exhaust particles could induce inflammation in cytokines (Mazzarella et al, 2007), cytokine/chemokine response (Øvrevik et al, 2010), cellular oxidative stress (Suzuki et al, 2008), mutation yield in human-hamster hybrid cells (Bao et al, 2007) etc. Diesel exhaust particles have been identified as a class 2A human carcinogen (International Agency for Research on Cancer, IARC) and related to an increase in the incidence of respiratory allergy, cardiopulmonary morbidity and mortality, and risk of lung cancer (Kizu et al., 2003).

Generally, diesel vehicles contribute only a small fraction of particulate matter (0.25-1.4% of $PM_{2.5}$) in the atmosphere (Hwang and Hopke, 2007; López-Veneroni, 2009), but most people are concerned with the health effects of diesel exhaust particles (Alföldy et al, 2009). Therefore, elucidating the chemical constituents of diesel exhaust is important to understand their toxicity (Lin et al., 2008a; Lin et al., 2008b; Schneider et al., 2008; Cheng et al., 2010). In addition, diesel fuel characteristics (i.e., sulfur content, fuel density, distillation point, cetane index) and engine operation conditions (power loading, exhaust temperature, engine speed, air/fuel ratio exhaust gas circulation) could affect the exhaust compositions and particulate size distribution (Lim et al., 2007; Lapuerta et al., 2007; Chung et al., 2008, Zhu et al., 2010). Most studies in the literature have investigated the constituents of diesel exhaust particles including carbon content (organic carbon and elemental carbon), metal, inorganic ions, polyaromatic hydrocarbons, etc. (Kawanaka et al., 2007; Maricq, 2007; Fushimi et al., 2008; Lin et al., 2008a; Cheng et al., 2010). Few studies have investigated the comprehensive chemical constituents of diesel exhaust particulate matter in detail. Typical mass fraction of diesel particle was mainly in accumulation mode, $0.050\ \mu m < Dp < 1.0\ \mu m$, with a maximum concentration between 0.1 and 0.2 μm and small mass peak in nuclei mode and coarse mode (Kittelson, 1998; Kittelson, 2002). Significant and fundamental changes have been made to the diesel engine combustion process and associated after-treatment technologies (i.e., catalyst, diesel particle filter, SCR catalyst) to meet stringent regulations and reduce emissions of NOx and particulate matter (Biswas et al., 2008). However, diesel vehicles are still a concern with regard to their pollution emission and health effects.

In general, two methods are used to measure vehicle emissions: the dynamometer test and real-world study (i.e., roadside and tunnel studies). The emission factors of specific engines can be determined by a dynamometer; measurements from individual cars are still the standard in dynamometer studies for many countries (Heeb et al., 2000, 2002, 2003; Nelson et al., 2008; Oanh et al., 2010).

Actual traffic emission data have been obtained from roadsides or road tunnels (De Vlieger, 1996; Lenaers, 1996; Pierson et al., 1996; Laschober et al., 2004; Stemmler et al., 2005; He et al., 2008); the emission factor has been determined by a mathematical method that does not reflect actual vehicle emissions. Because dynamometer testing is a standard method and determines tailpipe exhaust emission, it was selected in this work.

Detailed chemical constituents provide baseline information to determine the effects of diesel vehicle exhaust. Many studies have focused on diesel exhaust emission and composition using a dynamometer. However, detailed information about PM concentration and composition is still necessary to compare different areas. In this study, $PM_{2.5}$ and its compositions including elemental carbon, organic carbon, water-soluble ionic species, elements, and polyaromatic hydrocarbons were measured to determine their emission factors.

2. EXPERIMENT

2.1 Light-duty diesel vehicles and testing driving pattern

Six in-use light-duty vehicles were selected on the basis of accumulated mileage and produced year. All vehicles were without pollution control equipment, mileage ranged from 56,000 to 160,000 km, and the displacement volume ranged from 2184 to 2835 cc. **Table 1** presents more detailed information such as produced year, mileage, weight and engine capacity of all selected vehicles.

All selected vehicles were tested on a chassis dynamometer following test procedure FTP-75, which is used in Taiwan to certify new vehicles. The dynamometer is located in a certified laboratory located in ARTC (Automotive Research & Testing Center, Taiwan). All vehicles were visually examined for safety prior to testing on the following day. The distance and average speed of FTP-75 are 17.48 km and 34.1 km hr^{-1}, respectively.

2.2 Criteria pollutant sampling and analysis

All exhaust samples were taken from a constant volume dilution sampling system. The dilution system, designed to meet the specifications covered in the U.S. Federal Register (1986), was connected to a constant volume sampling system (Horiba, Japan) to dilute the exhaust flow rate to 9 m^3

min^{-1}. Exhaust samples, taken at the end of the entire cycle of the FTP, were analyzed for CO, HC, NO_x and CO_2 by auto-monitors (HORIBA MEXA-9200). The background concentrations of those pollutants were also analyzed routinely and deducted from the test results. Background concentrations were about 2 ppm for CO, 6 ppm C for HC, 0.1 ppm for NO_x and 0.1% for CO_2. The analytical errors for CO, HC, NOx and CO_2 were approximately 0.01-0.08%, 0.01-0.17%, 0.02-0.06% and 0.25-0.38%, respectively.

2.3 Particle sampling

A dilution tunnel and a monitoring system were installed downstream of the diesel exhaust to supply air for dilution and to measure particles and gas pollutants. A cascade impactor (Graseby Anderson Mark III) with quartz filters (with diameters of 64 mm, Pallflex, Pall Corporation, USA) is installed downstream of the dilution tunnel to collect size-resolved samples. These impactors can effectively separate the particulate matter into eight size ranges with the following equivalent cut-off diameters: 6.6-10.5 (stage 8), 4.4-6.6 (stage 7), 3.1-4.4 (stage 6), 1.9-3.1 (stage 5), 1.0-1.9 (stage 4), 0.6-1.0 (stage 3), 0.4-0.6 (stage 2), and <0.4 μm (stage 1). A linear interpolation method was employed to determine the mass concentration of $PM_{2.5}$ and PM_{10}. All quartz filters were baked at 900°C for 3h before use to ensure low concentrations of organic compounds on the blank filter materials. In addition, polyurethane foam (PUF) and an XAD-16 resin backup cartridge were utilized to collect PAHs in the vapor phase, which is connected after the particle sampling system.

2.4 Chemical analysis

2.4.1 Water-soluble ions

One-eighth of the particle filter sample of each stage was ultrasonically extracted for 2 h into 20 ml of deionized distilled water and passed through a Teflon filter of 0.45 μm nominal pore size. Ion chromatography (IC, Dionex, 120) was used to analyze the concentration of anions (Br^-, F^-, Cl^-, NO_2^-, NO_3^-, SO_4^{2-}) and cations (Na^+, NH_4^+, K^+, Mg^{2+}, Ca^{2+}). Anions were separated using an IonPac AS 12A (4×200 mm) analytical column, an AG 14 guard column with a 10 μl sample loop, and an anion self-regenerating suppressor-ultra. A solution of 2.7 mM Na_2CO_3/0.3 mM $NaHCO_3$ was used as an effluent at a flow rate of 1.5 ml min^{-1}. Cations were separated using an IonPac CS 12A (4×250 mm) analytical column and a CG 14 guard column, with a 50 μl sample loop, and a cation self-regenerating suppressor-ultra. A solution of 20 mM methanesulfonic acid was used as the eluent at a flow rate of 1 ml min^{-1}. The recovery ranged from 87% (Na^+) to 109%(F^-).

2.4.2 Elemental constituents in particulate matter

The one-eighth particle filter samples were mixed with a 20 ml acid mixture (HNO_3:$HClO_4$:HF = 5:3:2, v/v) in a Teflon-lined closed vessel and placed in a high-pressure digestion oven at 170^{o}C for 5h. The digested acid mixture was analyzed to determine the trace elements. A Perkin Elmer OPTIMA 3000 ICP-AES was used to determine the Al, Ca, Fe, K, Mg, Na, S, Co and Zn concentrations. Additionally, a SCIEX Elan Model 5000 ICP-MS manufactured by Perkin-Elmer was employed to determine As, Ba, Cd, Cr, Cu, Mn, Ni, Pb, Sb, Se, Sr and V concentration. Blank and duplicate samples were also analyzed in this study.

2.4.3 Organic and elemental carbon in particulate matters

Particulate samples intended for carbon analysis were collected on quartz-fiber filters that had previously been heated in air at 900^{o}C for 4h to lower their carbon blank level. The particle filter sample was stored below 4^{o}C until analysis. Total carbon (TC) and elemental carbon (EC) were measured with a C/H/N elemental analyzer (Carlo Erba EA 1110). The procedure performed in this study to determine particle carbon content is similar to the method described by Cachier et al. (1989). Samples one-eighth the amount of each filter were heated in advance in a 340°C oven for 100 min to expel the organic carbon (OC) content, then fed into the elemental analyzer to obtain the EC content. Another one-eighth sample was fed directly into the elemental analyzer without pre-treatment to obtain the TC concentration. EC could be determined by the difference of TC and OC. However, the EC fraction as measured by this method can be overestimated, so the use of thermo-optical techniques is highly recommended by other studies (Turpin et al., 2000; Schmid et al., 2001; Sillanpää et al., 2005).

2.4.4 Reference sample validation

To validate the analysis method, NIST Standard Reference Material SRM 1648 was used. About 10 mg of SRM 1648 and 1650a, which approximates the composition of urban particulate matter and diesel particulate matter, respectively, was used to examine the accuracy and reliability of the analysis method. Al, As, Ba, Co, Cr, Cd, Cu, Fe, K, Mg, Mn, Na, Ni, Pb, S, Sb, Se, Sr, V, and Zn were recovered in the acceptable range (recovery: 82-108%). In addition, the recovery of three water-soluble ionic species, F^-, Cl^-, and SO_4^{2-}, was 87-109%, which is in the acceptable range by the analysis method of ion chromatography.

2.4.5 Polyaromatic hydrocarbons (PAHs)

The 16 PAH (polyaromatic hydrocarbons) and 10 nitro-PAH standards (purity of >99%) including Naphthalene (NaP), Acenaphthylene (AcPy), Acenaphthene (AcP), Fluorene (Flu), Phenanthrene (PA), Anthracene (Ant), Fluoranthene (FL), Pyrene (Pyr), Benzo(a)anthracene (BaA), Chrysene (CHR), Benzo(b)fluoranthene (BbF), Benzo (k)fluoranthene (BkF), Benzo(a)pyrene (BaP), Indeno(1,2,3-cd)pyrene (IND), Dibenzo(a,h)anthracene (DBA) and Benzo(g,h,i)perylene (BghiP); and 2-Nitrofluorene (2-nFlu), 9-Nitroanthracene (9-nAnt), 3-Nitrofluoranthene (3-nFL), 1-Nitropyrene (1-nPyr), 7-Nitrobenzo(a)anthracene (7-nBaA), 6-Nitrochrysene (6-nCHR), 1,3-Dinitropyrene (1,3-DnPyr), 1,6-Dinitropyrene (1,6-DnPyr), 1,8-Dinitropyrene (1,8-DnPyr) and 6-Nitrobenzo(a)pyrene (6-nBaP), were purchased from Supelco Inc. (USA). Dichloromethane, n-hexane, acetone, acetonitrile, silica gel (0.063–0.200 mm, activated at 150°C for 18 h prior to use), anhydrous sodium sulfate (baked at 400°C for 4 h prior to use) and other reagents were pesticide analysis grade and/or residue analysis grade and purchased from E. Merck, Germany.

2.4.5.1 Sample extraction and cleanup

Combination samples of polyurethane foam (PUF) and XAD-16 resin were extracted using the Soxhlet extraction procedure in an all-glass Soxhlet system combined with an electro-thermal heating plate. The samples were extracted for 16 h with 300 ml of mixed solvent (dichloromethane-acetonitrile 3:1, by volume) in a 500-ml flat-bottom flask. The filters (cut size was larger than 1.9 μm) were mixed as one sample for consideration of low PAH content in large particles to ensure that the concentration was higher than the method detection limitation. Samples of quartz filter were extracted using sonication with the above solvent three times (3×40=120 ml) for periods of 15 min. The temperature of the sonication bath was maintained between 25 and 30°C. The extracts from the various procedures were concentrated on a rotary evaporator (EYELA, Japan) equipped with a water bath held at 40°C, and the solution volume was reduced to 1-2 ml. In the cleanup process, the residual solution was introduced into a silica column (1 cm internal diameter and 25 cm length), and the column was first eluted with 10 ml of n-hexane. About 2 cm height of anhydrous sodium sulfate was packed at the fore-end of the cleanup column to exclude water. The n-hexane fraction was discarded, and the available fractions were then obtained by elution with 20 ml of dicloromethane-hexane 1:2 and then 30 ml of acetone-hexane 1:2. The last two fractions were combined and concentrated just to dryness, then quantified to 2 ml (PUF+XAD-16) or 1 ml (quartz filter) with solvent acetone-hexane 1:2. The final solutions were analyzed with the gas chromatography (GC) method.

2.4.5.2. Gas chromatography method

PAHs were analyzed by GC-MS. The GC apparatus consisted of a Hewlett-Packard GC 6890 equipped with a mass (5973 N) and split/splitless injector. An HP-5MS capillary column (5% phenyl methyl siloxane, 30 m, internal diameter 0.32 mm, and film thickness 0.25 μm) was used. The injector program was set to 280°C at the pulsed splitless mode (12 psi for 1 min). The oven temperature program was 60°C for 1 min, 35°C min^{-1} to 170°C, 8°C min^{-1} to 210°C, 4°C min^{-1} to 300°C, and 15°C min^{-1} to 320, which was held for 3 min. The carrier gas (99.9995% nitrogen) flow rate was held at 1.5ml min^{-1}. MSD (mass selective detector) was operated in SIM (selected ion monitoring) mode, with the electron energy at 70 eV, the EI (electron ionization) source held at 175 °C and the interface temperature at 300 °C.

To analyze the nitro-PAHs, a ^{63}Ni electron-capture detector (ECD) was used for GC-ECD analysis under the same conditions as the PAH analyses. The ECD temperature was 300°C, and the total gas flow rate was 30 ml min^{-1} (makeup plus column). In a preliminary investigation for the above conditions, these PAHs and nitro-PAHs have a completely isolated chromatogram with retention time ranging from 4.66 to 27.39 min. The mixed stock solution was used to make five concentrations of mixed standard solution, which were required to establish calibration curves for PAH and nitro-PAH measurement.

The injection volume was 1μl for all samples. The spike was added to the blank sampling PUF+XAD-16 and quartz filter prior to extraction for recovery analysis. The average recovery of PAHs based on QA/QC ranged from 68% (naphthalene) to 93% (pyrene) and 71% (naphthalene) to 94% (Benzo(g,h,i)perylene) for the PUF+XAD-16 and quartz filter samples, respectively. The nitro-PAHs had lower average recoveries for the PUF+XAD-16 and quartz filter samples, which ranged from 59% (1,3-Dinitropyrene) to 87% (2-Nitrofluorene) and 61% (1,8-Dinitropyrene) to 89% (3-Nitrofluoranthene), respectively.

To validate the analysis method of PAHs in diesel particulate matter, NIST Standard Reference Material SRM 1650a was used. About 50 mg of SRM 1650a, which approximates the composition of diesel particulate matter, was used to examine the accuracy and reliability of the analysis method.

3. RESULTS AND DISCUSSION

3.1 Exhaust gas characteristics

The diesel fuel characteristics included carbon: 86.0%, hydrogen: 12.4%, heat value: 10821 cal g^{-1}, aromatic content: 32.4%, sulfur content: 0.0341% etc. The fuel characteristics could affect the emission factors of particulate matter. CO, CO_2, NOx and HC for the entire cycle are summarized in **Table 2**; some literature data are also included for comparison. The fuel consumption of these light-duty diesel vehicles was in the range of 0.106-0.132 l km^{-1}. The average emission factors of light-duty diesel vehicles were 0.171, 0.158, 1.395, and 1.735 g km^{-1} for THC, NMHC, CO and NOx, respectively. About 8% CH_4 contributed to THC.

In general, the PM emission factors are low for low-mileage vehicles, and the values increase with mileage accumulation and age. The average PM emission factor was 0.172±0.071 g km^{-1}. High fuel consumption reflects high

CO_2 and high NOx emission. In addition, little methane was emitted from the diesel exhaust. LDV-4 was the lowest reference weight, but high fuel consumption (about 20-50% high) and high pollution emission, i.e., CO (about 1.5-3.9 times), NOx (about 2.4-4.0 times). Results indicated that weight was not the main factor in high fuel consumption; engine characteristics are also important (Ceviz and Akin, 2010). High fuel consumption could cause incomplete combustion for high CO and high engine temperature for high thermal NOx.

PM, THC, CO, and NOx concentrations were in the range of California test guidelines for 1998, which are based on the FTP driving cycle (Norbeck etal., 1998). The average concentrations of PM and THC were low in this study, which could be attributed to the age of the California vehicles (1977-1993). These vehicles were older than those used in our tests.

3.2 PM mass distribution

Figure 1 shows the particle size distribution of the exhaust of light-duty diesel vehicles. Particulate matter concentration was 172 mg km^{-1}; 66% of particulate mass fraction was less than 0.4 μm (near the range of ultrafine particles). In addition, particulate size was 0.4-0.6, 0.6-1.0, and 1.0-1.9 μm corresponding to mass fractions of 6, 8 and 6%, respectively. Other particle size fractions were less than 4%. About 80% of the mass fraction of diesel particulate was less than 1.0 μm. Lin et al. (2008) indicated high mass fraction at a particle size < 1.0 μm, especially in the 0.166-0.52 μm range, and low mass fractions at particle sizes of > 0.52 μm and < 0.166 μm. Generally, the high mass fraction was less than 0.4 μm for diesel vehicles; the smallest cut size of the particulate sampler is about 0.4 μm, which could not clearly describe the particle size distribution; it could be a limitation of this study. Park et al. (2010) indicated that the mass concentration of diesel nano-particles was in the range of 0.131-0.230 μm. In addition, the average sizes of particles emitted in diesel exhaust is higher than particles emitted in gasoline exhaust under similar operating conditions. The peak of particle concentrations for mineral diesel was never less 0.040 μm; however, for gasoline engines, it could be as low as 0.020 μm under most operating conditions (Gupta et al., 2010).

3.3 Particulate compositions

3.3.1 Carbon content

The emission factor of diesel particulate matter was about 172 mg km^{-1}. Based on the interception of particle size distribution, the emission factor of PM_{10} was 167 mg km^{-1} and $PM_{2.5}$ was 151 mg km^{-1}. About 88% of particulate mass was less than 2.5 μm in diesel exhaust. Generally, the percent of particulate mass less than 10 and 2.5 μm was 99.4 and 95.1%, respectively (Norbeck et al., 1998), which was higher than the results of this study.

The carbon content was high, and its fraction was about 72% of particulate mass (**Table 3**). EC was about 66% of carbon content in particulate mass; the remainder was OC in $PM_{2.5}$. The fraction of EC was high compared to the results (EC and OC were almost the same level) of Norbeck et al., 1998. Generally, the EC content was higher than OC content in diesel particulate matter (Kleeman et al., 1999; Grieshop et al., 2006), which was similar to this study.

3.3.2 Elemental compositions

The emission factors of Al, S, Ca, and Fe were about 0.83-1.24 mg km^{-1} in $PM_{2.5}$ and 1.07-1.77 mg km^{-1} in PM_{10}, and the fractions of these elements were about 66-90% in $PM_{2.5}$ and others were in $PM_{2.5\text{-}10}$. Sulfur content in fuel could affect the formation of new particles during engine combustion in exhaust gas. Sulfur could form sulfate after the cylinder gas, leaving as exhaust. In addition, sulfur can be a catalyst poison in the exhaust control system of diesel motor vehicles. (Kozak and Merkisz, 2005). Therefore, the fuel sulfur could affect the formation of nucleation particulate matter during the combustion of diesel fuel (Schneider et al., 2005). Some studies have indicated that high sulfur and the oxidation catalyst are mandatory conditions for sulfate formation, which results in nucleation formation of particulate matter for light-duty diesel vehicles (Maricq et al., 2002; Vogt et al., 2003).

K, Zn, Na, and Mg were in the range of 0.18-0.48 mg km^{-1} in $PM_{2.5}$ and 0.29-0.82 mg km^{-1} in PM_{10}. Some toxic elements, i.e., Ni, Cr, Pb, Cu, Cd, and As, ranged from 0.01-0.09 mg km^{-1} in $PM_{2.5}$ and 0.02-0.22 mg km^{-1} in PM_{10}. Others were trace, i.e., Sb, Sr, V, and Se (the emission factors were less than 0.04 mg km^{-1} in $PM_{2.5}$). The element content in PM could be attributed to the engine wear and tear, pipe erosion of the vehicle, and fuel compositions (Wang et al., 2003).

3.3.3 Ionic species

Nitrate (0.82 mg km^{-1} in $PM_{2.5}$ and 1.33 mg/km in PM_{10}), sulfate (0.69 mg km^{-1} in $PM_{2.5}$ and 0.85 mg km^{-1} in PM_{10}), ammonium (0.41 mg km^{-1} in $PM_{2.5}$ and 0.54 mg km^{-1} in PM_{10}), nitrite (0.22 mg km^{-1} in $PM_{2.5}$ and 0.49 mg km^{-1} in PM_{10}) were the major ionic species in diesel PM. Other ionic species were less than 0.16 mg km^{-1}. Nitrate, nitrite and ammonium could be the result of the fuel composition and high-temperature combustion causing thermal NOx formation. Sulfur content in diesel fuel could be an important reason for the presence of sulfate in particulate matter (Maricq et al., 2002; Vogt et al., 2003). Shi and Harrison (1999) indicated that sulfuric acid/water (emitted from the fuel sulfur combustion) with subsequent condensation of organic substances in the diesel exhaust and the other species (i.e., ammonia) could be involved in the nucleation. In addition, Yu (2001) implied that chemiion could play a role in diesel exhaust nucleation.

The ionic species contents were high in diesel PM compared to those reported by Norbeck (1998). In addition, some alkali metals and alkali earth metals (Na, K, Mg, and Ca) were less than 0.17 mg/km in diesel PM.

The determined composition fractions of $PM_{2.5}$ were taken from diesel exhaust shown as **Figure 2**. Carbon content was high in PM, with low elements (3.8%) and ionic species (1.6). In addition, the composition of about 22% of PM mass could not be determined; it is a limitation of this study.

3.3.4 PAHs

The emission factors of PAHs are shown in **Figure 3.** Twenty-six PAHs including 16 PAHs and 10 nitro-PAHs were determined for diesel vehicle exhaust. The toxicity and cancer effects of PAHs are of greatest concern after exposure. The IARC identifies some PAHs to be probable human carcinogens (Group 2A, i.e. Benz(a)anthracene, benzo(a)pyrene, Dibenzo(a,h)anthracene etc.) and others to be possible human carcinogens (Group 2B, i.e. Benzo(b)fluoranthene (BbF), Benzo (k)fluoranthene (BkF), Indeno(1,2,3-cd)pyrene (IND), 2-Nitrofluorene (2-nFlu), 1-Nitropyrene (1-nPyr), 6-Nitrochrysene (6-nCHR), 1,6-Dinitropyrene (1,6-DnPyr), 1,8-Dinitropyrene (1,8-DnPyr) etc.) (IARC, 1983 and 2010). In addition, some PAHs have been classified in Group 3, a class of chemicals for which no human data is available on carcinogenesis and there is only limited or inadequate data in animals (i.e. Benzo(g,h,i)perylene (BghiP); 9-Nitroanthracene (9-nAnt), 3-Nitrofluoranthene (3-nFL), 7-Nitrobenzo(a)anthracene (7-nBaA), 1,3-Dinitropyrene (1,3-DnPyr), 6-Nitrobenzo(a)pyrene (6-nBaP) etc) (IARC, 1983 and 2010). Therefore, these PAHs are of concern due to their volatilization in diesel exhaust, persistent organic pollutants in the environment and toxicity in human health effect.

The emission factor of total PAHs was 3.62 mg km^{-1} in this study; about 40% was in the gas phase and 60% in the particulate phase (20% was determined in the particulate size > 1.9 μm, and 10% was in the particulate size less than 0.4μm). Naphthalene, acenaphylene, fluoranthene, fluorine, anthracene, pyrene, acenaphthene and phenanthrene are dominant PAHs, and their emission factors were over 0.12 mg km^{-1}. Naphthalene and indeno (1,2,3-cd) pyrene were dominant in the gas phase. We used the concept of toxic equivalent factor (TEF) to determine the carcinogenicity of chemicals. TEF data was investigated by LaGoy and Nisbet's study. In many risk assessments of complex pollutant mixtures, all carcinogenic PAHs have been considered to be as carcinogenic as BaP (Marty et al., 1994). Sixteen PAHs were transferred to TEF as BaP. Results indicated that the TEF of 16 PAHs was 0.24 mg-BaP km^{-1} and the Dibenzo(a,h)anthracene and BaP was about 90% TEF in diesel exhaust.

The content of nitro-PAHs (shown as **Figure 4**) was low, with most less than 0.04 mg/km. The emission factors of 1,6-dinitropyrene, 2-nitrofluorene and 1,8—dinitropyrene were in the range of 0.019-0.040 mg km^{-1}. The mass fraction of nitro-PAHs in total PAHs was less than 4%. But some nitrated aromatic hydrocarbons--i.e., 1,6-Dinitropyrene, 1,8-Dinitropyrene, 6-Nitrochrysene, etc.--revealed high toxic potency, with the potential for mutagenic and carcinogenic effects related to cell apoptosis of diesel exhaust (Landvik et al., 2007).

Only PAHs and nitro-PAHs were determined in PM contributing to low mass fraction of organic carbon in this work. Generally, PM organic classes included the n-alkanes and acids from $C_{13\text{-}30}$, PAHs, oxygenated/sulfur containing PAHs, hopanes, steranes, methoxylated phenols and others (Mcdonald et al., 2004).

4. CONCLUSIONS

Six light-duty diesel vehicles were selected to determine the pollutant emission factor of exhaust and following the FTP-75 driving cycle in a dynamometer. Fuel consumption was 0.126±0.022 l km^{-1}, and the high fuel consumption reflects high CO_2 and NOx emissions. The average emission factor of PM was

0.172±0.071 g km^{-1}, THC was 0.171±0.137 g km^{-1}, CO was 1.395±0.698 g km^{-1}, and NOx was 1.735±1.127 g km^{-1}. Carbon content was about 72% of particulate mass, and the EC portion was about 66% of carbon content, with the remainder being OC. Al, S, Ca, and Fe were about 1.0 mg/km, and K, Zn, Na, and Mg were less than 0.50 mg km^{-1} in $PM_{2.5}$. Some toxic elements, i.e., Ni, Cr, Pb, Cu, Cd, and As, were less than 0.1 mg km^{-1} and others were trace; i.e., Sb, Sr, V, and Se were less than 0.04 mg km^{-1} in $PM_{2.5}$. Nitrate, sulfate, ammonium, and nitrite were the major ionic species, and their emission factor was 0.22 (nitrite)-0.82 (nitrate) mg km^{-1} in diesel $PM_{2.5}$. The emission factor of total PAHs was 3.62 mg km^{-1}, and their mass was about 60% in the particulate phase. Emission factors of naphthalene, acenaphylene, fluoranthene, fluorine, anthracene, pyrene, acenaphthene and phenanthrene were in the range of 0.13-1.04 mg km^{-1}. The mass fraction of nitro-PAHs in total PAH was less than 4%, and1,6-dinitropyrene, 2-nitrofluorene and 1,8—dinitropyrene were in the range of 0.019-0.040 mg km^{-1}.

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Tables

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Figure 1 Particle size distribution of light-duty diesel vehicles

Figure 2 Composition fraction of $PM_{2.5}$ of light-duty diesel vehicle exhaust

Figure 3 PAH emission factor of light-duty diesel vehicle exhaust

Figure 4 Nitro-PAH emission factor of light-duty diesel vehicle exhaust