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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 (LDDV) was in the range of 0.106–0.132 l km^{-1}, and the average emission factors of NMHC (non-methane hydrocarbon), CO and NO_x 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 LDDVs 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 to 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 to 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}.

1. Introduction

Chemical constituents are an important issue in the study of diesel exhaust emission. Numerous epidemiological studies have shown that an increase in adverse cardiopulmonary effects is associated with an increase in particulate matter level (HEI, 2003; Pope et al., 2004). Recent studies have revealed that diesel exhaust particles can induce inflammation in cytokines (Mazzarella et al., 2007), cytokine/chemokine response (Øvrevik et al., 2010), cellular oxidative stress (Suzuki et al., 2008), and mutation yield in human-hamster hybrid cells (Bao et al., 2007). 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 and cardiopulmonary morbidity and mortality, as well as the 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 there is significant public concern about the health effects of diesel exhaust particles (Alföldy et al., 2009). Therefore, elucidating the chemical constituents of diesel exhaust is important to understand its toxicity (Lin et al., 2008a, 2008b; Schneider et al., 2008; Cheng et al., 2010).

Significant progress has been made in controlling duty diesel vehicle emission due to a combination of improved emission control technologies installed on new vehicles (i.e., catalytic converters, diesel particulate filters, new engine design, etc.) and reformulated fuel (i.e., low sulfur content). Most diesel vehicle studies have focused on the characteristics of heavy-duty vehicles and diesel school buses (Harley, 2009; Oanh et al., 2010); but only a few studies (for example, Norbeck et al., 1998; Oanh et al., 2010) have addressed the exhaust composition of small displacement diesel engines, i.e., light-duty diesel vehicles (LDDVs). Following the oil shortage and the resulting high price of oil, LDDVs have become popular due to their low oil consumption. Therefore, there is a need to characterize particulate emission rates and chemical composition for these vehicles.

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.,

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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 (Kittleson, 1998; Kittleson et al., 2002). Significant and fundamental changes have been made to the diesel engine combustion process and associated after-treatment technologies (i.e., catalytic converters, diesel particle filters, SCR catalyst) to meet stringent regulations and reduce emissions of NO_x 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 with different vehicle ages, cumulative mileage, engine displacement and fuel characteristics; 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); however, 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 (PAHs) including nitro-PAHs were measured to determine their emission factors.

2. Experiment

2.1. Light-duty diesel vehicles and testing driving pattern

Six in-use LDDVs 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. In addition, inline-four cylinder diesel engines were employed in this study including 4M40 (Mitsubishi), TD-27 (Nissan) and R2 (Mazda-Ford). Table 1 presents more detailed information such as the produced year, mileage, weight, manufacturer, model, engine type 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 (TEPA, 2011). 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 h^{-1}, respectively. In addition, vehicle emissions can be affected by many factors including driving pattern (idle, acceleration, deceleration, speed, etc.), vehicle age, vehicle inspection and maintenance programs, topography (road grade) and weather (temperature, humidity); these factors are not easily reflected in dynamometer testing, and it is necessary to test a large number of vehicle fleets to obtain representative data. Therefore, these factors could be a limitation of dynamometer testing.

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} and the dilution factor to about 14.06 ± 3.7. 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, NO_x 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) was 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 3 h 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

Table 1
Information of testing light-duty diesel vehicles (LDDVs).

Number	Manufacture date	Mileage (km)	Reference vehicle weight (kg)	Empty weight (kg)	Displacement (cc)	Manufacturer/Model	Engine type
LDDV-1	1994	102,238	2036	1858	2832	Mitsubishi/Canter	4M40
LDDV-2	1994	146,628	1970	1792	2664	Nissan/Cabstar	TD-27
LDDV-3	1995	153,519	1825	1647	2184	Ford/Econovan	R2
LDDV-4	1993	119,779	1581	1403	2184	Ford/Econovan	R2
LDDV-5	2003	55,666	2606	2428	2835	Mitsubishi/Canter	4M40-2AT
LDDV-6	2000	159,630	2616	2438	2835	Mitsubishi/Canter	4M40-2AT