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Chemical composition and source of fine and nanoparticles from recent direct injection gasoline passenger cars: Effects of fuel and ambient temperature

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HIGHLIGHTS

- Elemental carbon dominated the particulate mass.
- C_{20}–C_{28} hydrocarbons were dominant in both nano and accumulation-mode particles.
- Exhaust particles likely originated mainly from gasoline fuel.
- Less-volatile compounds in fuel seem to increase particulate emissions.

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ABSTRACT

Particle number, mass, and chemical compositions (i.e., elemental carbon (EC), organic carbon (OC), elements, ions, and organic species) of fine particles emitted from four of the recent direct injection spark ignition (DISI) gasoline passenger cars and a port fuel injection (PFI) gasoline passenger car were measured under Japanese official transient mode (JC08 mode). Total carbon (TC = EC + OC) dominated the particulate mass (90% on average). EC dominated the TC for both hot and cold start conditions. The EC/TC ratios were 0.72 for PFI and 0.88–1.0 (average = 0.92) for DISI vehicles. A size-resolved chemical analysis of a DISI car revealed that the major organic components were the C_{20}–C_{28} hydrocarbons for both the accumulation-mode particles and nanoparticles. Contribution of engine oil was estimated to be 10–30% for organics and the sum of the measured elements. The remaining major fraction likely originated from gasoline fuel. Therefore, it is suggested that soot (EC) also mainly originated from the gasoline. In experiments using four fuels at three ambient temperatures, the emission factors of particulate mass were consistently higher with regular gasoline than with premium gasoline. This result suggest that the high content of less-volatile compounds in fuel increase particulate emissions. These results suggest that focusing on reducing fuel-derived EC in the production process of new cars would effectively reduce particulate emission from DISI cars.

1. Introduction

Reducing the fuel consumption of passenger cars is urgently needed to combat global warming, and as a result, more fuel-efficient hybrid and diesel passenger cars have been placed in the market. At the same time, research and development of fuel-efficient cars with highly efficient gasoline engines and power-trains have been carried out. As a result, the next generation of gasoline cars, whose fuel economy is equivalent to hybrid cars, have recently been introduced in the European and Japanese markets. The techniques used to improve the fuel efficiency of these cars mainly depend on improved cycle efficiency by way of a high compression ratio or through friction loss reduction by downsizing. Many of these cars employ direct injection spark ignition (DISI) gasoline engines, which are suitable for these techniques. DISI

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gasoline cars are popular in Europe and Japan, and DISI engines are mounted on ≈35% (expectancy) of new model gasoline cars in Europe (Basheer and Frost, 2014) and ≈9% (based on the model number) of new model passenger cars in Japan in 2013 (JAF, 2013).

While DISI engines enable better fuel economy, DISI cars generally produce higher particulate matter emission than conventional port fuel injection (PFI) gasoline cars (Farron et al., 2011; Peckham et al., 2011; Samuel et al., 2010; Wei and Porter, 2011). The particulate emissions from heavy-duty diesel vehicles have attracted attention, but those from gasoline cars have not been fully investigated. However, the emissions from diesel cars have recently become cleaner with the help of exhaust gas after-treatment devices such as diesel particulate filter, therefore particulate emission levels from gasoline cars (especially DISI cars) are increasingly becoming noticeable (Gordon et al., 2014). As a result of this situation, emission regulations for DISI cars were introduced in the EU in 2014 but the regulatory value, based on particle number, was temporarily 10 times the value for diesel vehicles.

The number, mass, and size distribution of exhaust particles from DISI cars have been studied (Baral et al., 2011; Khalek et al., 2010; Kobayashi et al., 2012; Maricq et al., 2011). Consequently, DISI exhaust particles consist mostly of accumulation-mode particles (particles with a peak diameter of ≈0.05–0.10 μm on a number basis, which generally correspond to particles with a peak diameter of ≈0.1–0.3 μm on a mass basis), and volatile nanoparticles (diameter < 0.050 μm), that were remarkably observed in diesel exhausts (Fushimi et al., 2011; Kittelson, 1998), has not been observed (Khalek et al., 2010; Kobayashi et al., 2012; Maricq et al., 2011; Sakai et al., 2013).

When considering the controls on particulate emissions, information on the origin of particles is very important. Vehicle exhaust particles originate mainly from fuel and engine oil. For a PFI car, a predictive model that estimates the particulate number emission from fuel properties (vapor pressure and double bond equivalent of each component in gasoline) was proposed (Aikawa et al., 2010; Sobotowski et al., 2015). Furthermore, in general, this model can also reasonably predict the particulate number and mass for DISI cars (Aikawa and Jetter, 2014; Sobotowski et al., 2015).

The contribution of fuel and engine oil can be estimated from the chemical composition of exhaust particles. For diesel exhaust particles, these contributions have been investigated based on the organic components and elemental composition (Fushimi et al., 2011; Miller et al., 2007; Sakurai et al., 2003; Schneider et al., 2005). Fushimi et al. (2011) showed that the accumulation-mode particles from a diesel engine originate from both fuel and oil, but nanoparticles mostly originate from oil. These chemical characteristics of nanoparticles greatly affect their fate (e.g. life time) in the atmosphere (Fushimi et al., 2008). For gasoline PFI vehicles, exhaust particles have been characterized in detail (Kleeman et al., 2008; Lough et al., 2007; Schauer et al., 2002; Zielinska et al., 2004). Schauer et al. (2002) reported that the composition of *n*-alkanes emitted from catalyst-equipped gasoline powered vehicles is similar to the composition in the gasoline used. Kleeman et al. (2008) quantitatively estimated the contribution of fuel and oil to elemental carbon (EC) and organic carbon (OC) using two organic markers. Thus, EC and OC emitted from most categories of light-duty gasoline vehicles were dominated by gasoline fuel, whereas EC emitted from smoking gasoline vehicles and oxidation catalyst gasoline vehicles was dominated by oil. Esaki et al. (2013) investigated the formation origins, environments, and routes of deposits formed in different parts of gasoline PFI engines based on characterization by analytical techniques. However, there is little information on the chemical characteristics of fine particles (diameter < 2.5 μm) and nanoparticles and on their origin emitted from recent stoichiometric DISI cars.

In this study, first, the emission factors of particulate mass and the chemical compositions from recent stoichiometric DISI cars, not lean burn cars, were measured. Second, in order to understand the characteristic of the nanoparticles, the particulate mass and composition according to particle size were analyzed using a DISI car. Finally, particulate mass and chemical composition as a function of fuel type and ambient temperature were measured to quantitatively estimate the contribution of fuel and oil to the particles emitted from recent DISI cars and to understand what fuel property can affect particulate emission. To estimate the contribution of fuel and oil, two methods that use the gas chromatography/mass spectrometry (GC/MS) hump and quantitated elemental data were used. The sample amount that can be collected is limited for recent gasoline cars, and therefore, analytical methods that can be applied to trace samples such as thermal desorption GC/MS (TD-GC/MS) and particle induced X-ray emission (PIXE) were used for organic and elemental analyses, respectively.

2. Methods

2.1. Test vehicles, fuel, and ambient temperature

A total five cars, four of the recent stoichiometric DISI passenger cars and one PFI car, which is the same model as DISI-A used for comparison, were tested. Table 1 shows the main specifications of the test vehicles and experimental items. Particulate emission data from DISI cars (as reported in Europe and the United States) mostly represent turbocharged engines, but in this study, DISI-A and DISI-D are both mounted with naturally aspirated (NA) engines. DISI-B was produced by a European manufacturer, while the remaining four cars were produced by Japanese manufacturers.

Experiments were primarily conducted on DISI-A. First, in order to clarify emission factors and chemical composition, the particulate mass and chemical composition (carbonaceous compounds and organic compounds) of fine particles at an ambient temperature (room temperature of a test car on a chassis dynamometer) of 25 °C for all the cars were measured. For PFI, DISI-A, and DISI-B, elemental compositions and ions were also measured. Second, samples were collected by particle size and chemical analyses (carbonaceous compounds, elements, ions, and organic species) were carried out for DISI-A, in order to distinguish nano and accumulation-mode particles. Third, in order to clarify the impact of fuel type on particulate emissions, three of the regular gasoline DISI cars (DISI-A, DISI-C, and DISI-D) were measured using both premium and regular gasoline. Finally, in order to clarify particle origins and generation mechanisms, particulate mass and chemical compositions (carbonaceous compounds and organic species) were measured for DISI-A using four fuel types (commercial summer regular, summer premium, winter regular, and winter premium gasoline; Table 2) at three stages of ambient temperature (5, 25, and 35 °C). The summer regular gasoline was only used for the experiments at ambient temperatures of 25 °C and 35 °C. In the first, second, and third experiments, commercial summer gasolines were used. In all the experiments, manufacture-recommended engine oils were used.

2.2. Exhaust gas test

The exhaust gas test was conducted using a chassis dynamometer at the Low-Emission Vehicle Facility of the National Institute for Environmental Studies (Kobayashi et al., 2012). Raw exhaust gases were diluted using a full flow dilution tunnel. The dilution air was prepared from outdoor air after filtration by an ultra-low penetration air (ULPA) filter and controlling the temperature and relative humidity to 25 °C and 50%, respectively. For