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# Measurement of the light absorbing properties of diesel exhaust particles using a three-wavelength photoacoustic spectrometer

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## HIGHLIGHTS

- Light-absorbing properties of diesel exhaust particles were examined.
- No significant lensing effect was observed for either transient or constant driving.
- Significant light absorption of organics was observed under certain conditions.

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## ABSTRACT

Diesel-exhaust particles (DEP) are one of the main anthropogenic sources of black carbon (BC) and organic matter (OM). Understanding the optical properties of DEP, including the enhancement of light absorption by BC due to coating and light absorption by OM, is important for evaluating the climate impact of DEP. In this study, a three-wavelength photoacoustic soot spectrometer (405, 532, and 781 nm) was used to investigate the wavelength-dependent optical properties of DEP emitted from a diesel engine vehicle running on a chassis dynamometer in transient driving mode (JE-05) and at a constant speed (either idling or driving at 70 km/h). Optical properties were measured after passing the diluted exhaust through a heater, set at 20, 47, or 300 °C (transient driving mode) or between 20 and 400 °C (constant driving mode). The OM accounted for, on average, ~40 and ~35% of the total mass concentration of DEP during the transient and constant driving modes, respectively. In transient driving mode, enhancements of scattering coefficients at 20 and 47 °C, and of the mass concentration of organics, were observed during the high-speed driving period (~80 km/h) corresponding to driving on a highway. No difference was observed in the absorption coefficients between heated and unheated particles at 781 nm for either the transient (including the high-speed driving period) or constant driving modes. These results indicate a lack of enhancement due to the lensing effect, possibly because the BC was mainly mixed externally with the OM or because it was located at the edges of particles under these experimental conditions. Contributions to total light absorption at 405 nm by the OM were estimated by comparing the wavelength dependence of the absorption coefficients with and without heating. A significant contribution by light-absorbing OM (20 ± 7%) to total light absorption at 405 nm was observed during the high-speed driving period of the JE-05 mode, while the contributions were small during other periods in the JE-05 mode (0 ± 8%) and the constant driving mode (idling: 4 ± 12%; driving at 70 km/h: 0 ± 16%).



## 1. Introduction

Aerosol particles in the Earth's atmosphere influence both global and regional climate directly by scattering and absorbing incoming solar radiation and indirectly by acting as cloud condensation nuclei. Black carbon (BC) an important component of global

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warming in terms of direct forcing (e.g. Bond et al., 2013). It is defined operationally as carbonaceous material with a deep black appearance caused by a significant imaginary part of the refractive index (RI) and is roughly corresponding to elemental carbon (EC), which refers to nonvolatile carbon below a certain temperature (typically 550 °C) (Andreae and Gelencsér, 2006; Bond and Bergstrom, 2006). Although the definitions of BC and EC are different, BC and EC were considered equivalent for the purpose of this work.

Recently, class of organic matter (OM) called "brown carbon," which is defined operationally as light-absorbing carbonaceous material with a wavelength-dependent imaginary part of the RI, was suggested to have the ability to absorb solar radiation, particularly at ultraviolet (UV) and shorter visible wavelengths. This brown carbon was also considered to influences the radiation balance and photochemical reactions in the atmosphere (Andreae and Gelencsér, 2006; Moosmüller et al., 2009; Nakayama et al., 2013, and references therein). The difference in the wavelength dependence of BC and OM has been used to quantify BC and OM (e.g. Hadley et al., 2008).

Exhaust from motor vehicles such as diesel vehicles is one of the most important anthropogenic sources of fine particles in the atmosphere (e.g. Bond et al., 2013). Diesel exhaust particles (DEP) consist mostly of EC and OM, and the relative contributions of EC in DEP vary from 5 to 90% depending on the engine type, aftertreatment method, and operating conditions (e.g. Moosmüller et al., 2001; Maricq, 2007; Rönkkö et al., 2007; Fushimi et al., 2011). Light absorption by BC (or EC) can be enhanced when it is coated with other components, such as OM and inorganic salts, a phenomenon called the "lensing effect" (e.g. Schnaiter et al., 2005; Bond et al., 2006; Shiraiwa et al., 2010). If a significant amount of OM exists internally mixed with BC in DEP, light absorption by the BC may be enhanced. In addition, light-absorbing OM may be present in the DEP.

Recently, Adler et al. (2010) measured the optical properties of the water-soluble material (WSM) and organic-soluble material (OSM) extracted from DEP collected on a filter, and reported the imaginary part of the RI as 0.05 ± 0.02 (OSM) and 0.044 ± 0.001 (WSM) at 532 nm, and 0.11 ± 0.02 (OSM) and 0.07 ± 0.01 (WSM) at 355 nm. Using the RI values obtained, the influence of OM coating on the light absorption properties of BC was determined using the Rayleigh–Debye–Gans theory and the T-matrix method. The contributions of light-absorbing OM and the lensing effect on the light-absorbing properties of DEP depend on the mass ratio of BC to OM, size distribution and mixing state of the DEP, and the RI of the BC and OM, *i.e.*, depend on the driving conditions. However, no experimental studies that focus on the light-absorbing OM and lensing effect using real-time direct measurements of the wavelength dependence of the optical properties have been reported.

This report describes the real-time measurement of the optical properties of DEP using a three-wavelength photoacoustic soot spectrometer (Droplet Measurement Technologies, PASS-3) for investigating the contributions of light-absorbing OM and the lensing effect to light-absorbing properties of the DEP under a variety of driving conditions.

## 2. Experimental

The test diesel engine vehicle used in the present study was the same as that used by Yamada et al. (2011), Yamamoto et al. (2012), and Inomata et al. (2013), and was a light duty truck with a gross vehicle weight of 4485 kg and a 4.8 L engine equipped with a common rail injection system and diesel oxidation catalyst that complied with the emission regulations of Japan, 2003. Vehicle test runs were performed using a chassis dynamometer (Meidensha) in transient cycle (JE-05) or constant-speed (idling or driving at 70 km/h) driving modes. The JE-05 mode, which is the Japanese approval test cycle for heavy-duty vehicles, is employed in the Japanese 2005 emission standards. For the JE-05 mode, the vehicle was warmed using a preconditioning cycle before the measurements were taken.

A schematic of the experimental setup is shown in Fig. 1. The exhaust was diluted with air filtered using high efficiency particulate air (HEPA) and charcoal filters with a full flow constant volume sampler (CVS, Horiba, DLT-1860) at a flow rate of 40 $m^3$ $min^{-1}$. The exhaust gases and particles, which were sampled from the CVS, were additionally diluted with filtered air 6.4 and 3.3 times during the JE-05 and constant-speed modes, respectively. The diluted samples were passed through a heater and then introduced into the PASS-3. The heating system was used to separate BC and OM based on the difference in their thermal stabilities. The design of the heater was similar to that reported by Kondo et al. (2009) and consisted of a stainless steel tube and electronic jacket heaters. Most of the OM components should evaporate from particles in the heater maintained at 300–400 °C (Kondo et al., 2009), while the BC components in the particle do not evaporate at these temperatures. Detailed characteristics of the heater are described in the Supplemental Material (A1). The temperature of the heated tube was maintained at 20, 47, or 300 °C during the transient cycle mode and controlled between 20 and 400 °C during the constant-speed mode, as listed in Table 1. Flow rate through the heater was 1.0 or 1.3 L per minute (lpm) during the transient cycle and constant-speed modes, respectively, which correspond to a plug flow residence time of 2.9 and 2.3 s (calculated at 20 °C), respectively, in the heater. The heated tube temperature was monitored using a thermocouple. Particle transmission efficiency of the heater was tested in the laboratory using propane soot particles and found to be 0.80–0.98 depending on the heater temperature as described in the Supplemental Material (A1) and taken into account in the determinations of the optical properties and size distributions. Recondensation of evaporated materials on the remaining particles after passing through the heater was negligible because of the smaller surface of those particles compared to that of the wall of the sampling line.

A PASS-3 instrument was used to measure the absorption [$b_{abs}(\lambda)$] and scattering [$b_{sca}(\lambda)$] coefficients at 405, 532, and 781 nm. Information on the calibration procedures for the PASS-3 instrument is described in the Supplemental Material (A2). The $b_{sca}$ (532 nm) data obtained using the PASS-3 were not used in this study because of the strong dependence of the calibration factors on particle size. Uncertainties associated with the calibration were estimated to be 4, 9, 11, 7, and 11% for $b_{abs}$ (405 nm), $b_{abs}$ (532 nm),

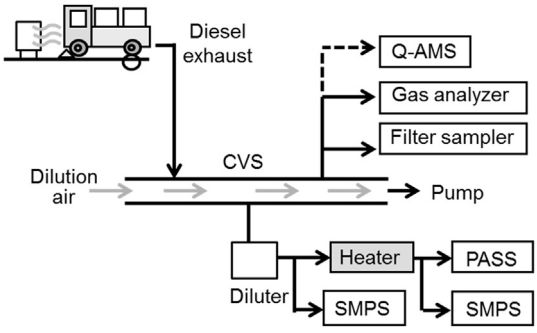


**Fig. 1.** Schematic diagram of the experimental configuration. CVS: constant volume sampler; SMPS: scanning mobility particle sizer; PASS-3: three wavelength photoacoustic soot spectrometer; Q-AMS: quadrupole-based aerosol mass spectrometer. The SMPS was used only during the constant-speed modes.