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Determination of single particle mass spectral signatures from heavy-duty diesel vehicle emissions for $PM_{2.5}$ source apportionment

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Abstract

The size and chemical composition of individual diesel exhaust particles were measured in order to determine unique mass spectral signatures that can be used to identify particle sources in future ambient studies. The exhaust emissions from seven in-use heavy-duty diesel vehicles (HDDVs) operating on a chassis dynamometer were passed through a dilution tunnel and residence chamber and analyzed in real time by aerosol time-of-flight mass spectrometry (ATOFMS). Seven distinct particle types describe the majority of particles emitted by HDDVs and were emitted by all seven vehicles. The dominant chemical types originated from unburned lubricant oil, and the contributions of the various types varied with particle size and driving conditions. A comparison of light-duty vehicle (LDV) exhaust particles with the HDDV signatures provide insight into the challenges associated with developing an accurate source apportionment technique and possible ways of how they may be overcome.

Keywords: Aerosol; Single particle mass spectrometry; Diesel; Chemical composition; Source apportionment

1. Introduction

One substantial anthropogenic source of atmospheric particulate matter (PM) is the exhaust emissions from diesel engines (Kirchstetter et al., 1999; Schauer et al., 1996). Although they compose only a small fraction of the mobile fleet (2% in California), the use of diesel engines is increasing worldwide given their higher fuel efficiency and lower maintenance costs (Dunlap, 1998). Nonetheless, PM mass emissions are 1–2 orders of magnitude higher from diesel engines than spark ignition vehicles (Kittelson, 1998). In London, approximately two-thirds of the mass of all particles with aerodynamic diameters smaller than 10 μm have been attributed to diesel engines (Colvile et al., 2001).

A number of previous studies have focused primarily on the size and number concentrations of particles emitted by diesel vehicles. The chemistry of the exhaust of heavy-duty diesel vehicles (HDDVs) constitutes a complex mixture of gaseous

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compounds and PM with many adsorbed and condensed gas-phase species (Kittelson, 1998; Yanowitz et al., 2000). Particles emitted by HDDVs conventionally are collected on filters and analyzed off-line after accumulating sufficient mass. One of the disadvantages of this method is the poor temporal resolution, prohibiting the study of variations in particle chemistry due to operating conditions (Moosmuller et al., 2001). Single particle mass spectrometry techniques, such as aerosol time-of-flight mass spectrometry (ATOFMS), are on-line analytical instruments that measure the size and chemical composition of individual particles (Suess and Prather, 1999). Obtaining size and chemical information of single particles coupled with high temporal resolution provides unique information on source emissions, which can be applied in apportioning ambient particles.

The goal of this study is to determine the unique associations of chemical species in single particles between 0.1 and 2.5 μm ($PM_{2.5}$) observed in the exhaust of HDDVs run on a chassis dynamometer that can be applied to near future source apportionment efforts. The results presented are part of a series of studies to identify and apportion aerosols to gasoline or diesel vehicles on a single particle basis. This series identifies the single particle signatures of exhaust emissions from light-duty (gasoline) vehicles (LDVs) (Sodeman et al., 2005), HDDV in the ultrafine size range (Toner et al., 2006), and HDDV in $PM_{2.5}$ (this work) and evaluates these dynamometer particle signatures in a real-world roadside apportionment study (Toner et al., 2007). Future publications will address the use of these source fingerprints for apportioning ambient particles that may have undergone atmospheric chemical processes during transport from the source to the receptor site.

2. Experimental methods

2.1. Sampling conditions

Exhaust emissions from seven HDDVs were analyzed between 26 August and 3 November 2001 at the Ralph's Distribution center in Riverside, CA. The trucks varied by vehicle year, manufacturer, and miles driven, as described in Table 1. The chosen vehicles were tested under the same sampling conditions, which include driving cycle and dilution conditions. The sampling procedure required driving each truck on a heavy-duty dynamometer operated by West Virginia University. The dynamometer system has been described elsewhere (Clark et al., 1995). For this study, a number of different driving cycles were employed to determine the effect of driving conditions on the exhaust aerosol chemical composition. The main driving cycle, developed by the California Air Resources Board (CARB), was composed of six regimes: idle, creep, transient, cruise, extended idle, and extended creep, which are described in the Supplementary Material and illustrated in Figure S1. All of the data represented in this work were collected under laden driving conditions, in which a load of 56,000 lbs was applied to each vehicle. The diesel exhaust flows through a dilution tunnel, which is part of the emissions testing laboratory, and then a portion of the dilute emissions is transferred to a residence chamber (McDonald et al., 2000). The residence chamber established an equilibrium between the gas and particle phase of the semivolatile organic components (Hildemann et al., 1989). The effect of the dilution conditions upon the particle chemical composition is described in the Supplementary Material. Dilution factors (based on the total carbon balance at the mixing point of raw exhaust

Table 1
Truck descriptions

CRC no.	Year	Type	Make	Engine	Model	Miles
3	1985	HDD tractor	International	Cummins	NTCC-300	501,586
6	1995	HDD tanker	Freightliner	Cummins	—	689,536
7	1990	HDD tractor	Peterbilt	Detroit Diesel	Series 60	399,224
8	1996	HDD tractor	Kenworth	Cummins	M11-300	507,855
9	1998	HDD tractor	Peterbilt	Caterpillar	C12	607,968
10	1998	HDD tractor	Sterling	Detroit Diesel	Series 60	21,631
11	2000	HDD tractor	Freightliner	Cummins	ISM	17,048