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Article

High-Time Resolution Measurements of Black Carbon Particles in the Exhaust Emissions of a Diesel Engine during Acceleration, Deceleration and Cruise Conditions

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Carbono negro (BC) é o componente principal de emissões de motores a diesel. Aethalometer® foi usado nas medições das concentrações de BC (com resolução temporal de 5 s) emitido pelo escapamento de uma caminhonete tipo pick-up a diesel Dodge RAM 2500 1995 equipada com catalisador de oxidação. As medições foram feitas com um dinamômetro de chassis durante os modos de aceleração, desaceleração e de *cruise* (velocidade constante) do arranque a quente do ciclo de ensaio MEC01 (versão 7.0). Partículas de exaustão foram coletadas em paralelo nos filtros de fibra de quartzo para a medição de carbono elementar (EC) e carbono orgânico (OC) pelo método termo-óptico por reflectância (TOR), e em filtros de Teflon® para determinação gravimétrica da massa total de partículas (PM). A rápida aceleração foi acompanhada por correspondentes aumentos nas emissões instantâneas de BC. Sob condições de aceleração totalmente aberta (WOT), a concentração de BC medida pelo Aethalometer® atingiu um pico de 1,2 mg m^{-3}, mas reduziu a apenas 0,03 mg m^{-3} em condições *cruise* de 20 mph. Estes resultados mostram que é possível medir as emissões especiadas de material particulado de motores a diesel em tempo real em função da carga do motor e outras condições de funcionamento.

Black carbon (BC) is a major constituent of diesel-engine exhaust emissions. Aethalometer® was used in the measurements of the BC concentrations (with time resolution of 5 s) in the exhaust of a truck model 1995 Dodge RAM 2500 diesel pick-up equipped with an oxidation catalyst. The measurements were made from a chassis dynamometer during the acceleration, deceleration and cruise (constant speed) modes of the hot start of the MEC01 test cycle (version 7.0). Exhaust particles were collected in parallel on quartz fiber filters for elemental carbon (EC) and organic carbon (OC) measurement by the thermal-optical reflectance (TOR) method, and on Teflon® filters for gravimetric total particle mass (PM). Rapid acceleration was accompanied by corresponding instantaneous increases in BC emissions. Under wide open throttle acceleration (WOT), Aethalometer® BC concentrations peaked at 1.2 mg m^{-3}, but reduced to only 0.03 mg m^{-3} under cruise conditions at 20 mph. These results show that it is possible to measure speciated diesel particulate emissions essentially in real time as a function of engine load and other operating conditions.

Keywords: high-time, black carbon, BC, diesel engine, exhaust emissions

Introduction

Combustion-derived aerosol consists mainly of solid carbonaceous particles, including BC (black carbon), sometimes denoted EC (elemental carbon), and OC (organic carbon) that is associated with a complex mixture of toxic organic species. BC emissions contribute significantly to fine particle mass and are an important cause of atmospheric visibility impairment. They change the atmospheric radioactive balance and influence the nucleation and optical properties of clouds, leading to perturbation of rainfall and a very important component of the forcing for global climate change. In addition, carbonaceous particulate matter contains absorbed/adsorbed toxics such as polycyclic aromatic hydrocarbons,[1] a class of compounds of concern that includes several potent mutagens and carcinogens.[2]

Diesel exhaust particles are usually found with a trimodal, lognormal form size distribution.[3] The coarse mode contains particles >1 μm aerodynamic diameter (dp). The

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accumulation mode, in the 0.1-0.3 μm dp range, contains most of the particle mass.[3] The nucleation (or Aitken) mode consists of particles in the 0.005-0.05 μm dp range, and contains more than 90% of the particle number.[3,4] It has been well established that ultrafine (dp <100 nm) particulate PAH measured in urban air and in roadway tunnels is found in the same size range as the black carbon component.[5] Recent changes in the composition of gasoline and diesel fuel and, more importantly, improvements in engine and emission control technologies are likely to have affected vehicle emissions. In California, for instance, low-aromatic, low-sulfur diesel fuel[6] has been used year-round since 1993, and reformulated gasoline7 has been used year-round since 1996. The introduction of electronic diesel fuel injection systems and the increasing fraction of catalyst-equipped light-duty vehicles on the road are examples of shifts in vehicle technology that have influenced emissions. For instance, beginning in 1988, control measures to reduce PM (total particle mass) emissions from diesel engines led to dramatic reductions in the particle mass emitted. However, it has been reported that some low-emission diesel engines emit much higher concentrations of ultrafine particles than older engine designs.[2] Particle in the nano-size range are formed by nucleation, which occurs during dilution and cooling of the exhaust.[3] Typically, these particles include hydrocarbons and sulfate, while the accumulation mode consists mainly of soot agglomerates formed directly by combustion,[3] in addition to oily droplets as shown by Flagan[4] and Miguel and co-workers,[5] and PAHs found both in the nuclei mode (dp < 30 nm) and the accumulation modes.[8]

A common practice of measurements of carbonaceous emissions from motor engine exhaust is by collection on quartz fiber filters, as described in the 1995 Code of Federal Regulations,[9] followed by laboratory analysis. These filter-based methods are time consuming and do not provide the rapid time resolution that is essential for the understanding of the load-dependent temporal behavior of emissions. The major goal of this study was to provide means of measuring the concentration of BC with high time resolution in the exhaust emissions of a diesel-fueled truck, during fast-changing load conditions. As has been shown in many studies, the emissions are dominated by older vehicles. The 1995 model vehicle used in this study will have emissions relevant to the vehicle fleets found in countries such as Brazil.

Experimental

Vehicle description and testing

The diesel-fueled truck tested was procured by the Vehicle Emissions Research Laboratory (VERL) staff at the University of California, Riverside Bourns College of Engineering Center for Environmental Research and Technology (CE-CERT), as part of an ongoing National Cooperative Highway Research Program (NCHRP) to evaluate the emissions from diesel engines.[10] The vehicle tested was a 1995 Dodge RAM 2500 diesel pick-up truck 5.9L V8 16 valve, fuel injection engine equipped with a 2-way oxidation catalyst, and is considered a normal emitter. It was operated on a Burke E. Porter 48" single-roll dynamometer, equipped with a Pierburgh CVS/dilution tunnel system, following phase one (hot start) of the MEC01 emission driving cycle (version 7.0) developed by Bart and co-workers,[10] for the NCHRP (Figure 1). A constant volume sampler (CVS) flow rate of 856 SCFM was used for the tests, and the vehicle was tested with the fuel in the tank at the time it was received, after an overnight soak at a temperature of 72 ± 2 °C. The specifications of the California reformulated diesel are shown in Table 1.

Table 1. Average specifications of reformulated diesel fuel

Specification	Pre-1993	California current	U.S.[a] current
Aromatics / vol.%	35	19-22	35
Sulfur / ppmw	440[b]	140[c]	360
Cetane No.	43	50-52	45
PNA	-	3	-
Nitrogen	-	150	110

[a]Alliance of Automobile Manufacturers Association (AAMA) National Fuel Surveys; [b]for Los Angeles area (greater than 3000 ppm in rest of California); [c]about 10-20% of total California volume is < 15 ppmv.

Analytical procedures

Aethalometer BC and FID C_3H_8 measurements

A single-wavelength aethalometer[11] (Magee Scientific, Berkeley, CA USA, model AE-16) was used to measure BC concentrations in the dynamometer tunnel with 5 s time resolution. After dilution of the engine-out emissions by a factor of 18.2 in the dynamometer tunnel, the aethalometer sample stream was further diluted with 1.0 L min^{-1} of particle-free ambient air. This secondary dilution was necessary to reduce BC concentrations to the normal working range of the instrument. Conductive silicone tubing of 0.25 inch OD was used to transfer the samples from the dynamometer tunnel to the aethalometer. This is critical for aerosol measurements because it reduces the buildup of static charge and minimizes particle loss to the tubing wall. The aethalometer uses a continuous filtration and optical transmission technique to measure

the concentration of BC in near-real-time. The sample was collected at flow rates of 3.3 L min^{-1} onto a 0.5 cm^2 area of quartz fiber filter material (Pallflex Tissuquartz type 2500QAO, which advances automatically to avoid optical saturation. Aerosol retention > 99.9% tested following ASTM D 2986-95A 0.3 μm (DOP) at 32 L min^{-1} *per* 100 cm^2 filter media. Quartz filters were pre-fired for 30 min at 800 °C in air to remove all organic contamination.

The transmission measurement determines optical absorption at 880 nm, which is converted to concentration of BC in the sample stream. The aethalometer records data internally and its timing was synchronized with the dynamometer instrumentation to ± 1 s. Gas-phase C_3H_8 measurements, performed with 1 s time resolution using a Horiba flame ionization analyzer (FID detector) helped us to understand the relationship and dynamics of both gas- and particle-phase exhaust emissions.

EC, OC and PM measurements

In order to get a measure of the emitted carbonaceous species, aerosol particles were collected during the entire modal emission cycle onto 47 mm diameter filters. Quartz filters were used for the determination of EC and OC, and Teflon filters were used for the determination of total particle mass (PM) using a Mettler microbalance accurate to ± 3 μg. EC and OC concentrations on the quartz filters were determined by combustion analysis using the thermal-optical reflectance (TOR) method.

Results and Discussion

Aethalometer and FID data

Table 2 summarizes the BC and C_3H_8 data taken under the specific power (SP) conditions of 100 and 150 mph^2 s^{-1} during the constant power and the WOT sections of the MEC01 emission driving cycle (Figure 1).

In the first event, occurring between ca. 400-470 s (Figure 2), the aethalometer BC and C_3H_8 concentrations peaked, respectively, at 0.6 mg m^{-3} and 5.0 ppmv during acceleration, and averaged 0.1 mg m^{-3} and 3.1 ppmv under cruise conditions at 20 mph. In the second event, between 500-550 s (Figure 2), BC and C_3H_8 concentrations peaked, respectively, at 0.5 mg m^{-3} and 5.8 ppmv during acceleration, and averaged 0.08 mg m^{-3} and 3.1 ppmv under cruise conditions at 20 mph. These data show several interesting features: first, fast accelerations are accompanied by corresponding instantaneous increases in BC and C_3H_8 emissions, which indicates that both components result from incomplete combustion of the fuel. Second, BC and C_3H_8 concentrations track each other quite well during acceleration, deceleration and cruise

Table 2. Aethalometer results for BC and C_3H_8 measurements made during the constant power and the WOT sections of the MEC01 emission driving cycle

	100 mph^2 s^{-1}		150 mph^2 s^{-1}		WOT	
Species	BC	C_3H_8	BC	C_3H_8	BC	C_3H_8
Cycle mode	μg m^{-3}	ppmv	μg m^{-3}	ppmv	μg m^{-3}	ppmv
Acceleration max.	600	5.0	542	5.8	1,214	6.5
Cruise mean	99	3.1	84	3.1	29	2.5

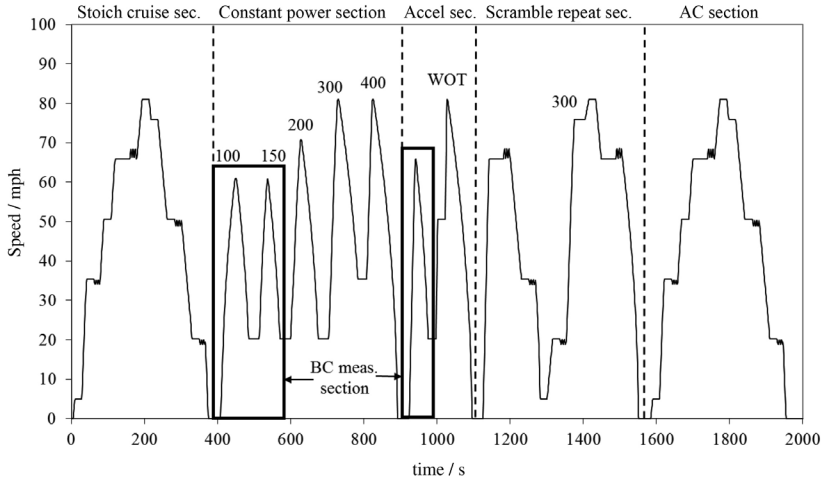

Figure 1. MEC01 emission driving cycle (version 7.0). BC and C_3H_8 measurements were made, respectively, with 5 and 1 s resolution, during the constant power section of the cycle at specific power (SP) ratings of 100 and 150 mph^2 s^{-1}, and under wide open throttle acceleration (WOT), as indicated in the boxes. The dilution factor for cycle was 18.2. The mean test cell and tunnel interior temperatures were, respectively, 26.3 and 52.0 °C. These measurements are shown graphically in Figures 2 and 3.

conditions at 20 mph. Third, during cruise conditions at 20 mph, there is a slow, but continuous increase in the concentration of both components, rising slowly up to the point where acceleration is re-started. One possible explanation of this observation is that, when acceleration is ceased, the immediate decrease in the exhaust temperature is accompanied by a reduction in the thermophoretic losses to the walls of the dilution tunnel. Although thermophoretic forces are small, the high mobility of nano- and ultrafine-size diesel exhaust particles is high enough to promote losses of particles to the tunnel walls, a phenomenon routinely observed when sampling with Teflon bags.[12] For instance, McMurry and Rader[13] showed that the maximum (stirred tank) and the minimum (gentle mixing) thermophoretic deposition rates for a 16 K difference are 851 K cm^{-1} and 62 K cm^{-1}, respectively, for diesel particle collection onto a Teflon bag. During the dynamometer test, the difference in temperature between the dynamometer cell compartment and the interior of the dilution tunnel averaged 26 K. For this reason, it is reasonable to assume that the largest particle losses are expected to occur during the fast acceleration modes (stirred tank) of operation of the MEC01 emission driving cycle, when the engine operates at higher temperatures than under deceleration and cruising conditions.

Under wide open throttle acceleration (WOT), BC and C_3H_8 concentrations peaked, respectively, at 1.2 mg m^{-3} and 6.5 ppmv, although they averaged only 0.03 mg m^{-3} and 2.5 ppmv during cruise conditions at 20 mph (Figure 3). The same concentration profiles and features are observed under this condition, which corresponds to the fastest acceleration mode of the modal emission cycle.

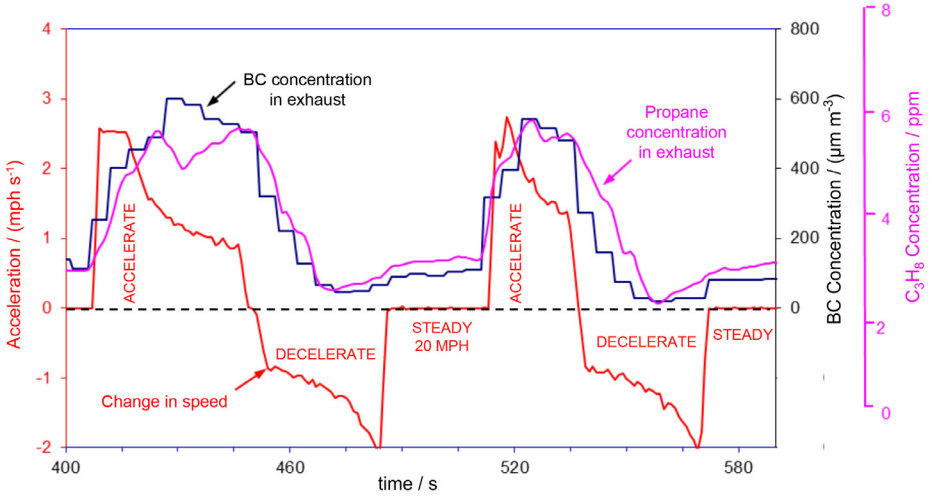

Figure 2. Results of aethalometer BC and FID C_3H_8 concentrations during the acceleration, deceleration and cruise conditions of the constant power section of the MEC01 emission driving cycle.

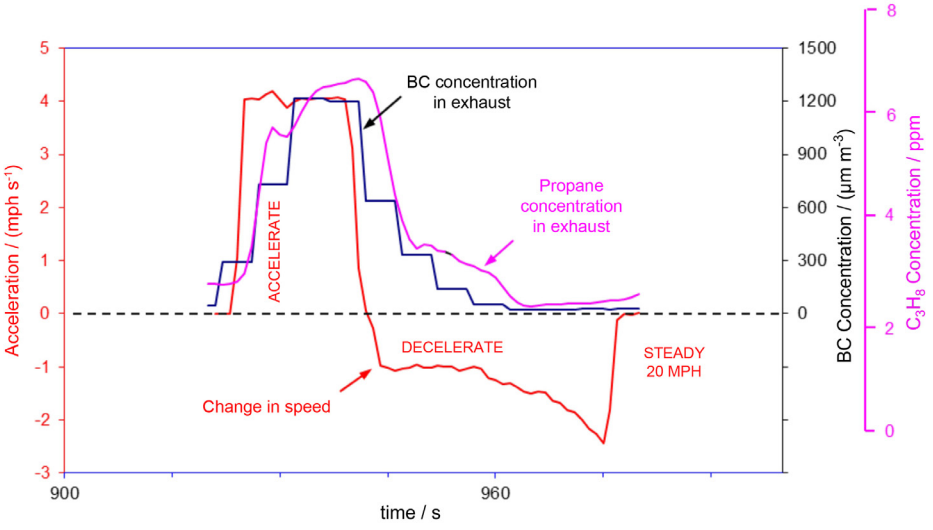

Figure 3. Results of aethalometer BC and FID C_3H_8 concentrations during the acceleration, deceleration and cruise conditions of the wide open throttle (WOT) section of the MEC01 emission driving cycle.

Table 3. Results of EC, OC and PM filter measurements of engine-out and diluted (18.2 times) exhaust concentrations obtained during the entire phase 1 (hot start) of the MEC01 emission driving cycle

Component	Engine-out / (mg m^{-3})	Diluted / (μg m^{-3})	EC/TC	OC/TC	TC/PM	EC/PM
EC concentration	14.1	774				
OC concentration	14.8	814				
TC (EC+OC) conc.	28.9	1,588				
PM concentration	34.0	1,686				
Concentration ratios			0.49	0.51	0.85	0.41

OC, EC and PM filter data for phase 1 of the MEC01 emission driving cycle

Filter measurements of EC concentrations using the TOR method generally agree quite well with aethalometer BC concentrations.[14] These parallel filter measurements provide additional information on the concentrations of the important major classes of carbonaceous species present. For this reason, it was measured EC, along with OC and PM concentrations (Table 3) during the entire phase 1 of the MEC01 emission driving cycle.

Taking into consideration a (constant) dilution factor of 18.2 for phase 1 of the MEC01 emission driving cycle, the calculated mean EC, OC, TC and PM engine-out exhaust and diluted concentrations are shown in Table 3. EC represented 49% of TC, i.e., 41% of the gravimetric particle mass, while TC accounted for 85% of the PM (Table 3). The remaining 15% contains ash, sulfate, and other components typically found in diesel engine exhaust.[3] The EC/PM ratios observed in the present study are consistent with EC/PM2.5 average ratios of 0.52 found by Kirchstetter *et al.*[15] for 1977 California HD diesels in the Caldecott Tunnel, located in a commuter route east of Berkeley. Dallmann *et al.*[16] measured PM2.5 emissions, but with an un-calibrated instrument. Their results suggest a BC/PM2.5 ratio between 0.5 and 1, i.e., that the direct diesel particulate emissions were primarily composed of BC.

Conclusions

Aerosol black carbon concentrations were measured by an aethalometer with 5 s time resolution in the exhaust emissions of a diesel-engine pick up truck during acceleration, deceleration and cruise operating conditions of the first phase (hot start) of the MEC01 emission driving cycle. Rapid increases in vehicle speed during acceleration were accompanied by corresponding instantaneous increases in BC (and C_3H_8) concentrations, reaching a (diluted) value of 1.2 mg m^{-3} under wide open throttle acceleration, and dropping down to 0.03 mg m^{-3} under cruising conditions at 20 mph. Fast acceleration under a specific power of 100 mph^2 s^{-1} produced a BC concentration peak of 0.6 mg m^{-3}, and 0.1 mg m^{-3} under cruising conditions at 20 mph. A slow increase in the BC concentration from the beginning to the end of the cruise conditions at 20 mph suggests the occurrence of a decrease in thermophoretic losses to the walls of the dilution tunnel as a result of decreased exhaust temperature during deceleration. Gas-phase propane emission concentrations measured concurrently with 1 s time resolution closely followed the BC concentrations, suggesting that both components result from incomplete combustion of the fuel. These results show that it is possible to measure speciated diesel particulate emissions essentially in real time, as a function of engine load and other operating conditions.

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