

See discussions, stats, and author profiles for this publication at: <https://www.researchgate.net/publication/9068318>

On-Road Measurement of Particle Emission in the Exhaust Plume of a Diesel Passenger Car

ARTICLE *in* ENVIRONMENTAL SCIENCE AND TECHNOLOGY · OCTOBER 2003

Impact Factor: 5.33 · DOI: 10.1021/es0300315 · Source: PubMed

CITATIONS

116

READS

85

4 AUTHORS, INCLUDING:



Volker Scheer

Ford Motor Company

41 PUBLICATIONS 1,431 CITATIONS

SEE PROFILE



Thorsten Benter

Bergische Universität Wuppertal

149 PUBLICATIONS 2,246 CITATIONS

SEE PROFILE

On-Road Measurement of Particle Emission in the Exhaust Plume of a Diesel Passenger Car

RAINER VOGT,^{*,#} VOLKER SCHEER,[#]
ROBERTO CASATI,^{#,†} AND
THORSTEN BENTER^{*,†}

Ford Forschungszentrum Aachen GmbH, Süsterfeldstrasse 200,
52072 Aachen, Germany, and Bergische Universität
Wuppertal, FB 9 Chemie, Gauss Strasse 20,
42097 Wuppertal, Germany

Particle size distributions were measured under real world dilution conditions in the exhaust plume of a diesel passenger car closely followed by a mobile laboratory on a high speed test track. Under carefully controlled conditions the exhaust plume was continuously sampled and analyzed inside the mobile laboratory. Exhaust particle size distribution data were recorded together with exhaust gas concentrations, i.e., CO, CO₂, and NO_x, and compared to data obtained from the same vehicle tested on a chassis dynamometer. Good agreement was found for the soot mode particles which occurred at a geometric mean diameter of approximately 50 nm and a total particle emission rate of 10¹⁴ particles km⁻¹. Using 350 ppm high sulfur fuel and the standard oxidation catalyst a bimodal size distribution with a nucleation mode at 10 nm was observed at car velocities of 100 km h⁻¹ and 120 km h⁻¹, respectively. Nucleation mode particles were only present if high sulfur fuel was used with the oxidation catalyst installed. This is in agreement with prior work that these particles are of semivolatile nature and originate from the nucleation of sulfates formed inside the catalyst. Temporal effects of the occurrence of nucleation mode particles during steady-state cruising and the dynamical behavior during acceleration and deceleration were investigated.

1. Introduction

The current public debate on airborne particulate matter (PM) is driven by the results of epidemiological studies, which show correlations of the occurrence of ambient PM and adverse health effects (1, 2). In most studies the mass of ambient PM with an aerodynamic diameter smaller than 10 μm (PM₁₀) and smaller than 2.5 μm (PM_{2.5}) is considered. Recently, a correlation of daily mortality with ultrafine particles smaller than 0.1 μm in diameter was reported. However, it was commented by the Health Effects Institute (HEI) that there exists no relative or temporal difference of fine and ultrafine particle effects with respect to associated health effects (3). Due to the unclear role of fine and ultrafine particles there has been considerable interest in the characterization of ambient particle size distributions and their emission sources.

In this paper we focus on measurements of tailpipe particle emissions from motor vehicles. Although a lot of progress has been made in understanding the contribution from diesel engines, there are still large uncertainties in the measurement of their exhaust particle number size distributions. It is widely accepted that the soot mode occurs at a particle mobility diameter of 50–100 nm and that the mean diameter and size distribution is largely independent of engine technology (4–6). However, a large uncertainty remains concerning the occurrence of nucleation mode particles of 10–20 nm size, which may be generated under certain engine operation conditions through nucleation and condensation processes during cooling of the exhaust gases. While it is well-known that diesel particles consist of elemental carbon, organic carbon, sulfuric acid, and some metal ash, there is only very limited information available on the chemical composition of the nucleation mode particles.

Nucleation mode particles are often observed near motorways, e.g., urban streets, or adjacent to freeways, where the number size distribution is dominated by particles in the 10–30 nm size range (7, 8). Ambient measurements at a German “Autobahn” (high-speed freeway) site showed a bimodal size distribution with a maximum mode at 10–20 nm in addition to the much less abundant soot particle mode (9, 10). Measurements using a thermodenuder and a volatility twin differential mobility analyzer (VTDMA) revealed that most of the particles in this size range were volatile and could be evaporated around 130 °C. Apparently, these particles do not have a solid core (9). This is consistent with the hypothesis that the particles are comprised of sulfuric acid and/or unburned hydrocarbons which undergo hygroscopic growth (11). The sole investigation on the chemical composition of the nucleation mode particles was done on a heavy-duty diesel engine by Tobias et al. (12) who reported that the volatile material of particles smaller than 50 nm consisted mainly of aliphatic hydrocarbons and a much smaller content of ~10% sulfuric acid.

It has been suggested that the dilution conditions applied in the vehicle emissions test laboratory have a significant influence on the presence of nucleation mode particles (13, 14). Maricq et al. (15) reported on possible artifacts, which could be generated upon evaporation of deposits when sampling through a transfer hose into the dilution tunnel. Kittelson et al. (16) reported particle size distributions measured in the exhaust plume of a heavy-duty diesel truck. Nucleation was found to be highly nonlinear and very sensitive to ambient conditions, e.g., temperature. Shi et al. (17) studied total particle number emissions from passenger vehicles driving by a measurement site. From the concurrent measurement of the CO₂ mixing ratio and particle number density, the particle emission rate was estimated for vehicles operated on different diesel and gasoline technologies. However, no particle size distribution was measured, and the vehicle speed and engine operation condition were not well defined. Therefore, to validate laboratory sampling techniques a comparison with real-world atmospheric sampling directly from the exhaust plume appears to be prudent.

In this paper we report the first on-road determination of particle emission from a diesel passenger car under well controlled conditions on a test track and comparison to laboratory measurements. Real-world particle size distributions and emission factors were measured in the vehicle exhaust plume. The Ford Mobile Laboratory which was equipped with particle measurement instrumentation and trace gas analyzers followed closely the test vehicle on a test

* Corresponding author phone: 49-241-9421204; fax: 49-241-9421414; e-mail: rvogt@ford.com.

[#] Ford Forschungszentrum Aachen GmbH.

[†] Bergische Universität Wuppertal.

track. First, the experimental method of sampling from the exhaust plume is described, and the recorded data are compared with conventional chassis dynamometer measurements. Second, effects on the occurrence of nucleation particles due to the fuel sulfur content in combination with the presence of an oxidation catalyst are reported. Finally, temporal effects during steady-state cruising and the dynamics of acceleration and deceleration were investigated.

2. Experimental Methods

The experiments were performed using two European model diesel passenger cars (vehicle 1: EURO III, 1.8l turbo-charged direct injection (DI) with oxidation catalyst; vehicle 2: EURO III, 2.0l turbo-charged DI with oxidation catalyst). The vehicles were operated with European reference diesel fuels (RF73-A-93, RF-06-99, Carcal55) with sulfur levels of 350 ppm S, 40 ppm S, or 10 ppm S. Vehicle 1 was equipped with four temperature sensors to record temperatures postcatalyst, premuffler, postmuffler and at the tailpipe end. The temperature, fuel consumption, and vehicle speed were recorded with an on-board data acquisition system.

For comparison the gaseous and particulate emissions were measured at the emissions research laboratory of the Ford Forschungszentrum Aachen. The 48-in. single roll chassis dynamometer and dilution tunnel is essentially identical to the setup described in refs 15, 18, and 19. For PM size measurements the exhaust was sampled by a rotating disk diluter (MD19-2E, Matter Engineering AG), which was operated with particle free synthetic air. The diluter was directly connected to the tailpipe by a 15 cm stainless steel line of 4 mm inner diameter. To avoid artifacts through evaporation of condensed material this sampling line was cleaned regularly and heated to 200–220°C, which was slightly above the exhaust temperature. The rotating disk diluter was operated at a dilution factor of 100. For particle size measurements the vehicle was warmed on the dynamometer at constant speed for 10 min. Subsequently, a scanning mobility particle sizer (SMPS, Model 3934L, TSI Inc.) recorded three size scans of 5 min duration each, followed by a 1 min down scan and a 1 min delay. Sheath air and sample air settings were 6 L min⁻¹ and 0.6 L min⁻¹, respectively, which yielded a size range between 9 and 453 nm. The exhaust was directed via an insulated and heated corrugated stainless steel hose (6 m length, i.d. = 100 mm) into the stainless steel dilution tunnel. Particles were sampled more than 10 tunnel diameters downstream to permit thorough mixing. For PM emission measurement the standard gravimetric method was performed by sampling through standard 47 mm Teflon-coated filters. During a typical experiment three bag samples for subsequent NO_x, CO, and HC analysis and three filters for PM mass were drawn in parallel to the size scans.

The on-road measurements were performed on a high-speed oval track of 4 km length per lap. To avoid interferences from other sources no other vehicles were allowed on the test track during all measurements. The exhaust plume was sampled by the Ford Mobile Laboratory (FML) which closely followed the test car. The distance between the two vehicles was kept approximately constant by towing a thin rope and following the end mark at the selected distance. The FML was originally constructed on the basis of a Ford Transit van to operate as a stand-alone experimental platform for the investigation of ambient particles (10). For these experiments a battery pack and an on-board power supply were installed which allowed operation of various pumps, a scanning mobility particle sizer (SMPS, Mod. 3934L TSI, Inc.), total number count (condensation nucleus counter, CPC Model 3022, TSI Inc.), CO and NO_x analyzers (Models 300 and 200A, API), and data acquisition instruments while driving. The SMPS was operated at 10 L min⁻¹ sheath air and 1.0 L min⁻¹

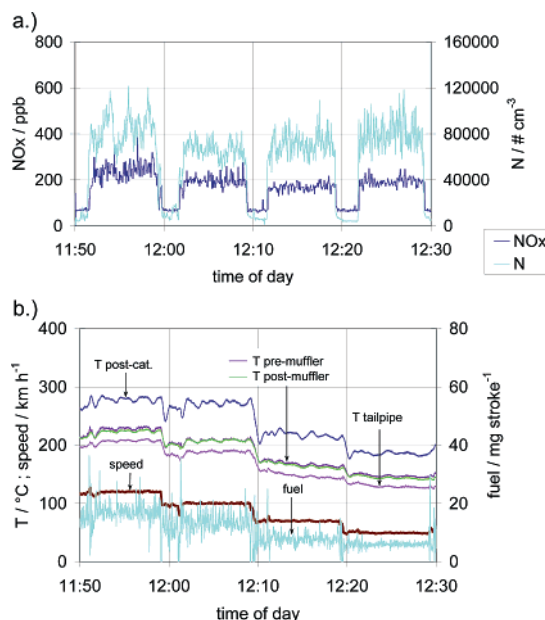


FIGURE 1. (a) Observed NO_x and total particle number concentrations while chasing diesel vehicle (1) at 14 m distance at 120 km h⁻¹, 100 km h⁻¹, 70 km h⁻¹, and 50 km h⁻¹. Between the speed changes, background air was sampled. (b) Vehicle speed and exhaust temperatures at four different locations (left axis) and fuel consumption (right axis).

sample air which yielded a size range between 7 and 316 nm. Sampling was performed through a 4 mm i.d. stainless steel inlet in front of the radiator grill. A 10.3 mm i.d. stainless steel line of 420 cm length connected the sampling probe with the inside of the FML. Air was drawn at a volume flow of 17 L min⁻¹, from which the filtered sheath air for the SMPS was taken and the instruments sampled at their specified flow rates. The residence time inside the stainless steel line was 1.2 s. The different response and delay times of the gas and aerosol analyzers were adjusted further downstream.

3. Results

3.1. Sampling from the Vehicle Exhaust Plume and Determination of Dilution Factor. In a typical experiment the test car was warmed at a constant speed of 120 km h⁻¹, while the FML was driving in front and sampling background air. Figure 1 shows how the exhaust plume was sampled starting from 11:53, when the test car passed the FML. The distance of 14 m was kept constant within 1 m for 8 min, when the FML passed the test car a second time to sample background air. During this time the speed was adjusted to 100 km h⁻¹, and at 12:03 the exhaust plume was sampled again. In Figure 1(a), (b) the NO_x and total particle number concentration are shown together with fuel consumption, vehicle speed, and exhaust temperatures. In Table 1 the NO_x concentrations measured with the same vehicle at the chassis dynamometer and during the chasing experiments are presented. To calculate the dilution factor for the chasing experiments it is assumed that the NO_x emissions are identical with the laboratory values. At 14 m distance the dilution factor varies from DF = 926 at 50 km h⁻¹ to DF = 1051 at 120 km h⁻¹. In one set of experiments the distance was increased to 100 m. Clearly, the exhaust plume was sampled, and the DF was determined to be 9300 at 100 km h⁻¹. During the experiments the ambient wind speed was low, and it was further reduced by the surrounding trees. We did not observe effects from perpendicular winds.

3.2. Measurement of the Particle Size Distribution. While the FML was following the test vehicle running on 40 ppm S fuel at constant speed and distance the particle size

TABLE 1. Measured NO_x Concentrations on the Chassis Dynamometer and during Sampling of the Exhaust Plume of Diesel Vehicle (1)^a

	50 km h ⁻¹	70 km h ⁻¹	100 km h ⁻¹	120 km h ⁻¹
[NO _x] _{laboratory} /ppb	116000	122000	158000	179000
[NO _x] _(14 m) /ppb	125	103	127	170
DF _(14 m)	926	1185	1248	1051
[NO _x] _(50 m)			26.8	
DF _(50 m)			5900	
[NO _x] _(100 m)			17.0	
DF _(100 m)			9300	

^a The dilution factor (DF) was determined from $[\text{NO}_x]_{\text{laboratory}}/[\text{NO}_x]_{\text{(chasing)}}$.

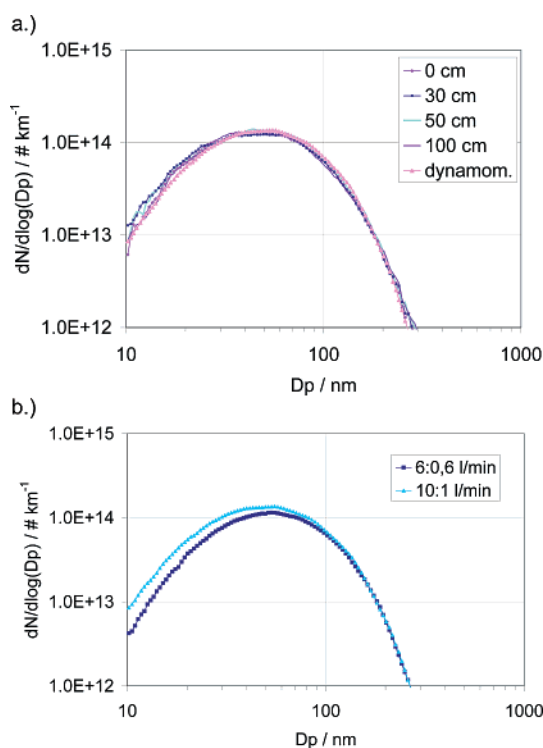


FIGURE 2. (a) Particle size distributions measured at 100 km h⁻¹ at 14 m distance in the exhaust plume of diesel vehicle (1) with different extension lengths of the sampling probe. The sulfur content of the diesel fuel was 40 ppm; $T = 17\text{--}20^\circ\text{C}$, $\text{RH} = 56\% - 80\%$. For comparison data obtained running the same vehicle on the dynamometer at 100 km h⁻¹ are included (triangles). **(b)** Effect of different SMPS flow settings on measured particle size distributions during the 100 km h⁻¹ dynamometer test. The SMPS flows were 6 L min⁻¹ sheath air and 0.6 L min⁻¹ sampling flow (squares) and 10 L min⁻¹ sheath air and 1.0 L min⁻¹ sampling flow (triangles). Sampling was performed from an excess flow under identical dilution conditions through a T-connector mounted directly at the SMPS impactor.

distribution was measured by the SMPS. Four subsequent size scans were averaged. Using the dilution factors as given in Table 1 the raw data were converted to number size distributions expressed as emission rate per km. To test the optimum length of the sampling probe extension in front of the radiator grill of the FML particle size distributions were measured at 100 km h⁻¹ with four different length extensions, as shown in Figure 2. The size distributions were unimodal with a geometric mean diameter of approximately 45 nm. A unimodal size distribution represents the soot-mode particles and is typical for a light-duty diesel vehicle running on low sulfur fuel (4–6). No change was observed upon varying the sampling probe extension from 0 to 100 cm, cf. Table 2. This

result clearly indicates that no dead air space or unusual air circulation in front of the FML disturbs the measurement procedure, most likely because the air stream partly flows into the FML radiator housing. For simplicity, the following experiments were done without sampling hose extension (0 cm).

For comparison, the particle size distributions of the same vehicle at the same speed were measured on the chassis dynamometer. These data are also included in Figure 2a and Table 2, respectively. The particle size distributions measured with tailpipe dilution were again unimodal, with virtually the same particle diameter and size distributions. During the chasing experiments the SMPS flow settings were 10 L min⁻¹ sheath air and 1.0 L min⁻¹ sample air flow. In Figure 2b it is shown for a dynamometer test at 100 km h⁻¹ that the lower SMPS flows used during the laboratory tests (6 L min⁻¹ and 0.6 L min⁻¹) resulted in a somewhat larger geometric mean diameter and a smaller geometric standard deviation, if compared to a size distribution measured under identical dilution and engine conditions, but with 10 L min⁻¹ sheath air and 1.0 L min⁻¹ sample air flow. This illustrates that diffusion losses of small particles in the SMPS instrument occur and are not corrected by the SMPS software. Using the same SMPS flow settings there was very good agreement of the integrated particle number of $9.1\text{--}9.5 \times 10^{13}$ particles km⁻¹, during the chasing experiment, and 9.3×10^{13} particles km⁻¹ as measured on the dynamometer (Table 2). Also, the geometric mean diameters were essentially identical.

3.3. Fuel Sulfur and Oxidation Catalyst Effect. To explore the effect of the fuel sulfur content and the presence of an oxidation catalyst diesel vehicle (1) was operated on high sulfur fuel (350 ppm S). In Figure 3 a.) the particle size distribution measured with the FML chasing the exhaust plume at 14 m distance are shown for speeds of 50, 70, 100, and 120 km h⁻¹. At 50 km h⁻¹ and 70 km h⁻¹ unimodal size distributions were observed, which are typical for soot mode particles and which are in agreement with dynamometer measurements. However, at 100 km h⁻¹ and 120 km h⁻¹ a second particle mode appeared with a number count maximum at about 10 nm particle diameter. The nucleation mode showed some fluctuations, which are not averaged during the 15 min duration of the measurement. The instability of the nucleation mode is related to the engine load which is adjusted by the driver, especially when exiting the curve from the high-speed oval. This effect will be further examined in section 3.4.

Upon removal of the oxidation catalyst from the vehicle unimodal size distributions were observed, as shown in Figure 3b. Nucleation mode particles could not be detected, and the particle size distribution represents well the soot mode. The ambient temperature and relative humidity were nearly identical, thus it appears unlikely that changes of the ambient conditions caused the disappearance of the nucleation mode. Most likely, at the 100 km h⁻¹ and 120 km h⁻¹ runs the exhaust temperatures are sufficiently high (see also Figure 1b), and the fuel sulfur is converted to sulfuric acid in the presence of the oxidation catalyst. Subsequently, the H₂SO₄ generated forms condensation nuclei during cooling of the exhaust plume. From this study it remains open if sulfuric acid, hydrocarbons, and/or water lead to particle growth into the observable size range of the SMPS (12).

To further explore the role of the fuel sulfur content and the formation conditions of the nucleation mode diesel vehicle (2) was operated on ultralow sulfur fuel (10 ppm S). The particle size distribution was measured with the FML chasing the exhaust plume. As shown in Figure 4, even at 120 km h⁻¹ a unimodal size distribution and no nucleation mode particles were observed. At the same day and virtually identical ambient conditions the fuel was changed back to regular sulfur content (360 ppm S), and a similar bimodal

TABLE 2. Measured Particle Size Parameters and Total Particle Number Emissions Recorded during Chasing of Diesel Vehicle (1) Running on 40 ppm S Fuel with Different Extensions of the Sampling Probe of the Mobile Laboratory^a

speed (km h ⁻¹)	extension of the sampling probe	geometric mean (nm)	geometric SD	total concn (# km ⁻³)	PM mass (mg km ⁻³)
50	0 cm	46.0	1.82	1.2×10^{14}	
50	dynamometer	51.5	1.77	9.7×10^{13}	20.4
70	0 cm	47.6	1.82	1.1×10^{14}	
70	dynamometer	55.6	1.75	9.3×10^{13}	22.5
100	0 cm	45.1	1.84	9.1×10^{13}	
100	30 cm	43.8	1.88	9.0×10^{13}	
100	50 cm	45.2	1.86	9.5×10^{13}	
100	100 cm	44.8	1.83	9.1×10^{13}	
100	dynamometer	50.4	1.80	7.5×10^{13}	16.8
100	dynamometer ^a	46.7	1.84	9.3×10^{13}	16.8
120	0 cm	41.9	1.90	1.1×10^{14}	
120	dynamometer	48.2	1.82	9.8×10^{13}	24.4

^a The data obtained using the dynamometer are shown for comparison. The SMPS flows during chasing were 10 L min⁻¹ sheath air and 1.0 L min⁻¹ polydisperse aerosol, for the dynamometer measurements 6 L min⁻¹ and 0.6 L min⁻¹, respectively. ^a This test was done with the same SMPS flow setting as during the chasing experiments (sheath air 10 L/min, 1.0 L/min polydisperse aerosol).

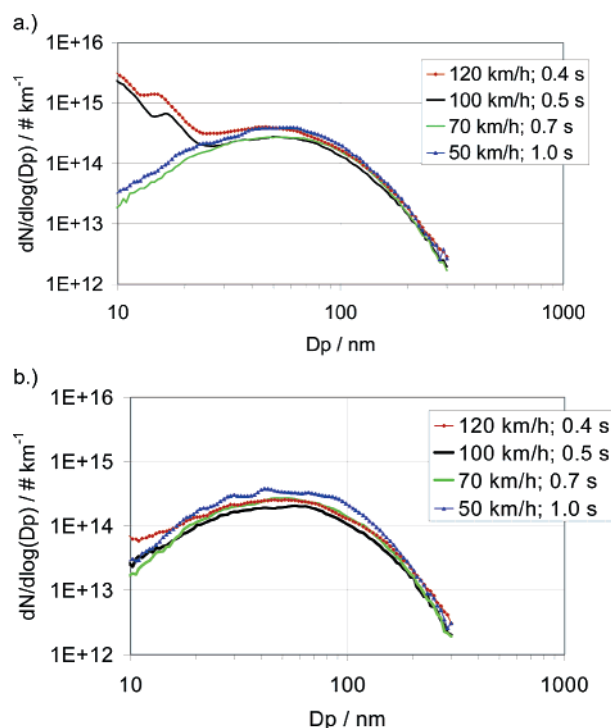


FIGURE 3. (a) Particle size distributions measured at different speeds in the exhaust plume of diesel vehicle (1) running on 360 ppm S fuel with an oxidation catalyst installed. The distance between vehicle tailpipe and sampling inlet was 14 m, which corresponds to an atmospheric residence time of 0.4 s. $T = 14^\circ\text{C}$, $\text{RH} = 50\%$. (b) Same measurement as panel a, but with the oxidation catalyst removed. $T = 17^\circ\text{C}$, $\text{RH} = 40\%$.

size distribution was observed as described and shown above (Figures 3 and 4). Upon removal of the oxidation catalyst the nucleation mode was no longer detectable. Under these conditions, the size distribution was almost identical to the results obtained in the 10 ppm S fuel experiment with oxidation catalyst present (Figure 4). These experiments show that both high fuel sulfur content as well as the presence of an oxidation catalyst are prerequisite conditions for the occurrence of nucleation mode particles in the real exhaust plume. This finding is in general agreement with the results reported by Maricq et al. (20) and will be further discussed in section 4.

3.4. Temporal Stability of Nucleation Mode Particles.

During chasing experiments at constant vehicle speed of

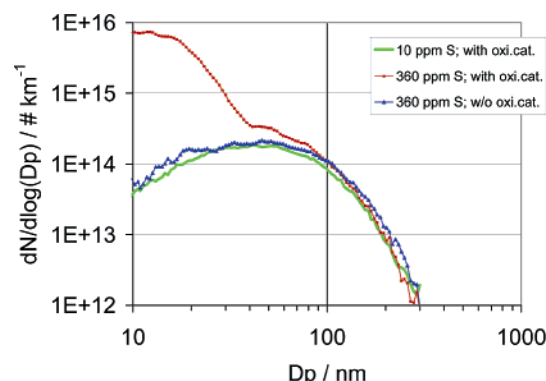


FIGURE 4. Particle size distributions measured at 120 km h⁻¹ in the exhaust plume of diesel vehicle (2) running on 360 ppm S fuel with (squares) and without (triangles) oxidation catalyst installed. The black line represents a measurement with 10 ppm S fuel with oxidation catalyst installed. The distance between test vehicle and sampling inlet was 14 m, corresponding to 0.4 s atmospheric residence time before sampling. $T = 20^\circ\text{C}$, $\text{RH} = 60\%$.

100 km h⁻¹ the appearance of the nucleation mode at 10–20 nm particle size had an induction time of typically 20 min. In Figure 5 the size distributions measured during 35 min of chasing diesel car 1 operated on 320 ppm S are shown together with the temperatures measured at different locations of the exhaust line. The post-cat temperature is measured directly behind the oxidation catalyst. Within 5 min this temperature is constant at $T = 270^\circ\text{C}$. At the other measurement positions, i.e., pre- and postmuffler, and at the tailpipe, constant temperatures were also reached within five minutes. Therefore, a simple change of temperatures coupled with a release of material previously deposited inside the exhaust system cannot account for the retarded evolution of the nucleation mode. Figure 5 shows that the soot particle mode located at about 50 nm is present from the beginning of the experiment, as expected. These observations may be compared to dynamometer tests of Mathis (21), who reported that the stabilization of the nucleation mode took at least 10 min, while the soot mode was stable immediately after a given load change of the diesel engine. In contrast to this result we find that virtually no nucleation mode was present for the first 15 min of the experiment.

The fuel consumption, ambient temperature, and relative humidity all remained constant during the run. A plausible explanation for the delayed occurrence of the nucleation mode is that the oxidation catalyst produces a constant amount of sulfuric acid, which is stored inside the catalyst,

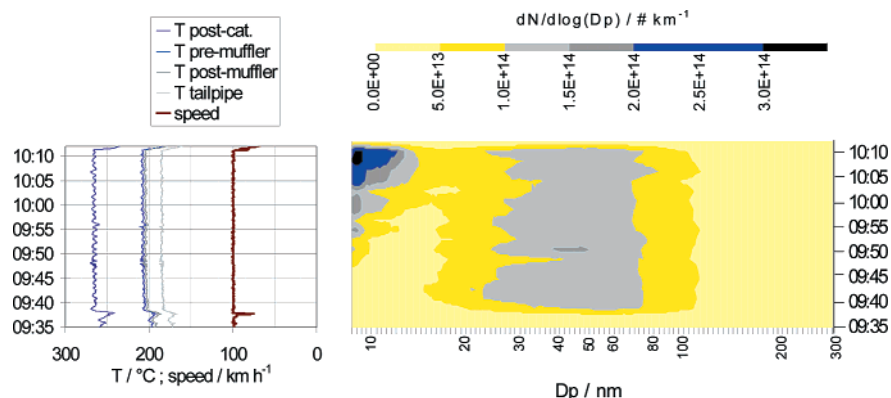


FIGURE 5. Evolution of particle size distributions measured in the exhaust plume of diesel vehicle (1) running on 320 ppm S fuel with oxidation catalyst installed during 35 min of chasing at 100 km h⁻¹. The chasing distance was 14 m corresponding to an atmospheric residence time of 0.5 s ($T = 17^\circ\text{C}$, RH = 57%). The diagram on the left shows temperature profiles as measured at four different locations and additionally the vehicle speed.

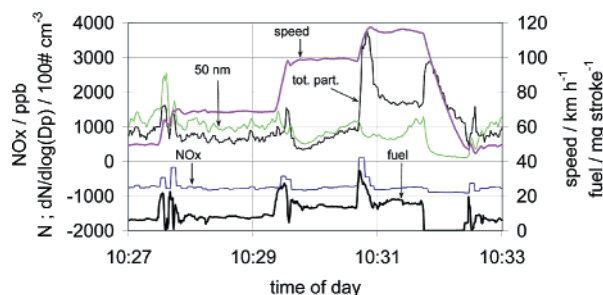


FIGURE 6. NO_x, total particle number N, particle number $dN/d\log(Dp)$ at 50 nm (left axis), speed and fuel consumption (right axis) as measured during acceleration and deceleration in the exhaust plume of diesel vehicle (1) running on high sulfur fuel (320 ppm S) with the oxidation catalyst installed. The NO_x concentration has been shifted by -1000 ppb for clarity.

muffler, and exhaust pipe. After some time of driving the storage capacity of the system is exceeded and sulfuric acid is emitted at large enough quantities to serve as condensation nuclei, which grow due to condensation into the observed region.

As shown in Figure 5, also a periodic variation of the exhaust temperatures is observed. There are two temperature peaks per 2.5 min, which corresponds to the time needed for one lap in the high-speed oval at 100 km h⁻¹. The two peaks result from the small load increase which the driver uses to adjust the velocity after leaving the curve of the oval. These load changes cause periodic patterns in the particle emissions, especially in the nucleation mode (Figure 5). However, the time resolution of the SMPS is not sufficiently high to entirely resolve these fluctuations.

3.5. Particle Emissions during Acceleration and Deceleration. To investigate particle emissions during speed changes the diesel car (1) (320 ppm S) was accelerated from 50 km h⁻¹ to 70 km h⁻¹, from 70 km h⁻¹ to 100 km h⁻¹, and from 100 km h⁻¹ to 120 km h⁻¹. This speed ramp was followed by tipping out and deceleration to 50 km h⁻¹. The FML was kept at 14 m distance, only during the acceleration it was sometimes larger (~by a factor of two). In Figure 6 the fuel consumption curve clearly marked the acceleration and deceleration phases. The time resolution of the NO_x analyzer and the particle counter of ~5 s was sufficient for tracing the increased NO_x and particle levels during acceleration. The SMPS was set to sample 50 nm particles only. As expected the total number of particles measured by the CPC generally tracked the number measured at 50 nm. When comparing the particle number values in Figure 6 it should be noted that particles at 50 nm are given in $dN/d\log(Dp)$, resulting

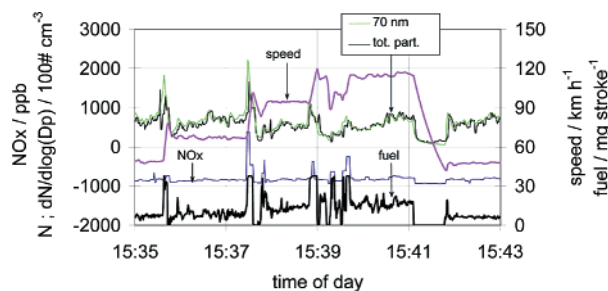


FIGURE 7. NO_x, total particle number N (CPC), particle number $dN/d\log(Dp)$ at 70 nm (left axis), speed and fuel consumption (right axis) as measured during acceleration and deceleration in the exhaust plume of diesel vehicle (1) running on low sulfur fuel (40 ppm S) with the oxidation catalyst installed. The NO_x concentration has been shifted by -1000 ppb for clarity.

in somewhat larger values than the total particle count. During the first two accelerations and during the constant cruise at 100 km h⁻¹ the ratio of total particle number and particles at 50 nm remains approximately constant. However, during the acceleration to 120 km h⁻¹ and during the subsequent deceleration the total number of particles was strongly increased. Especially, during deceleration the 50 nm particles decreased concurrently with fuel shut off, while the total number of particles increased and fell off with a distinct delay (Figure 6).

The stronger increase of total particle number concentration is an indication for the occurrence of nucleation particles. During acceleration the air-to-fuel ratio is decreased, and the exhaust contains a larger amount of hydrocarbons from unburned fuel. This volatile material can either condense on existing particles, thus increase the volatile organic fraction (VOF), or form new particles. The competition between nucleation and condensation on existing particles is a reasonable explanation of the increased total particle count during deceleration: Immediately after power reduction the amount of soot particles drops (cf. Figure 6, 50 nm trace), reducing the available surface area for condensation of organic material, and sulfuric acid and thus nucleation occurs. This effect is similar to observations made during chassis dynamometer/dilution tunnel measurements by Gruber et al. (22) and Combustion Inc. (23), although nucleation particles were not observed during the acceleration, likely due to different engine, catalyst, and temperature conditions.

The experiment was repeated with low fuel sulfur content (40 ppm S). In Figure 7 results are depicted which show elevated particle and NO_x emissions during acceleration. However the trace representing soot particles (here at 70 nm

particle size) and the total particle number are closely correlated. No increase due to nucleation particles was observed during acceleration from 100 to 120 km h⁻¹ or during deceleration. Since all other ambient conditions were kept constant, the lower fuel sulfur content and lower sulfuric acid formation are most likely the cause for the absence of nucleation particles.

4. Discussion

The goal of this work is to better understand dilution processes and to define laboratory measurement conditions which most reliably reflect real world emission and exhaust dilution. Particle size distributions measured in the exhaust of a diesel passenger car (EURO 3; 40 ppm fuel sulfur content) sampled directly from the tailpipe on the chassis dynamometer were unimodal with a geometric mean diameter around 50 nm, which is at the lower end of the diameter range of 50–70 nm typically reported in the literature (5). This particle mode is common for soot particles.

Particle size distributions were measured in the exhaust plume of the same diesel passenger car at a high-speed test track using the Ford Mobile Laboratory. The measurements showed good agreement of the size and number emissions of the soot mode particles. At 100 and 120 km h⁻¹, using 360 ppm sulfur fuel and the standard oxidation catalyst mounted, an additional nucleation mode at 10–20 nm was observed. Using low sulfur fuel (S < 10 ppm) this nucleation mode was not observed. This result clearly indicates that fuel sulfur is oxidized to sulfuric acid which efficiently forms particle nuclei. The effects of the oxidation catalyst and fuel sulfur level on the occurrence of nucleation particles has recently been investigated in a wind tunnel study (20). It was shown that the presence of an active catalyst and 350 ppm sulfur fuel are required to observe nucleation particles. At 112 km h⁻¹ vehicle speed sampling was carried out at 5.5 and 1.5 m distance behind the tailpipe. While at 1.5 m the nucleation mode was absent, it was clearly observed at 5.5 m (20). This is in general agreement with our finding that the nucleation mode is already present at 14 m sampling distance (100–120 km h⁻¹) and does not change up to 100 m distance. Maricq et al. found that lowering the wind speed had a distinct impact on the nucleation mode. In contrast to our work in which vehicle speed was always equal to wind speed they found only a small nucleation mode at equal vehicle and wind speed of 112 km h⁻¹. The nucleation mode became more dominant at lower wind speed of 64–80 km h⁻¹. This shows how complex dilution and nucleation processes are and the need for real world on-road measurements.

In contrast to most prior work we report particle emission rates per km, which would allow a more quantitative assessment of soot mode and nucleation mode particles. Shi et al. (20) estimated particle number emission rates in a drive-by study under weakly defined conditions. They reported emission rates of 3.0×10^{14} and 1.1×10^{15} particles km⁻¹ for diesel vehicles with and without oxidation catalyst, respectively. The order of magnitude is well comparable with our results, although Shi et al. found the higher number in the absence of an oxidation catalyst. Obviously, there is much more work needed to further quantify emission rates of nucleation particles, which not only are dependent on fuel, catalyst, and engine operation but also are influenced by ambient conditions.

Kittelton et al. (24) observed particle size distributions during chasing the exhaust plume of a heavy-duty diesel truck. The nucleation mode was much smaller, when the truck engine was operated on 100 ppm sulfur California diesel fuel, instead of 300 ppm sulfur EPA diesel fuel. Similar results were reported by Baumgard and Johnson (25) on heavy-duty engine dynamometer studies using 100 ppm low sulfur fuel. Abdul-Khalek et al. (14) observed the same effect;

however, the reduction was only 48% at 1 s residence time. Qualitatively, these results are in agreement with our measurements. An explanation for the quantitative differences could be the different light-duty and heavy-duty engine concepts and the different sulfur contribution from oil consumption.

There have been very limited investigations on the simulation of the dispersion of exhaust components in the wake of a vehicle (26). Kim et al. (27) described a computational fluid dynamics (CFD) model, which was used to simulate the dilution of condensable exhaust gases of a heavy-duty truck in comparison to wind tunnel data. The model included nucleation, condensation, and coagulation processes of sulfuric acid particles formed from oxidized fuel sulfur, but it neglected the presence of elemental carbon particles. In general, the CFD model could reproduce the measured particle mode at 50–70 nm, though it was predicted to consist of volatile material, and it missed a shoulder in the size distribution of the experimental data which was possibly due to nucleation particles. For modern light duty diesel applications it has been shown that the 50–70 nm particle mode mainly consists of solid material, while a nucleation mode at 10–20 nm as also observed in this work is comprised of volatiles (5, 20). It would be interesting to apply a CFD model to the exhaust plume study presented here; however, the model should include solid diesel soot particles.

Using the 40 ppm sulfur fuel there was excellent agreement between particle size distributions measured in the exhaust plume and on the chassis dynamometer. However, running on 360 ppm high sulfur fuel the bimodal size distribution was only observed during chasing (28). To avoid adsorption losses the short sampling line from the tailpipe to the diluter was heated at or slightly above the exhaust temperature. Obviously, the tailpipe dilution method does not reproduce real world dilution, which is a function of temperature and concentration gradients, dilution ratio, and relative humidity. Future work will address these parameters in more detail to further gain insight into particle formation conditions and to establish reliable measurement procedures for nucleation particles.

Literature Cited

- (1) Vedral, S. J. *Air Waste Manage. Assoc.* **1997**, 47, 551–581.
- (2) Dockery, D. W.; Pope, C. A. *Annu. Rev. Public Health* **1994**, 15, 107–132.
- (3) Wichmann, H.; Spix, C.; Tuch, T.; Wölke, G.; Peters, A.; Heinrich, J.; Kreyling, W. G.; Heyder, J. *Research Report 98*; Health Effects Institute: Cambridge, MA, November 2000.
- (4) *ACEA programme on emissions of fine particles from passenger cars*; ACEA: Brussels, Belgium, 1999.
- (5) *ACEA programme on emissions of fine particles from passenger cars [2]*; ACEA: Brussels, Belgium, 2002.
- (6) Maricq, M. M.; Harris, S. J. *Aerosol Sci.* **2001**, 32, 749–764.
- (7) Whitby, K. T.; Clark, W. E.; Marple, V. A.; Sverdrup, G. M.; Sem, G. J.; Willeke, K.; Liu, B. Y. H.; Pui, D. Y. H. *Atmos. Environ.* **1975**, 9, 463–482.
- (8) Wahlin, P.; Palmgren, F.; Van Dingenen, R. *Atmos. Environ.* **2001**, 35, S63–S69.
- (9) Wehner B.; Philippin, S.; Wiedensohler A.; Scheer V.; Vogt, R. *J. Aerosol Sci.* **2001**, 32 Suppl. 1, S117.
- (10) Vogt, R.; Kirchner, U.; Scheer, V.; Hinz, K. P.; Trimborn, A.; Spengler, B. *J. Aerosol Sci.* **2003**, 34, 319–337.
- (11) Baltensperger, U.; Streit, N.; Weingartner, E.; Nyeki, S.; Prévôt, A. S. H.; Van Dingenen, R.; Virkkula, A.; Putaud, J. P.; Even, A.; ten Brink, H.; Blatter, A.; Neftel, A.; Gaggeler, H. W. *J. Geophys. Res.* **2002**, 107, doi: 10.1029/2001JD001292.
- (12) Tobias H. J.; Beving D. E.; Ziemann P. J.; Sakurai H.; Zuk M.; McMurphy P. H.; Zarling D.; Waytulonis R.; Kittelson D. B. *Environ. Sci. Technol.* **2001**, 35, 2233–2243.
- (13) Shi J. P.; Harrison R. M. *Environ. Sci. Technol.* **1999**, 33, 3730–3736.
- (14) Abdul-Khalek, I.; Kittelson D.; Brear F. *SAE Tech. Pap. Ser.* **1999**, No. 1999-01-1142.
- (15) Maricq M. M.; Chase R. E.; Podsiadlik D. H.; Vogt R. *SAE Tech. Pap. Ser.* **1999**, No. 1999-01-1461.

- (16) Kittelson, D.; Johnson, J.; Watts, W.; Wei, Q.; Drayton, M.; Paulsen, D.; Bukowiecki, N. *SAE Tech. Pap. Ser.* **2000**, No. 2000-01-2212.
- (17) Shi, J. P.; Harrison, R. M.; Evans, D. E.; Alam, A.; Barnes, C.; Carter, G. *Environ. Technol.* **2002**, 23, 1–14.
- (18) Maricq, M. M.; Podsiadlik, D. H.; Chase, R. E. *Environ. Sci. Technol.* **1999**, 33, 1618.
- (19) Maricq, M. M.; Podsiadlik, D. H.; Chase, R. E. *Environ. Sci. Technol.* **1999**, 33, 2015.
- (20) Maricq, M. M.; Chase, R. E.; Xu, N.; Laing, P. *Environ. Sci. Technol.* **2002**, 36, 283–289.
- (21) Mathis, U. *Proceedings of the 6. International ETH– Conference on Nanoparticle Measurement 19–21 August 2002*.
- (22) Gruber, M.; Lenz, H. P.; Reischl, G. P. *Proceedings of 22. Internationales Wiener Motorensymposium 2001*; 26.–27. 4.2001, VDI Reihe 12, No. 455, pp 165–191.
- (23) Cambustion Ltd. Cambridge CB1 8DH, U.K. 2002.
- (24) Kittelson, D. B.; W. Watts; Johnson J. *Proceedings of the 6. International ETH– Conference on Nanoparticle Measurement 19–21 August 2002*.
- (25) Baumgard, K. J.; Johnson, J. H. *SAE Tech. Pap. Ser.* **1996**, No. 960131.
- (26) Hider, Z. E.; Hibberd, S.; Baker, C. J. *J. Wind Eng. Ind. Aerodyn.* **1997**, 67&68, 733–744.
- (27) Kim, D.; Gautam, M.; Gera, D. *Aerosol Sci.* **2002**, 33, 1609–1621.
- (28) Vogt, R.; Scheer, V. *Proceedings of the 5. International ETH– Conference on Nanoparticle Measurement 6.-7 August 2001*.

Received for review February 20, 2003. Revised manuscript received July 7, 2003. Accepted July 10, 2003.

ES0300315