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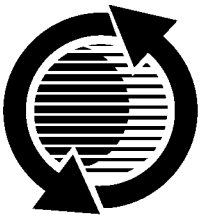

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ABSTRACT

This paper explores the extent to which standard dilution tunnel measurements of motor vehicle exhaust particulate matter modify particle number and size. Steady state size distributions made directly at the tailpipe, using an ejector pump, are compared to dilution tunnel measurements for three configurations of transfer hose used to transport exhaust from the vehicle tailpipe to the dilution tunnel. For gasoline vehicles run at a steady 50 - 70 mph, ejector pump and dilution tunnel measurements give consistent results of particle size and number when using an *uninsulated* stainless steel transfer hose. Both methods show particles in the 10 - 100 nm range at tailpipe concentrations of the order of 10^4 particles/cm^3. When an *insulated* hose, or one containing a *silicone rubber coupler*, is used to test small 4 cylinder gasoline vehicles, a very intense nanoparticle / ultrafine mode at < ~30 nm develops in the dilution tunnel particle size distribution as the vehicle speed is increased to 60 and 70 mph. This nanoparticle mode coincides with a rise of the transfer line temperature to about 180 - 250 °C. It is much less evident for the full size gasoline sedan, which has cooler exhaust. Both tailpipe and dilution tunnel measurements of diesel vehicle exhaust reveal an accumulation mode peak of ~10^8 particles/cm^3, centered at 80 -100 nm. In this case, even with the uninsulated transfer hose an intense ultrafine peak appears in the dilution tunnel size distributions. This mode is attributed to desorption and/or pyrolysis of organic material, either hydrocarbon deposits on the walls of the steel transfer hose or the silicone rubber, by hot exhaust gases, and their subsequent nucleation in the dilution tunnel. This substantially limits the ability to make accurate particle number and size measurements using dilution tunnel systems.

INTRODUCTION

Prompted by potential health concerns, the past few years have witnessed a growing interest in particulate matter (PM) measurements, both ambient and from a wide variety of emissions sources. These measurements are conventionally performed by recording PM mass. The ambient standards are written in terms of mass concentrations, and emission regulations are based on mass rates. However, in order to understand better the nature of the mobile source contribution to ambient PM, many research groups are currently extending their investigations to include measurements of the numbers and sizes of particles in motor vehicle exhaust. Because the standard procedure for tailpipe PM measurements utilizes a dilution tunnel to cool the exhaust and to prevent water condensation, concerns have emerged that the test cell measurements of motor vehicle PM do not reflect the “real world” emissions.

The root of the concern is that vehicle exhaust, a hot, complex, mixture of gaseous emissions and particles, is transformed differently when diluted in a tunnel as compared to the “real world”. Particles are not immutable; they readily undergo transformations, such as coagulation, condensation, and adsorption, and new particles can be created by nucleation of gaseous particle precursors in the diluted and cooled exhaust. Under “real world” conditions, motor vehicle exhaust is diluted rapidly, in less than one second, and by a large amount, a dilution ratio of greater than 100, into air of variable temperature and humidity. In the test cell, the exhaust is conducted to the dilution tunnel, typically by a 10 cm diameter by 5 m long tube, where it is then diluted by a factor of between 5 and 50, depending on test conditions, using dry air at room temperature. This discrepancy between dilution times, extents, temperature, and humidity can potentially lead to significant differences in the nature of the particulate emissions.

Kittelson[1,2] has extensively discussed the possible ways in which coagulation, adsorption, and nucleation can differ between these two dilution scenarios and potentially affect particle number emissions and the nature of the size distributions. However, the interpretation of these processes in a specific situation depends a great deal on the nature of the test vehicle: Does it have a diesel or gasoline engine? Is the fuel conventional or low sulfur? Does the exhaust aftertreatment include a catalyst? A particle trap? For example, ultrafine, or nanoparticles, might be formed by sulfate nucleation in the diluted exhaust from a diesel vehicle using sulfur-containing fuel and incorporating a particle trap. Whereas, in the absence of the particle trap, the sulfates condense on the carbonaceous particles normally formed during diesel combustion, and many fewer ultrafine particles are observed.[3] Similarly, it might be anticipated that removal of gaseous hydrocarbons would make condensation less of a factor for a catalyst equipped vehicle as compared to a non-catalyst vehicle, and that coagulation might be less important in gasoline vehicle exhaust as compared to diesel exhaust, because of the inherently lower gasoline engine PM emissions.

That dilution conditions, such as the dilution ratio, affect particulate mass has been appreciated for some time.[4,5] Recently, the effect of dilution ratio, temperature and humidity on particle size distributions has also begun to receive attention.[2,3,6,7] As seen in the present work, the transit of the hot exhaust through the transfer line to the dilution tunnel further enhances the likelihood that the particle distribution measured in the tunnel does not match what comes out of the tailpipe. Particle number is in principal more sensitive to the dilution process than particulate mass, because coagulation alters the number of individual particles, but not the overall PM mass, and, though nucleation can create large numbers of nanometer size particles, they contribute relatively little to the total PM mass because of their small size.

The purpose of the present paper is twofold: First, it compares two distinctly different combustion particle sampling methodologies, namely the ejector pump and the dilution tunnel. Secondly, whereas previous work[1,2] has emphasized the possibility that dilution tunnel measurements may miss nanoparticles attributable to vehicle exhaust, the present paper explores the complementary issue of particle “artifacts”, i.e., particles not emitted by the tailpipe, but nonetheless recorded in the dilution tunnel. Two sources of artifacts are identified: deposits on the interior walls of the transfer line and shedding of materials used in the transfer line. In a similar vein, Kittelson[1,2] has given examples of long stabilization times needed after transient changes in diesel engine load, and attributed this to the storage and release of volatile particle precursors in the engine and sampling system. In both the previous and present work, these particles are primarily in the ultrafine, or nanoparticle, mode. Whereas these “artifacts” modify the appearance of diesel exhaust particle size distributions, they can completely overwhelm, in terms of particle number, the PM emissions from current model port injection gasoline vehicles. The artificial sources yield higher numbers of particles with an increase in exhaust temperature; thus, they serendipitously mimic the behavior one might expect from increasing vehicle speed or load and can easily be confused as “real” vehicle effects. They may be responsible for some of the comments appearing in the literature that “gasoline vehicles emit less PM mass, but as large a particle number as diesel vehicles”.

EXPERIMENT

PARTICLE SIZE DETERMINATION – Particles, sampled either from the tailpipe or from the dilution tunnel, are analyzed using two model 3934 scanning mobility particle sizers (SMPS) from TSI Inc. Large particles in the sample stream are removed with a 577 nm 50% cutoff impactor. The remaining particles are brought to a Boltzmann charge equilibrium by passing them through a ^{85}Kr bipolar charger and are injected along the outer periphery of a cylindrical cavity that constitutes the differential mobility analyzer (DMA). A voltage applied between the outer wall and the central cylindrical electrode induces a drift of the positively charged particles through the sheath flow and towards the central electrode. Particles exhibiting the correct charge to mobility ratio exit through an aperture at the downstream end of the DMA, are transported to a model 3010-S condensation nuclei counter (CNC), and counted. The size resolution of the instrument typically ranges from ±0.5 nm at 15 nm to ±30 nm at 500 nm at the classifier flow settings used in the present experiments (0.4 L/min aerosol flow and 4.0 L/min sheath flow). A correction for multiply charged particles is applied using the manufacturer provided algorithm.

Two minute scans were used to record particle size distributions simultaneously at the tailpipe and from the tunnel. The scans were performed at approximately 3 - 5 minute intervals. For the gasoline vehicles, the particle emissions are sufficiently small that typically 5 scans are averaged in order to minimize statistical noise that would otherwise result in a “spiky” appearance for the size distributions. Consistency of the two SMPS instruments was confirmed by connecting both instruments to the tunnel and verifying that the size distributions are essentially identical.

Number weighted particle size distributions are plotted as $dN/dlog(D_p)$, i.e., as the number concentration of particles in a given size channel normalized by the logarithmic width of the channel. The values have been appropriately scaled to give tailpipe concentration. These are converted to mass weighted distributions by multiplying by D_p^3 and the particle’s density, either known or guessed. The two types of tailpipe concentrations can be converted further to number or mass emission rates, respectively, by multiplying by the relevant exhaust flow rate. The total number or mass emission rates are then computed by integrating over particle diameter.

TEST VEHICLES – Four vehicles are used in the tests reported here: a small, U.S., 4-cylinder, 1997 model, passenger car equipped with a three-way catalyst (car labeled US4); a European, 4-cylinder, 1997 passenger car, with three-way catalyst (E4); a 1996, full size, 8-cylinder, U.S. car (US8); and a 1998, direct injection, diesel passenger car, with an oxidation catalyst (DV). All are relatively low mileage vehicles that meet the current gaseous and PM emissions standards.

The following fuels are used: California Phase II summer regular grade gasoline for the 4 cylinder U.S. car, European certification fuel for the 4 cylinder European gasoline car, California Phase II summer premium grade gasoline for the 8 cylinder U. S. vehicle, and European certification premium #2 diesel fuel for the diesel passenger car.

DILUTION TUNNEL – The test cell and chassis dynamometer have been described in detail previously[8,9]. Here, it is primarily the dilution process that is of interest. Exhaust gas from the test vehicle is transferred to the dilution tunnel through a corrugated stainless steel tube. Separate transfer tubes, as well as dilution tunnels, are used to test gasoline and diesel vehicles. For the gasoline vehicle tests the transfer tube is 9.1 cm in diameter and 5.8 m long; whereas the diesel transfer tube is 10.4 cm in diameter and 7.6 m long. Table 1 lists the dilution specifications for the various vehicle type and speed combinations that were tested. The exhaust flow rates range from about 0.6 m^3/min for the 4 cylinder gasoline vehicles running at 50 mph to about 1.7 m^3/min for the diesel vehicle and the large gasoline vehicle at 70 mph. Thus, the transit time between tailpipe and dilution tunnel ranges from 1.3 to 3.1 seconds for the gasoline vehicle tests and from 2.2 to 5.7 seconds for the diesel vehicle tests.

Table 1. Test vehicles and exhaust dilution conditions.

Vehicle	Speed (mph)	Exhaust flow (m^3/min)	Tunnel flow (m^3/min)	Primary dilution ratio	Second. dil. ratio	Tailpipe dilution ratio	Transfer hose[a] temperature (°C)
US4	50	0.63	19.8	31.5	1	8	120 – 160
	60	0.85	19.8	23.3	1	8	175 – 215
	70	1.19	19.8	16.6	1	8	260– 300
E4	31	0.44	9.9	22.4	1	8 & 58	~ 113[b]
	44	0.59	9.9	16.6	1	8 & 58	130 – 145
	63	1.00	9.9	9.87	1	8 & 58	160 – 260
US8	50	0.83	19.8	23.7	1	8	~ 113[b]
	60	1.16	19.8	17.1	1	8	113 – 121
	70	1.58	19.8	12.5	1	8	160 – 177
DV	50	0.88	19.8	22.4	8	57	~ 113[b]
	60	1.27	19.8	15.5	8	57	120 – 140
	70	1.78	19.8	11.1	8	57	160 – 180

[a]Applies only to insulated transfer hose; the uninsulated line remains below about 175 °C.
[b]Minimum temperature maintained by heater.

The dilution tunnels are constructed from 30.4 cm diameter electropolished stainless steel tubing. Heated (38 °C), filtered, low humidity (-9 °C dewpoint) dilution air enters at the upstream end through a subsonic venturi (smooth approach orifice). The exhaust gas is introduced in the downstream direction, along the dilution tunnel axis, and just upstream of an orifice plate, which is used to ensure rapid mixing of the exhaust with the dilution air. The tunnel operates in the turbulent regime at a constant total (exhaust + diluent) flow of between 10 and 30 m^3/min. In the present study, vehicles US4, US8, and DV were tested at a tunnel flow of 20m^3/min and vehicle E4 at 10 m^3/min. The corresponding primary dilution ratios, listed in Table 1, range from 10 to 32.

A sample of the tunnel flow is withdrawn at a distance of more than 10 tunnel diameters downstream from the orifice plate. A 0.95 cm diameter, J-shaped, tube pointing upstream parallel to the tunnel axis is used to extract the sample at a flow rate of 0.4 L/min. This sampling is not isokinetic, but for the 10 - 500 nm particle range relevant to exhaust particulate matter, this provides a representative sample regardless. For the gasoline vehicle tests, the sample is directly introduced, using Tygon tubing, into the SMPS. The diesel vehicle particulate emissions are sufficiently high to require secondary dilution. This is accomplished by using an ejector pump to extract a sample from the tunnel via the aforementioned J tube. The output flow from the ejector pump is then sampled at 0.4 L/min into the SMPS for particle size measurements.

As the curve marked “tunnel background” in Figure 1 shows, the filtered dilution air is not entirely free of particles; however, about 90% of the particles have been removed. It is also apparent from the figure that the gasoline vehicle particulate emissions are sufficiently low as to require subtraction of this background signal. After subtraction, there is good agreement between the tailpipe and dilution tunnel measurements of particle size distribution (see also Figures 3 and 4 below). Background subtraction for the ejector pump is not required since it employs particle free N_2 (or air) for dilution.

The tunnel PM measurements are carried out in three configurations: 1) using the corrugated stainless steel transfer tube, 2) insulating and heating the transfer line, and 3) employing a short section of silicone rubber tubing to connect the tailpipe to the transfer tube. The heater only operates during cold start to prevent water condensation; subsequently the exhaust gas is sufficient to maintain the transfer tube to above the dewpoint.

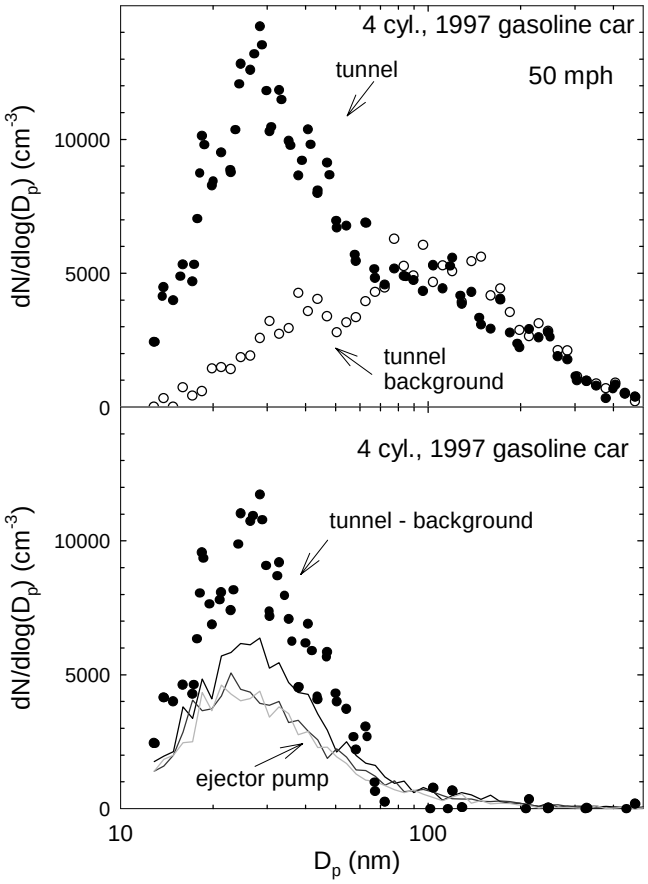

Figure 1. Top panel: Dilution tunnel particle size distributions recorded with and without vehicle (E4) exhaust. The uninsulated transfer tube is used to conduct the exhaust to the tunnel. Bottom panel: Comparison of ejector pump measurements of exhaust particle size with tunnel measurements after subtracting the background. All concentrations are converted to equivalent tailpipe concentrations.

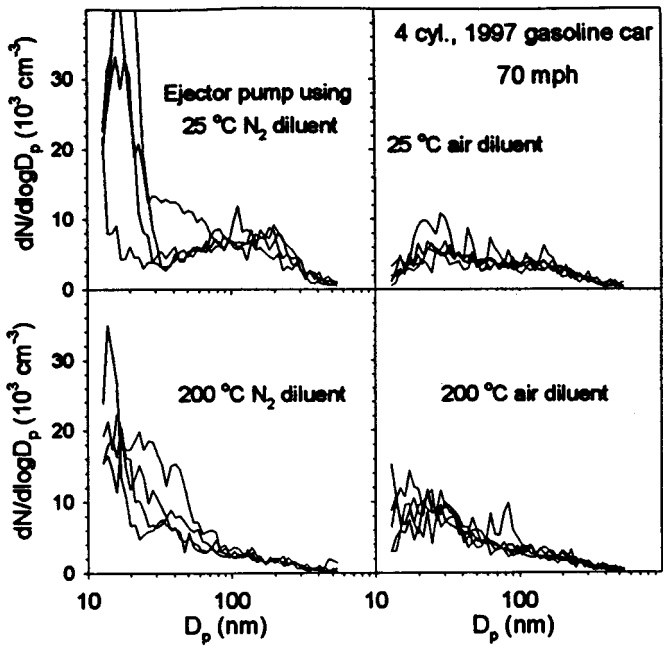

Figure 2. A comparison of ejector pump measurements of tailpipe PM concentration using N_2 and air diluent at either 25 °C or 200 °C. The measurements are made sequentially and are thus subject to fluctuations in the vehicle emissions.

During the 70 mph steady state tests, the exhaust can heat the transfer tube as high as 300 °C. Although at our test facility flanges are added to the tailpipes of test vehicles to enable an entirely metal connection to the tunnel, it is a common practice at many other facilities to employ a flexible silicone rubber coupler to connect the tailpipe to the dilution system, hence the reason for the third test configuration.

EJECTOR PUMP SAMPLING – Ejector pump diluters, from Dekati Ltd., are used to sample vehicle exhaust directly from the tailpipe. The ejector pump is mounted onto the tailpipe with a short, J shaped, 0.6 cm diameter, tube extending into the tailpipe via a compression fitting, and facing open end upstream. Particle free air, or N_2, at 2 atm overpressure is forced at high velocity past a small orifice in the ejector causing a pressure drop, due to the Bernoulli effect, which acts to pump some exhaust from the tailpipe. The same air, or N_2, then serves as the diluent. The dilution ratio for the ejector pump is fixed by the orifice size. It is nominally about 8, but varies from one unit to another due to small differences in orifice size. In these experiments, we use the manufacturer specified dilution ratio. Higher dilution ratios are readily achieved by cascading two or more units.

In our standard approach, we use N_2 as the diluent because of its ready availability. The first ejector stage, as well as the N_2 supplied to it, is heated to about 200 °C. The second stage, when used, remains uninsulated and employs room temperature N_2. In order to ascertain possible effects of this combination of diluent and tempera-

ture on the particle size distribution, the following comparison was performed: the ejector pump was operated with 1) N_2 at 25 °C, 2) N_2 at 200 °C, 3) air at 25 °C, and 4) air at 200 °C. As seen from Figure 2, the temperature of the first ejector stage appears to have little effect on the particle size distribution. Compared to the distributions recorded using air diluent, those obtained with N_2 show higher and more variable particle concentrations in the 10 - 30 nm range. However, relative to the sampling effects that are discussed below, i.e., order of magnitude differences in particle size distribution, the variations between the distributions obtained using N_2 versus air diluent are minor. It is unclear whether they are due to the choice of N_2 versus air diluent, minor examples of the artifacts described below, or simply normal variations in the engine emissions.

RESULTS

GASOLINE VEHICLE: *UNINSULATED* TRANSFER LINE – Prior to a set of steady state tests, each vehicle is warmed up over at least Phase 1 of the FTP drive cycle, followed by 5 or more minutes of steady driving at 50 mph. For many, but not all, of these preparatory drives the exhaust is directed outside the test cell and not into the transfer tube and dilution tunnel. In this case additional time is allowed for the vehicle exhaust to heat the transfer line to above the dewpoint prior to making the particle size measurements.

Figures 3 and 4 compare tailpipe and dilution tunnel measurements of particle size at 50, 60, and 70 mph for vehicles US8 and US4, respectively. These tests utilize the *unheated/uninsulated* exhaust transfer line. Note that the US8 data in Figure 3 are plotted using a linear scale for particle concentration; whereas, the US4 vehicle data are plotted on a logarithmic concentration axis. For vehicle US8, ejector pump sampling at the tailpipe and dilution tunnel measurements are in very good agreement with respect to both the numbers and sizes of the particles. The particle number recorded from the tunnel is perhaps 20% higher than determined by the ejector pump measurement; however, the difference, possibly due to our reliance on the stated ejector pump dilution factors, is comparable to the test to test variation.

The exhaust particle concentration, in Figures 3 and 4, is essentially independent of vehicle speed over the 50 - 70 mph range. This implies that the “efficiency” of forming particles remains nearly constant over the 3 engine rpm/load points corresponding to 50, 60, and 70 mph. Although the exhaust concentration does not change, the particle number emission rate at 70 mph is nearly double that at 50 mph because of the higher exhaust flow. The corresponding PM mass emission rates, as calculated by assuming a particle density of 1 g/cm^3, mass weighting the particle size distributions, integrating over size, and scaling the result by exhaust flow and vehicle speed, are also listed in Figure 3. Note that these are extremely small, on the order of a few micrograms per mile. The 2σ error in the mass emission rate is estimated at ± 50%, originating roughly equally from test to test variability, and the uncertainty in particle density.

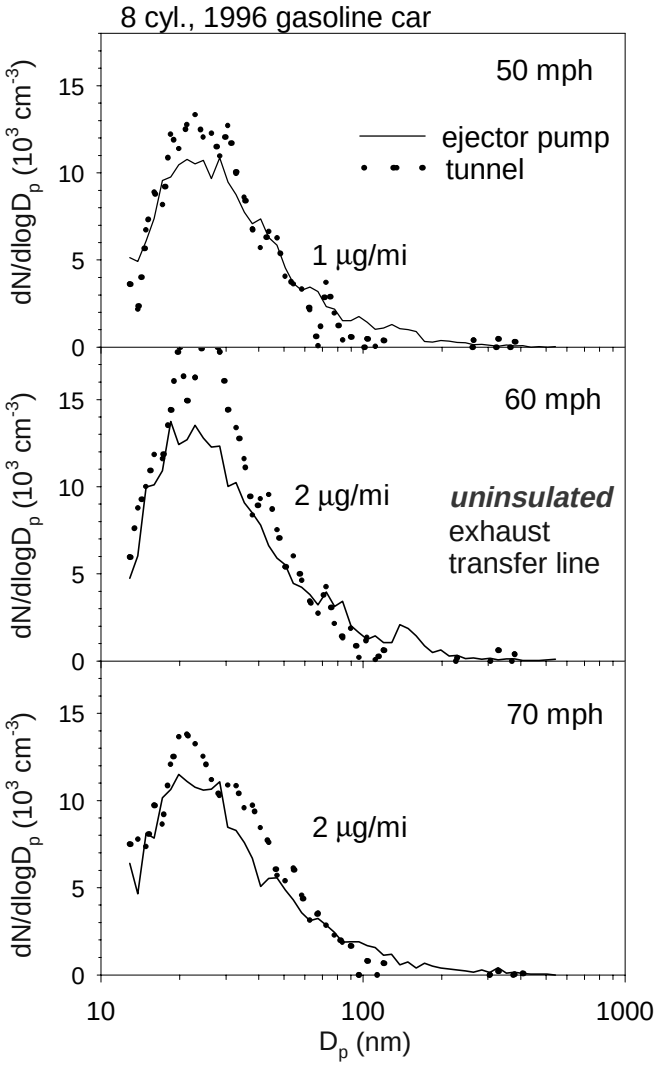

Figure 3. Comparison of ejector pump and dilution tunnel particle size distributions for the 8-cylinder gasoline car at 50, 60, and 70 mph when using the *uninsulated/unheated* transfer line. Note linear concentration axes. The tunnel background has been subtracted. Mass emission rates are estimated from the size distributions.

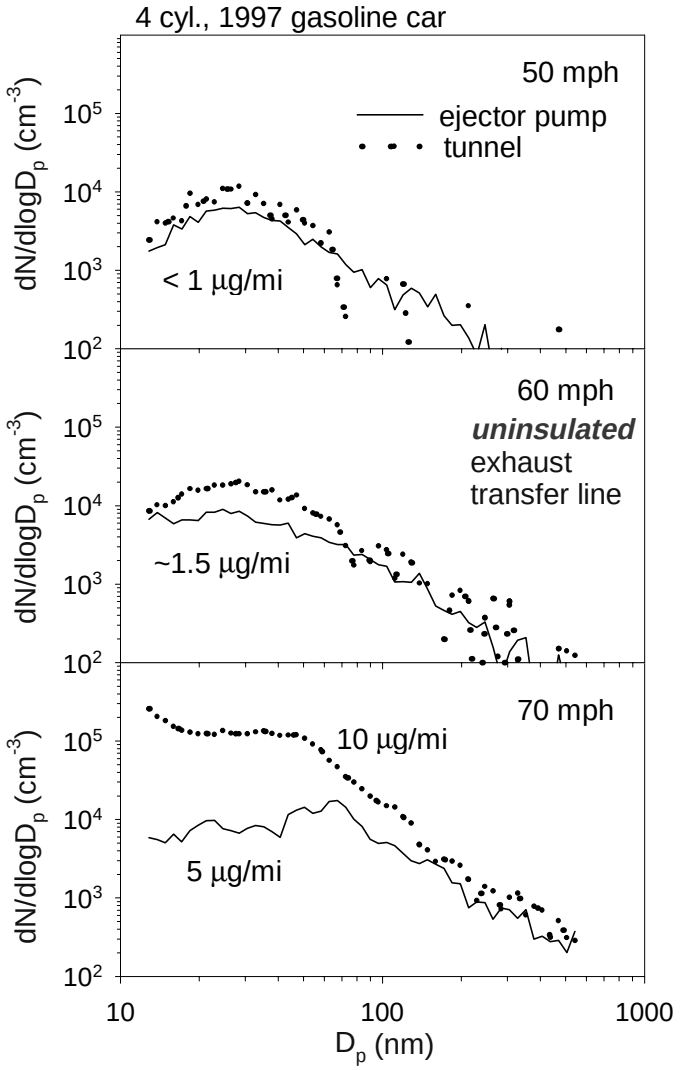

Figure 4. Comparison of ejector pump and dilution tunnel particle size distributions for the 4-cylinder, U.S., gasoline car at 50, 60, and 70 mph when using the *uninsulated/unheated* transfer line. Note logarithmic concentration axes. Mass emission rates are estimated from the size distributions.

At 50 and 60 mph in Figure 4, particle number emissions for vehicle US4 recorded from the dilution tunnel are 1.5 and 2 times the ejector pump results, respectively. Both sampling techniques show similar shapes of size distribution, with particles present primarily in the 10 - 60 nm regime. Tests performed on vehicle E4 at 31, 44, and 63 mph mimic those shown in Figure 4, both with regard to the shapes of the size distributions and the level of agreement between ejector pump and dilution tunnel measurements. As with vehicle US8, PM mass emission rates deduced from these size distributions, and those for vehicle E4, are a few μg/mi. At 70 mph, the particle number recorded from the tunnel exceeds the ejector pump result by an order of magnitude, primarily at the small size end of the distribution. The increase coincides with large variations, by factors > 2, in the scan to scan variability in the size distributions and is attributed to the hydrocarbon storage - release artifacts discussed below.

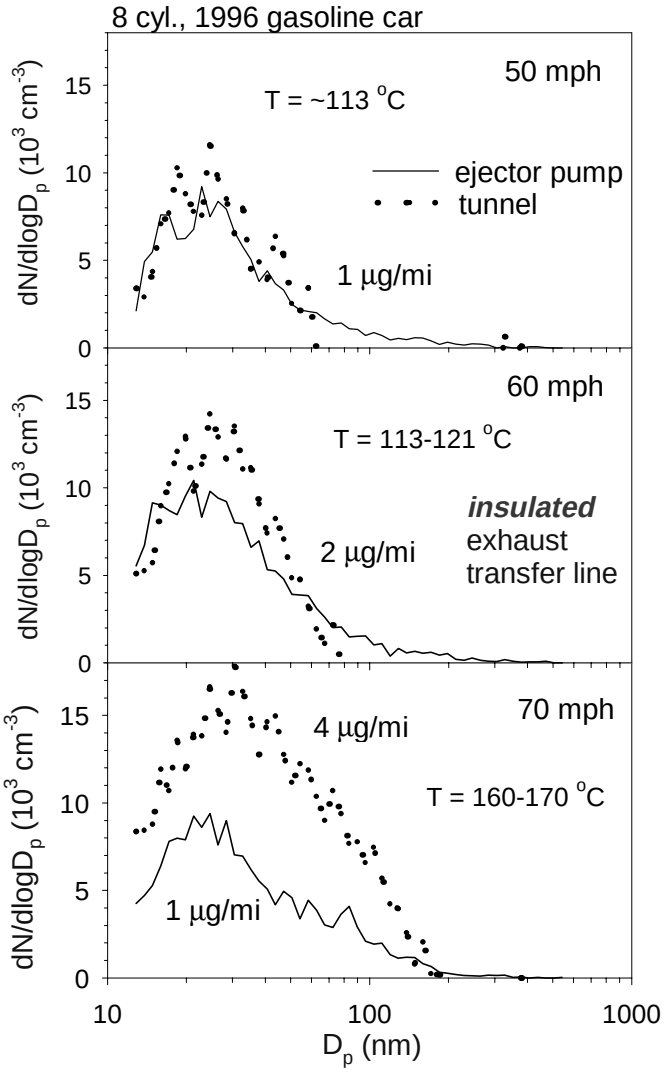

Figure 5. Comparison of ejector pump and dilution tunnel particle size distributions for the 8-cylinder gasoline car at 50, 60, and 70 mph when using the *insulated/heated* transfer line.

GASOLINE VEHICLE: *INSULATED* TRANSFER LINE – The vehicle tests presented in the preceding section were repeated using an *insulated and heated* transfer line, with the heater employed solely to maintain a minimum temperature of 113 °C. In this case agreement, or disagreement, between dilution tunnel and ejector pump measurements depends on the test vehicle and its speed. Figure 5 illustrates agreement within ~20% for vehicle US8 at 50 and 60 mph, which deteriorates to a greater than factor of two disagreement at 70 mph. The particle size distributions, peaking at about 25 nm, are essentially the same at the tailpipe as in the tunnel, both for the uninsulated and insulated transfer tube, except that at 70 mph the tunnel based distribution broadens toward the large diameter side.

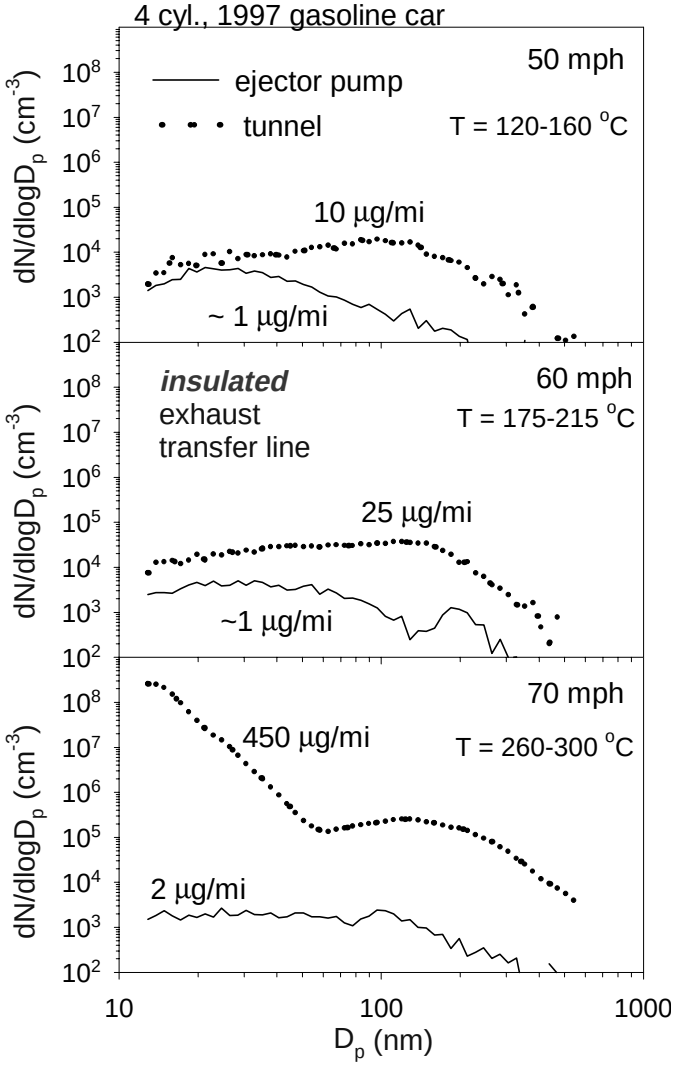

Figure 6. Comparison of ejector pump and dilution tunnel particle size distributions for the 4-cylinder, U.S., gasoline car at 50, 60, and 70 mph when using the *insulated/heated* transfer line.

In contrast, use of the *insulated* transfer line has an enormous effect on the particle number emissions for vehicle US4, as shown in Figure 6. Comparison of the ejector pump based size distributions in Figures 4 and 6 indicates that PM emissions from the vehicle have not changed; they remain broadly distributed over the 10 - 60 nm range. However, the main feature in the tunnel derived size distributions, at 50 and 60 mph, is now an accumulation mode peak at about 100 nm. At 70 mph, an ultrafine particle mode forms at < 15 nm with particle number concentrations 3 - 4 orders of magnitude higher than observed from the ejector pump. Essentially the same behavior is observed for vehicle E4; the differences in ejector pump versus tunnel based size distributions at 31 and 44 mph are smaller than for the 50 and 60 mph tests in Figure 6, but a similar 3 order of magnitude increase in ultrafine particles in the dilution tunnel is found at 63 mph (see Figure 9). For both vehicles US4 and E4, these changes coincide with an increase in transfer line temperature to above roughly 180 °C (this value is likely quite sensitive to the previous testing history), as measured at the middle of the transfer hose (see Table 1). Due to the significantly cooler exhaust, the insulated transfer line only reaches about 170 °C at 70 mph when testing the larger displacement 8 cylinder US car. This is less than the temperature reached for the 4 cylinder vehicle tests at 60 mph; thus, for vehicle US8 the relatively small factor of two increase in particle number observed at 70 mph when using the insulated transfer line (see Figure 5) is consistent with the 4 cylinder vehicle data.

The large increase in ultrafine particles observed when using the insulated transfer tube is not quantitatively repeatable; that is, the increase as compared to the tailpipe measurements can range from a factor of 100 to 10000, the peak in the ultrafine mode can vary from 25 nm to < 10 nm, and the transfer line temperature at which the mode appears can vary from ~160 °C to > 250°C. Size distributions recorded from one series of 70 mph tests on vehicle US4 performed in succession are illustrated in Figure 7. Here, particle number and mean size increase as the temperature rises from 150 °C to about 220 °C, and then subsequently decrease. In other tests, depending on their length and on the previous testing history, only the increase or decrease in ultrafine particles is observed during a specific test sequence.

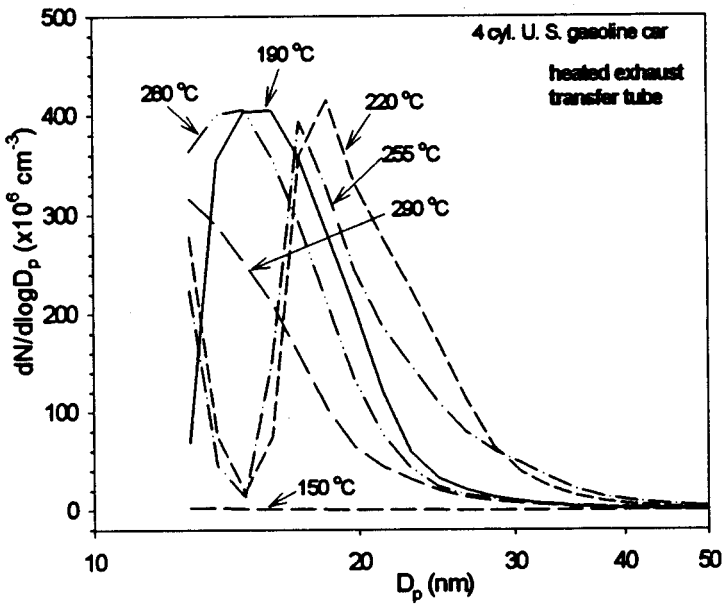

Figure 7. Variation in the ultrafine mode with a sequence of SMPS scans, over which the transfer line temperature climbs progressively higher.

That the intense ultrafine mode is observed in the tunnel, but not at the tailpipe, implies that the transfer line is the source of the particles. That the appearance of this mode is very sensitive to temperature and to the prior history of vehicle tests, suggests that the particles originate from the desorption or pyrolysis of particle precursors from hydrocarbon materials previously deposited on the transfer tube walls. This is corroborated by ejector pump measurements, which in Figure 8 reveal the presence of the ultrafine mode at the downstream end of the *insulated* transfer line just prior to the dilution tunnel. As with the tunnel data, the ultrafine mode is not quantitatively reproducible; rather it depends on the temperature of the tube and the testing history.

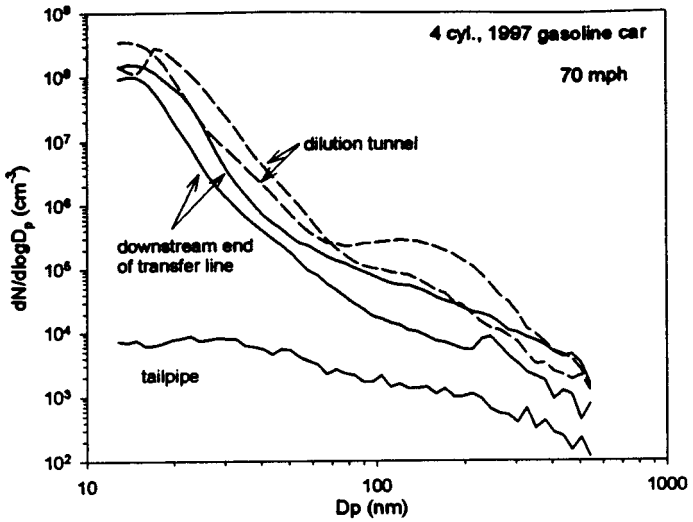

Figure 8. Ejector pump particle size distributions measured at the downstream end of the *insulated/heated* transfer line.

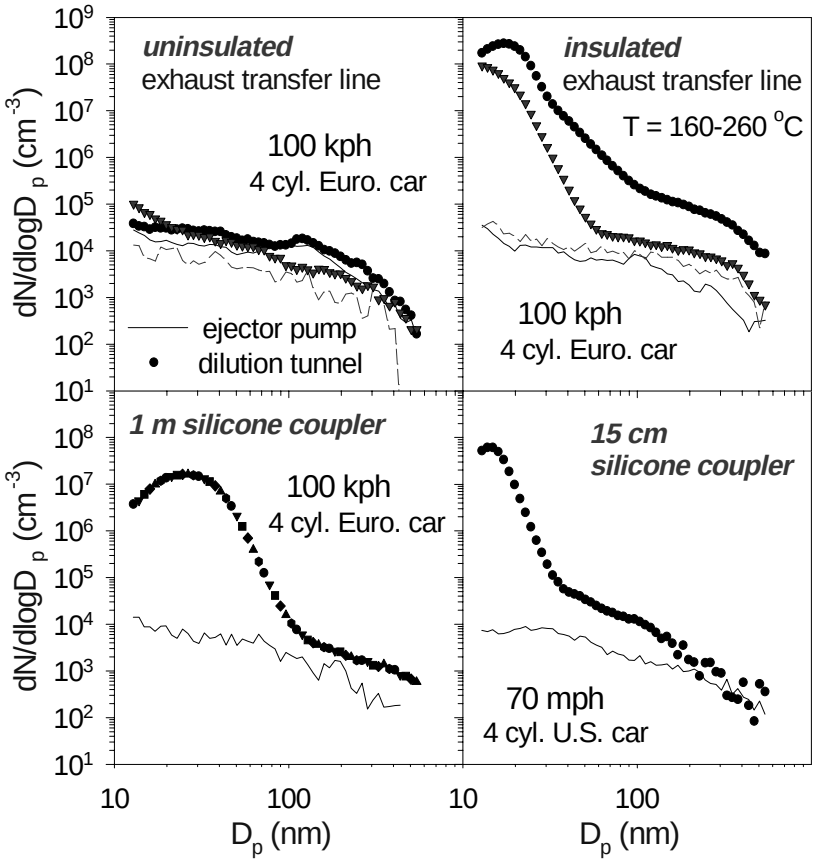

Figure 9. Comparison of particle size distributions for the 4 cylinder European gasoline car taken by ejector pump versus dilution tunnel when using a 1) *uninsulated* transfer line, 2) *insulated* transfer line, 3) *uninsulated* transfer line plus a 1 meter silicone rubber coupler, and 4) *uninsulated* transfer line plus a 15 cm silicone rubber coupler. In the top two panels, two sets of data are compared. Mass emission rates are estimated from the size distributions.

GASOLINE VEHICLE: SILICONE RUBBER COUPLER – The third test configuration utilizes an *uninsulated/unheated* transfer line, but inserts a silicone rubber coupler between the tailpipe and the transfer line. A 1 meter coupler was used in tests at 31, 44, and 63 mph with vehicle E4 and a 15 cm coupler was used in tests at 50, 60, and 70 mph with vehicle US4. Below 60 mph, the dilution tunnel and ejector pump particle size distributions are in good agreement, analogous to what is observed in Figures 3 and 4 without the coupler. In stark contrast, as shown in Figure 9, a very sizable ultrafine mode develops in the tunnel derived size distributions at 63 mph for vehicle E4 and at 70 mph for vehicle US4, although it is not observed in the ejector pump tailpipe measurements. After initially bringing the vehicle speed to 70 mph (or 63 mph for E4), the intensity of this mode increases with time, presumably because the silicone coupler gets hotter. In this case, the ultrafine particles are attributed to desorption / pyrolysis of the silicone rubber material by the hot exhaust gases.

DIESEL VEHICLE – Size distributions of diesel exhaust PM recorded from the tailpipe are compared to dilution tunnel measurements in Figure 10 for the case of the *uninsulated/unheated* transfer line. Each of the distributions, at the various speeds and sampling locations, exhibits an accumulation mode of ~10^8 particles/cm^3 that is centered at roughly 100 nm. At 60 and 70 mph a major discrepancy becomes apparent, namely the tunnel derived distributions are bimodal whereas those from the tailpipe show only the accumulation mode. The ultrafine mode of ~18 nm particles in the tunnel version of the 60 mph test exceeds the accumulation mode by a factor of 10 in particle number. This mode shifts to larger particle size, ~35 nm, and increases another fivefold in intensity in the 70 mph test.

Unlike the accumulation mode, the ultrafine mode is not always stable from one scan to the next. Figure 11 displays a sequence of size distribution scans made after raising the vehicle speed from 50 to 60 mph. The top panel shows the dilution tunnel data, whereas the lower panel gives the corresponding tailpipe measurements. The interpretation is as follows: The accumulation mode represents the distribution of particle sizes actually emitted in the engine exhaust. The increase in exhaust temperature, from raising the vehicle speed, desorbs and/or pyrolyzes hydrocarbon deposits on the j-tube probe used for ejector pump sampling, thereby creating a temporary source of ~20 nm particles. After a short time, the hydrocarbon deposits are “burned off” and this ultrafine mode disappears. The ultrafine mode is not at first observed in the dilution tunnel. It grows in with time as the transfer hose is heated by the vehicle exhaust sufficiently high for the desorption / pyrolysis of the hydrocarbon material to begin. The artifact can persist for a long time because considerable hydrocarbon storage is available in the 7.6 m corrugated hose. It is in principal possible that hydrocarbons stored in the exhaust / aftertreatment systems of the vehicle can also give rise to an ultrafine mode, but in the present situation this is inconsistent with the opposite trends observed for the intensity of this mode in the tunnel versus from the tailpipe.

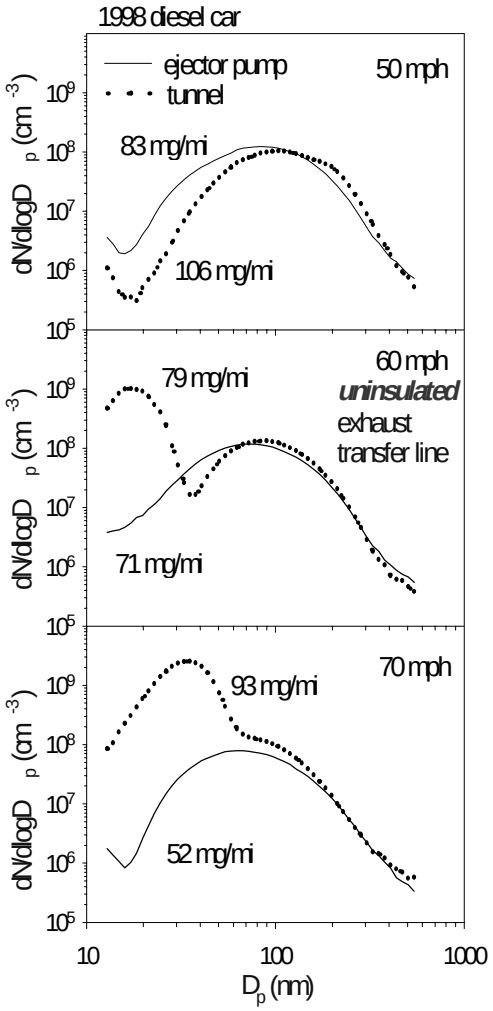

Figure 10. A comparison of diesel vehicle exhaust particle concentration taken with the ejector pump versus dilution tunnel when using the *uninsulated/unheated* transfer line.

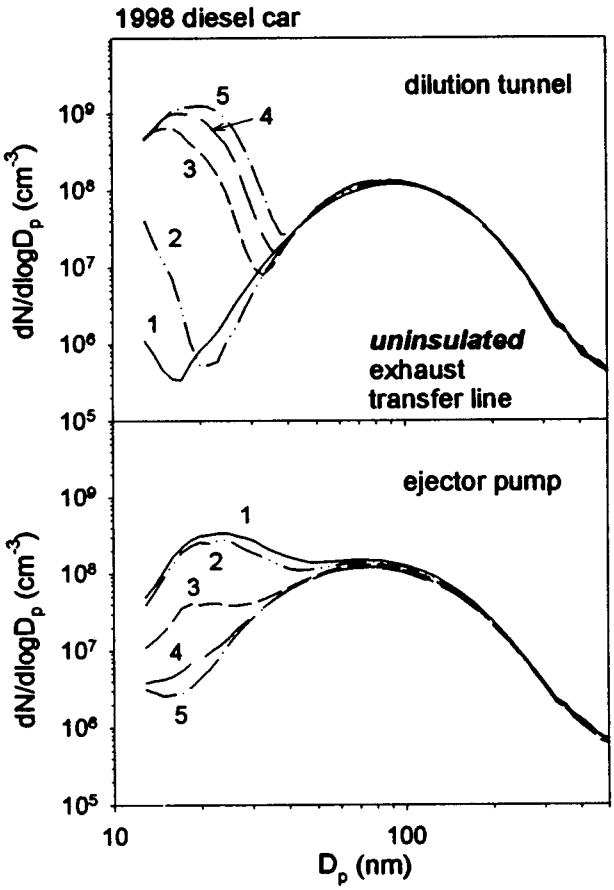

Figure 11. Sequence of size distributions taken at 3 minute intervals following an increase in vehicle speed from 50 to 60 mph. Top panel illustrates the growing in of the 20 nm artifact due to heating of the transfer hose. Bottom panel shows a transient artifact from hydrocarbon build-up that "burns off" of the j-tube sample probe in the tailpipe.

It should be noted that special precautions were observed in these tests for the tailpipe probe. The vehicle was warmed up without the j-tube probe in place. It was stopped and a clean probe inserted into the tailpipe. The vehicle was restarted and taken to the 50 mph, and then 60 mph, test speeds. Hydrocarbons deposited on the probe prior to it reaching the tailpipe exhaust temperature are assumed responsible for the ultrafine particles temporarily observed in the initial few 60 mph size distributions in Figure 11. In other tests, for which the j-tube probe is in place throughout the vehicle warm up cycle, the ultrafine mode can persist for considerably longer than a few scans, presumably from the larger amount of hydrocarbons that deposit during the cold start.

The accumulation mode, both as measured from the tailpipe and dilution tunnel, is reproducible to about ±15%. However, the tailpipe and tunnel versions differ from each other. Examination of Figure 10 shows the accumulation mode to be shifted to smaller particle size by about 25 nm at the tailpipe as compared to the dilution tunnel. Also noticeable is the more rapid falloff of the small diameter side of the distribution in the tunnel measurement. These differences are likely a manifestation of particle coagulation occurring in the transfer hose during transport of the exhaust from the tailpipe to the tunnel.

To get an idea of how important coagulation might be, let us assume that the "typical" particle on the small side of the distribution is 30 nm. An approximate, "hard sphere", rate constant for coagulation between two particles is $k_c = (2)^{-½}\ \sigma\ \langle v \rangle$, where $\sigma = \pi D_p^2$ is the collision cross section between two spherical particles and $\langle v \rangle = (8kT/\pi m)^{½}$ is the thermal mean speed of the particles. Here k represents Boltzmann's constant and m is the particle mass. For particles of unit density at a transfer line temperature of 150 °C, $k_c = 2.1\ 10^{-9}$ cm^3 s^{-1}. Over the 2 - 5 second transit time through the transfer hose, a second order rate law employing this rate constant, and an initial concentration of $5x10^7$ particles/cm^3 (approximate number of particles in the small half of the accumulation mode), predicts that about 1/3 of the "typical" small particles coagulate to form larger particles. This is qualitatively consistent with the shift to larger particles observed in the dilution tunnel.

Because the PM artifacts consist primarily of ultrafine particles, they have negligible, or at least relatively small, effects on PM mass emission rates. This is apparent from comparing the mass emissions that are listed in Figure 10 alongside each size distribution. At 60 mph, the ultrafine artifact, though ten times higher in particle number than the accumulation mode, contributes almost nothing to the particulate mass. At 70 mph, the increase in size of the artifact particles to about 35 nm begins to affect the PM mass emissions; thus, PM mass recorded from the tunnel is 79% higher than what is determined from the tailpipe data. PM emissions measured from the dilution tunnel when using the *insulated/heated* transfer hose lead to qualitatively the same results as observed in Figure 10. The tunnel based size distributions are bimodal at 60 and 70 mph, except that the ultrafine artifact is more pronounced than when using the *uninsulated* hose.

DISCUSSION AND CONCLUSION

The major conclusion to emerge from this study is that hydrocarbon storage in the transfer hose that is used to transport exhaust from the vehicle to the dilution tunnel, and its subsequent release by the hot exhaust gases from the vehicle, can have a profound influence on the number and character of the measured particles. As a result, whether or not one is able to record a representative size distribution using a dilution tunnel depends on a number of factors: Is a gasoline or diesel vehicle being tested? Is the engine displacement large or small? What is the nature of the test: FTP, US06, or steady state? What material is the transfer hose constructed from? And, what is the previous testing history of the transfer hose and tunnel?

Although Kittelson et al.[2,7] has noted occasions when long stabilization periods are needed after switching between diesel engine test modes and attributed this to the release of stored hydrocarbons in the exhaust and sampling systems, the extent to which this can alter the appearance of particle size distributions has not been fully appreciated. Instead, the shortcomings of the dilution tunnel have been seen primarily in terms of how it might limit observation of ultrafine, or nanoparticle, emissions that might occur under “real world” conditions. However, the storage - release artifacts can substantially alter the appearance of vehicle exhaust particle size distributions. In the case of the diesel test vehicle the artifact adds an ultrafine peak to the accumulation mode of diesel exhaust particles producing a bimodal appearance. In the case of recent model gasoline vehicles, the situation is even worse. The artifacts completely overwhelm the exhaust particulate matter. They raise the normal gasoline exhaust levels of 10^4 particles/cm^3 by 3 - 4 orders of magnitude, effectively making the gasoline PM emissions look like those from a diesel vehicle. Moreover, the artifacts can mistakenly be attributed to the test vehicle since they often appear as speed and load are increased, but this is an indirect consequence of the hot exhaust gases.

For recent model gasoline vehicles, as long as the artifacts are avoided, dilution tunnel measurements appear to give accurate renditions of the exhaust particle size distribution. This can be seen from the good, ~20%, agreement between tunnel and tailpipe measurements for vehicle US8 in Figure 3 and at the lower speeds for vehicle US4 in Figure 4, when the *uninsulated* transfer hose is used and remains relatively cool. The high exhaust flow, ~1 m^3/min, and large diameter of the transfer tube, ~ 9 cm, minimize thermophoretic, diffusional, and electrostatic losses en route to the tunnel. Efficient reduction of hydrocarbon emissions by the catalytic converter significantly limits the extent to which adsorption, condensation, and especially nucleation occur. Finally, gasoline exhaust PM concentrations of 10^5 particles/cm^3 are too low for coagulation to be effective. Hence, the agreement between tailpipe and tunnel PM measurements is consistent with the physical characteristics of the dilution tunnel system and the nature of gasoline vehicle exhaust.

Dilution tunnel measurements of transient PM number and size during the FTP, or ECE urban, cycle are likely to be accurate for current model gasoline vehicles. The vehicle speed is moderate, only briefly rising above 55 mph during the FTP, thus limiting the extent to which the transfer hose is heated. One must be more careful with regard to the more aggressive US06 cycle, during which the vehicle speed reaches above 70 mph. Transient measurements of particle number during the US06 cycle reveal the particles to be emitted in a series of narrow peaks in time that coincide with vehicle acceleration.[10] Between these peaks, the particle emissions return to near background levels, suggesting that the artifacts play at most a minor role. In the course of our previous study [10] we sometimes noticed a curious “lifting” of the baseline toward the end of the US06 cycle for small, < ~30 nm, particles, which we now attribute to the hydrocarbon release artifact. Of all the tests, steady state measurements of particle size are the most prone to interference from artifacts, since these are the most likely to be carried out under prolonged high speed or high load vehicle operation.

There are two sorts of difficulties in using a dilution tunnel to measure particle size distributions for diesel vehicles. One is the artifact problem discussed above with respect to gasoline vehicles; the second is coagulation. As with the gasoline vehicles, the artifacts are likely not a problem for FTP or ECE urban drive cycles where high speed driving is not an issue. US06 tests may prove more of a challenge, since the transfer hose for diesel testing is expected to be dirtier than its gasoline vehicle counterpart and, therefore, the stored hydrocarbon material may begin to desorb at a lower temperature. Even if the artifact emissions are avoided, however, dilution tunnel measurements of particle size in diesel exhaust are distorted from what exits the tailpipe. Above tailpipe concentrations of about 10^7 particles/cm^3, particle coagulation begins to play an increasingly important role. Thus, in Figure 10 the mean particle size of 75 nm at the tailpipe grows to about 100 nm by the time the exhaust reaches the dilution tunnel. It can be avoided to some degree by minimizing the length of transfer hose.

In contrast to some reports[11,12] that suggest gasoline vehicle PM number emissions can be nearly as high as those from a diesel vehicle, the present work shows that recent model port fuel injection vehicles have very low particulate emissions, by number and mass, even at high speed operation. This is consistent with the low emissions recently noted during tests over the US06 transient cycle, for which emission rates of < 10 mg/mi were measured.[10] It is also consistent with the very low “baseline” particle emissions observed for a gasoline vehicle by Graskow et al.[13] (however, the random high PM emission “spikes” observed by these researchers were not found for the vehicles in the present study). The present results do not mean that gasoline vehicles never emit high particle concentrations. High PM emissions are readily observed under rich engine operation.[10] They would be expected as well from malfunctioning vehicles, “oil burners”, and perhaps older technology carburetor vehicles.

A number of recommendations regarding motor vehicle exhaust particle measurements are suggested by the present study. 1) The dilution tunnel, transfer hose, and particle sampling probes should be kept clean, especially when measuring newer technology low, and ultralow, emitting vehicles. 2) Separate transfer hoses and dilution tunnels should be used for gasoline and diesel vehicle particle number measurements. While one might argue that a single dilution tunnel may be adequate for PM mass measurements, since the ultrafine mode artifact contributes relatively little mass, this arrangement is certainly not legitimate for particle number measurements.

3) The temperature of the transfer line should be monitored. A temperature of greater than 100 °C is desirable to prevent water condensation and to reduce hydrocarbon vapor deposition; however, temperatures above about 180 °C (perhaps even lower depending on the condition of the transfer hose) are sufficiently high to desorb or pyrolyze stored organic material. 4) Silicone rubber and other similar materials should be avoided. Clean stainless steel is preferable. Even with these precautions, however, it appears that artifacts will be hard to avoid when measuring particle number and size at high speeds and loads.

ACKNOWLEDGMENTS

We would like to thank Mike Loos and Jim Weir for their help and patience in making these combined tailpipe and dilution tunnel particle measurements.

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Nanoparticle formation in diesel vehicle exhaust: A comparison of laboratory and chasing experiments

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Introduction

The currently ongoing public debate on the emission of particulates is focused around air quality and health concerns. Sources of particulates include industrial processes, road transport, and natural
emissions from primary sources and secondary particle formation. Regarding diesel particle emissions there are still large uncertainties during the measurement of particle number/size. It is clear that diesel particles consist of EC, OC, sulfuric acid, and some metal ash. The largest uncertainty is the formation of ultrafine particles of 10-20 nm

size.

Open questions include:
How does exhaust dilution effect PM size distribution?

What is the effect of the fuel sulfur and oxidation catatalyst?

Abstract

Exhaust particle size distributions from a diesel passenger car operated on a chassis dynamometer were measured with a scanning mobility particle sizer (SMPS). The exhaust was either sampled after secondary dilution from the dilution tunnel, or was directly taken from the tailpipe using two mini-diluter systems. The influence of the dilution ratio, the relative humidity of the dilution air, and the residence time of the diluted exhaust has been studied with a special emphasis on the formation of condensed particles.

One important question is how well the exhaust dilution in the emission laboratory reflects real atmospheric dilution? To address real world dilution the Ford Mobile Laboratory (FML) was used. This is a "state of the art" laboratory based on a Ford Transit. While carefully following vehicles under controlled conditions, air from their exhaust plume is continuously sampled and analyzed inside the mobile laboratory. Exhaust particle size distribution data together with exhaust gas concentrations are collected and is compared with measurements obtained in the emission test laboratory.

The test vehicle is a current production turbo charged DI Diesel passenger vehicle with oxidation catalyst which was operated with 350 ppm fuel sulfur. To investigate the effect of the oxidation catalyst and fuel sulfur some chasing experiments were conducted with low (10 ppm S), or with normal S fuel and without oxidation catalyst. Significant effects on the nucleation mode particles were observed, depending on the presence of fuel sulfur and the oxidation catalyst.

Dynanometer exhaust dilution & sampling

Fig. 1: Dynanometer exhaust dilution & sampling. For direct tailpipe sampling two ejector-pump diluters or a rotating disk diluter (Matter Engineering AG) were used.

Effect of residence time

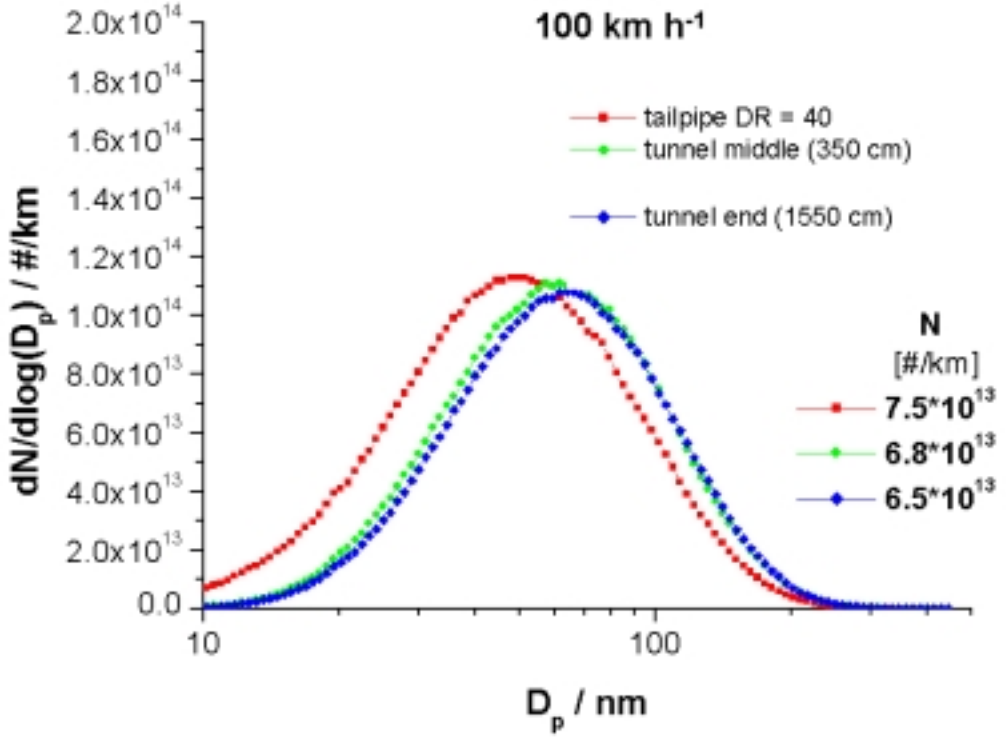

Fig. 2 Comparison of particle size distribution measured at three sampling location with the Matter diluter. The diesel vehicle was running at constant speed of 100 km h^{-1}. The Matter diluter was set to a dilution ratio of 1:40. At the tunnel the total dilution ratio was 1:440.

Effect of residence time

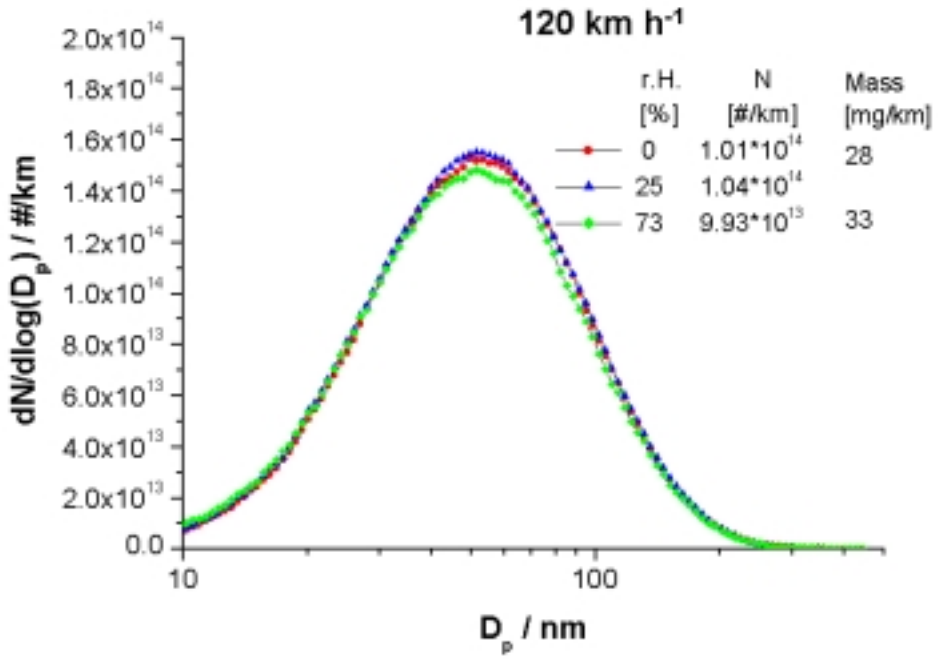

Fig. 3: Comparison of particle size distribution measured with the Matter diluter at the tailpipe of the diesel vehicle. The short sampling line was heated and the exhaust was diluted with humidified synthetic air at the given relative humidity (r.H.) values

On-road chasing of exhaust plume

Fig. 4. Chasing of exhaust plume with Ford Mobile Laboratory

Exhaust chasing of diesel vehicle

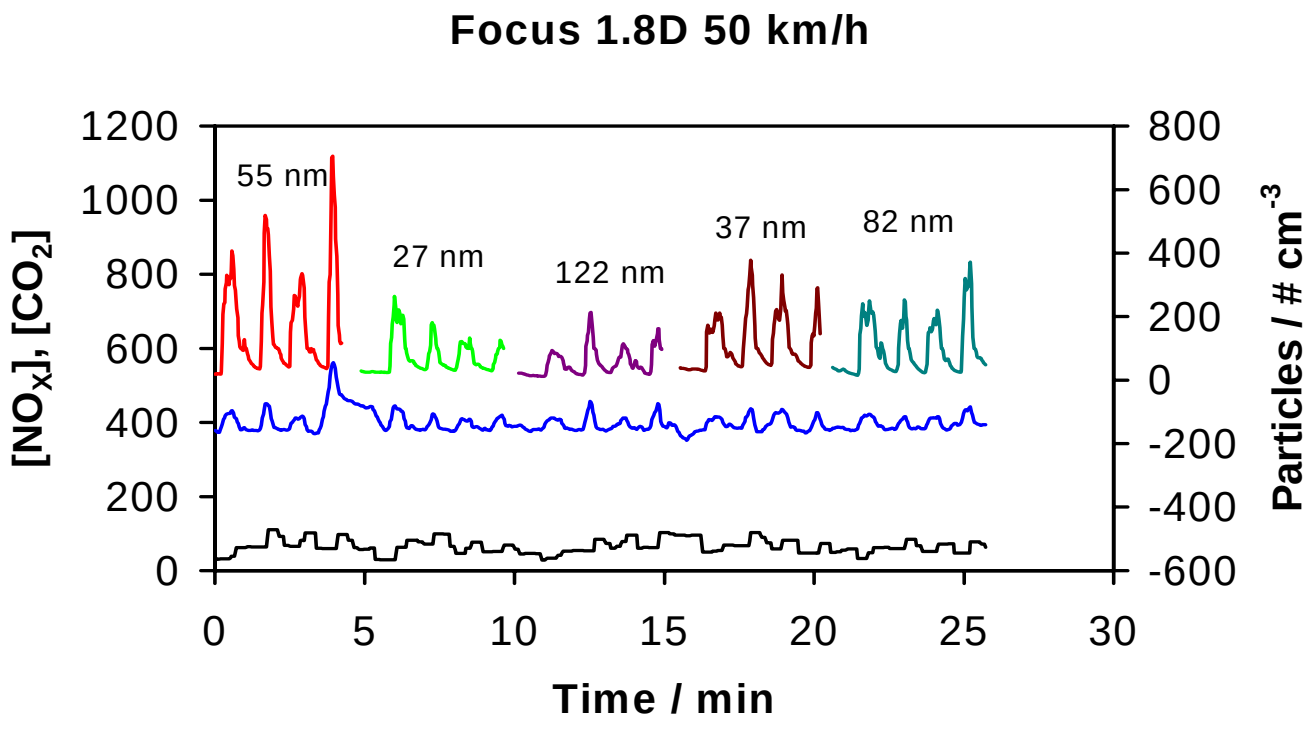

Fig. 5. NO_x, CO_2 and particles measured at a fixed SMPS size bin while drive in and out of the exhaust plume of the diesel test vehicle.

PM size distribution during chasing of diesel vehicle

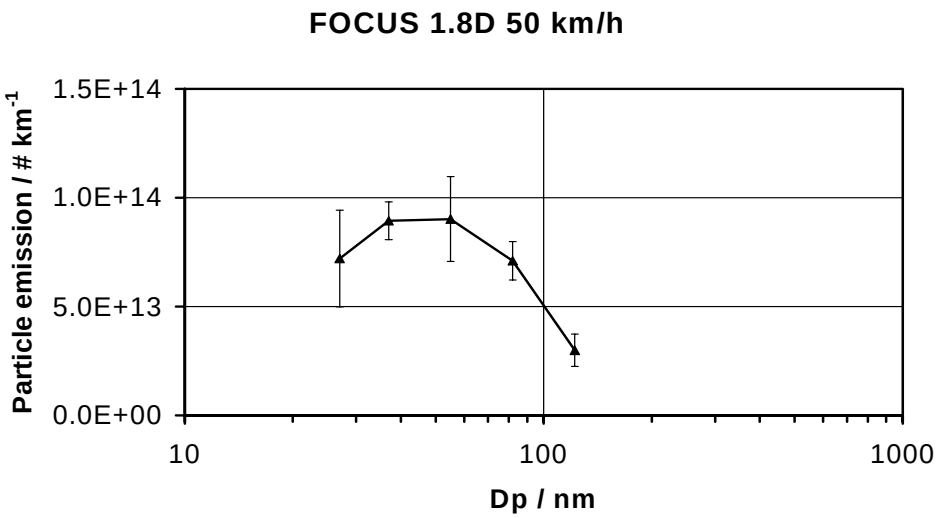

Fig. 6. Constructed size distribution from chasing experiments. The dilution ratio is calculated from the measured NO_x and CO_2 concentration and the known NO_X and CO_2 emission at constant speed.

PM size distribution during chasing at different speeds

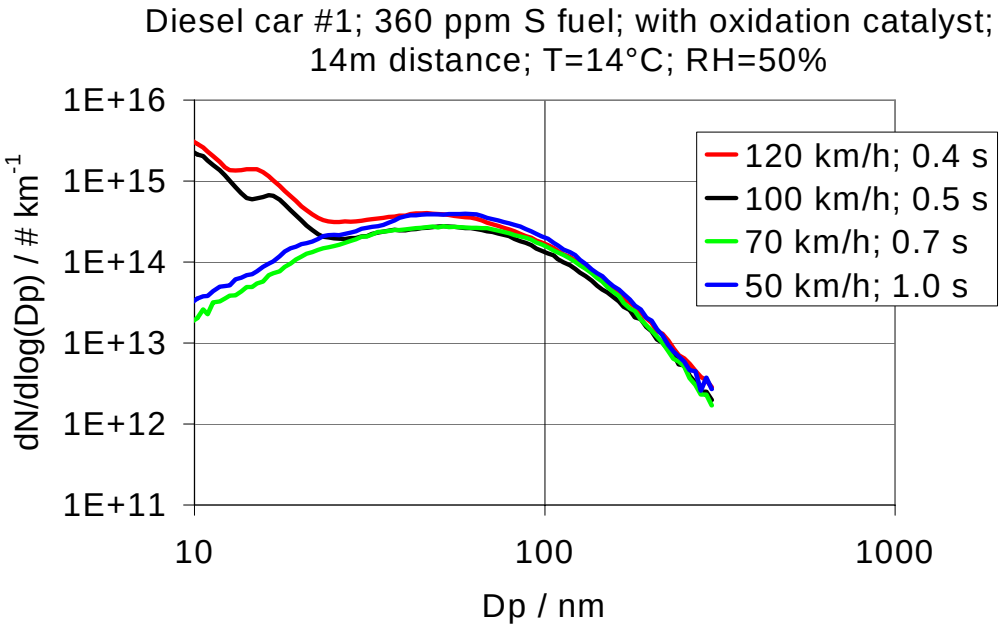

Fig. 7: Size distributions measured at different speeds in the exhaust plume of the test vehicle. running on 360 ppm S fuel and oxidation catalyst.

PM size distribution during at different speeds at dynanometer

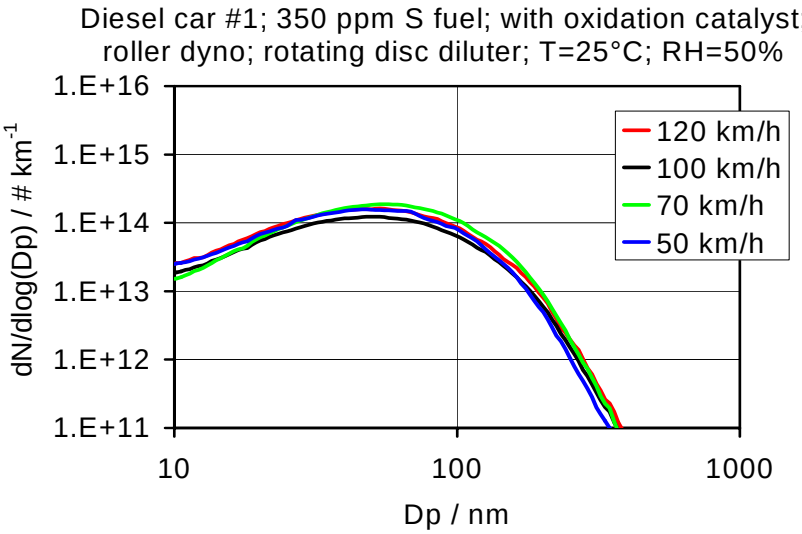

Fig. 8: Same test vehicle as Fig 7 operated at different speeds at chassis dynanomter. No nucleation mode particles were observed with rotating disc diluter.

PM size distribution during chasing at different speeds: no oxidation catalyst

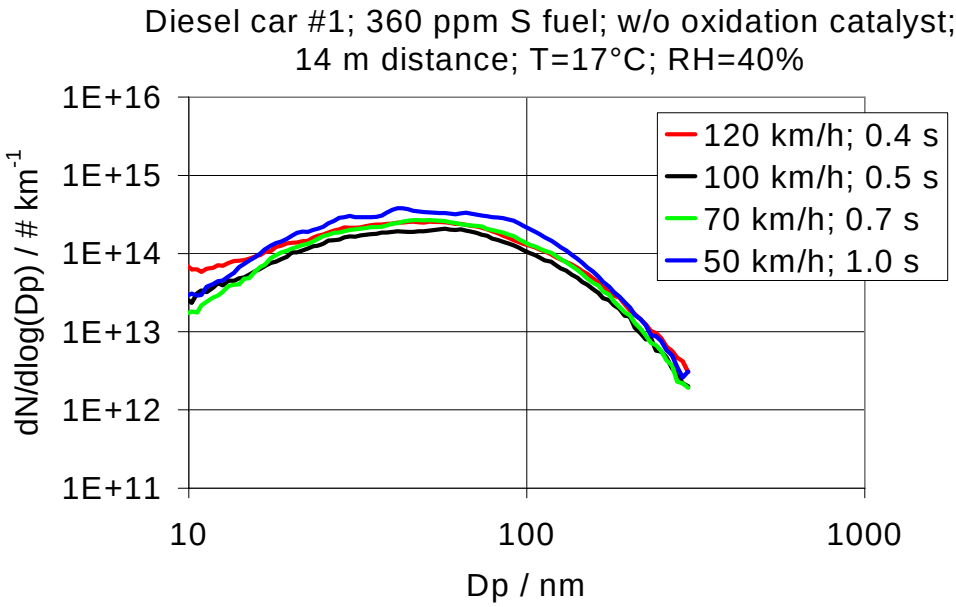

Fig. 9. PM size distributions measured in exhaust plume of test vehicle with 360 ppm fuel S and no oxidation catalyst.

Fuel-S and oxidation catalyst effect

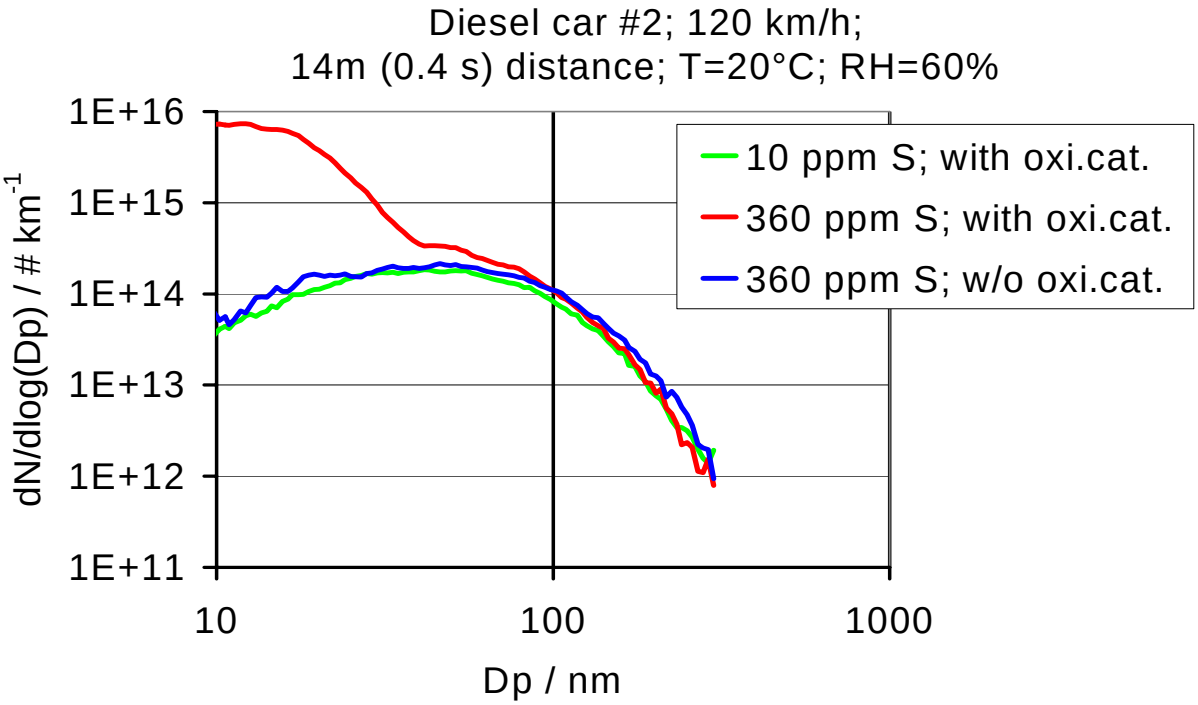

Fig. 10. PM size distributions measured in exhaust plume of test vehicle with different S fuel, with and w/o oxidation catalyst

Time evolution of nucleation mode particles

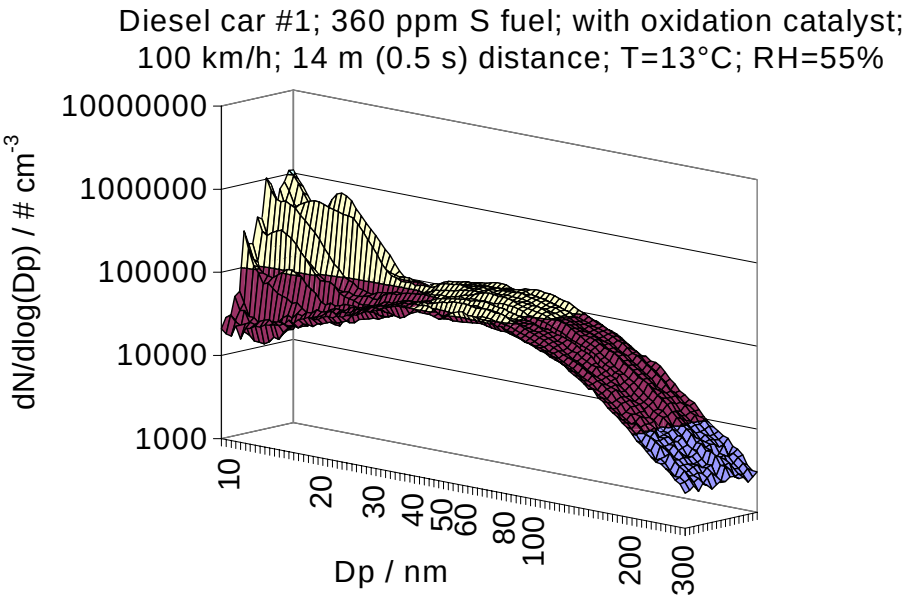

Fig. 11. Evolution of nucleation mode in PM size distribution during 40 min chasing at 100 km h^{-1}.

Evolution of nucleation mode particles and vehicle parameters

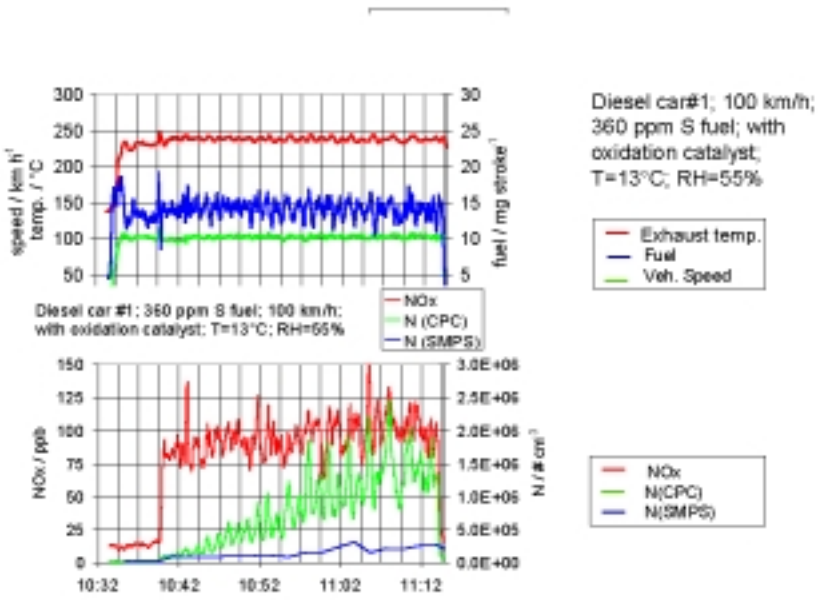

Fig. 12. Evolution of number emission (CPC and integrated SMPS) in PM size distribution during 40 min chasing at 100 km h^{-1} and fuel consumption, exhaust temperature and vehicle speed.

Summary

- Diesel vehicle particle size distributions measured at the dynanometer were unimodel (340 ppm S; with oxidation cat)

- Number/size distribution varied depending on sampling condition

- Good agreement of tailpipe sampling and exhaust chasing for soot mode particles

- Nucleation particles occur during atmospheric dilution only at 100 and 120 km h^{-1}, if 360 ppm S fuel and oxidation catalyst are used

-

- Using 10 ppm S fuel, no nucleation particles were observed

R. Vogt and V. Scheer "Particles in diesel vehicle exhaust: A comparison of laboratory and chasing experiments".
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Graz 19-21.6.2002, pp 79-84, Univ.-Prof. Dr. R. Pischinger, Graz, ISBN 3-901351-59-0.

Particles in diesel vehicle exhaust: A comparison of laboratory and chasing experiments

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ABSTRACT

Exhaust particle size distributions from a diesel passenger car operated on a chassis dynamometer were measured with a scanning mobility particle sizer (SMPS). The exhaust was either sampled after secondary dilution from the dilution tunnel, or was directly taken from the tailpipe using two mini-diluter systems. The influence of the dilution ratio, the relative humidity of the dilution air, and the residence time of the diluted exhaust were studied with a special emphasis on the formation of condensed particles.

To address real world dilution a mobile laboratory was used. While carefully following a test vehicle under controlled conditions, air from the exhaust plume is continuously sampled and analyzed inside the mobile laboratory. Exhaust particle size distribution data together with exhaust gas concentrations were collected and are compared with measurements obtained in the emission test laboratory. First results show good agreement for soot mode particles measured in the exhaust plume, if compared with the emission lab. However, significant differences were observed for nucleation mode particles, which occur only under real atmospheric dilution conditions, depending on the presence of the oxidation catalyst, fuel sulfur content and the vehicle speed.

Key words: Diesel particles, size distribution, exhaust dilution, real world dilution, oxidation catalyst, fuel sulfur

1. INTRODUCTION

The current public debate on the emission of particulate matter is focused on ambient air quality and health concerns. Sources of particulates include industrial processes, road transport, and natural

emissions from primary sources and secondary particle formation. Regarding diesel particle emissions there are still large uncertainties on the measurement of number/size distributions. It is well understood that diesel particles consist of elemental carbon, organic carbon, sulfuric acid, and some metal ash. While it is widely established that the number/size distribution of the soot mode particles has its maximum at a mobility diameter of 50-80 nm and that the particle mean diameter is independent of engine technology (ACEA (1999); Maricq et al. (1999)), a large uncertainty remains with the occurrence of ultrafine particles of 10-20 nm

size. Close to an urban street, or at a parking lot next to an Autobahn, the number/size distribution is often dominated by particles in the 10-30 nm size range (Wahlin et al. (2001); Wehner et al. (2001)). However, it was shown that this size mode is made of volatile material, which may be evaporated using a thermodenuder and that the particles do not have a solid core (Wehner et al., (2001).

It has been suggested that the dilution conditions applied in the emission test laboratory have a significant influence on the presence of nucleation mode particles in the 10-30 nm size range (Shi & Harrison (1999); Abdul-Khalek et al. (1999)). Here we investigate under carefully defined conditions the influence of parameters like the dilution method, dilution time and relative humidity of the dilution air on the measured size distribution. The next important question is, how well the exhaust dilution applied in the emission laboratory

reflects real atmospheric dilution? Measurements using the Ford Mobile Laboratory which closely followed the exhaust plume of a diesel passenger car are presented.

2. EXPERIMENTAL METHODS

Test were performed with a European model diesel passenger car (1.8l turbo-charged DI and oxidation catalyst, EURO 3) and regular sulfur fuel (approx. 350 ppm S). The vehicle was warmed up at a chassis dynamometer for 10 min at constant speed. Subsequently, three size scans (each 5 min measurement and 2 min SMPS down scan) were measured in conjunction with three gas bag samples and three filters for PM mass. As stated below some experiments were conducted with low sulfur fuel (10 ppm S), or with the oxidation catalyst removed.

2.1. Exhaust Sampling in the Emission Laboratory

Two types of diluters were explored: the ejector diluter (Dekati Inc.) and the rotating disk diluter (Matter Engineering AG). Both diluters were operated with particle free air and connected through a 10-15 cm stainless steel line (6mm diameter) directly to the tailpipe. In order to avoid artifacts through evaporation of condensed material this sampling line was regularly cleaned and heated to 220°C. Two ejector diluters (dilution ratio of about 1:9 each) were cascaded, connected by a reservoir volume which inserted 2 s residence time in order to provoke nucleation. The diluters were not heated.

The rotating disk diluter was operated at a dilution ratio between 40 and 100. For some experiments the dilution air was humidified between 0 % and 73 % relative humidity. The test vehicle exhaust is conducted via an insulated and heated corrugated stainless steel hose (6 m length) to a stainless steel dilution tunnel. Particles are sampled on paper filters from the tunnel following the legislated procedure. For particle size measurements an ejector diluter is connected at the same position.

2.2. Sampling from the exhaust plume with the Ford Mobile Laboratory

The Ford Mobile Laboratory (FML) was constructed on the basis of a Transit van to operate as a stand-alone experimental platform for the investigation of ambient particles at one location for a given time period. For these experiments an on-board power supply has been installed which allows operation of pumps, SMPS, CO and NO_X analyzers and data acquisition instruments while driving. Sampling is performed through a 6 mm stainless steel inlet and 12 mm sampling line which opens in front of the radiator grill. The FML was driven at varying distances to the same test vehicle which was used in the emission test facility. Tests are performed on a high speed test track in the absence of other vehicles.

3. RESULTS

3.1. Comparison of dilution conditions

In Fig. 1 particle size distributions are shown which were measured with the diesel passenger car running with constant speed at 100 km h^{-1} and 120 km h^{-1}. The Dekati and Matter diluters were connected directly to the exhaust pipe. At 120 km h^{-1} the particle number is somewhat larger (approx. 20 %) than at 100 km h^{-1}, however the Dekati and Matter diluters show the same tendency. The two dilution systems are in reasonable agreement (2-20%), considered that the measurements were done on different days and no absolute calibrations of the diluters or the SMPS were available. During none of the experiments a nucleation mode was observed.

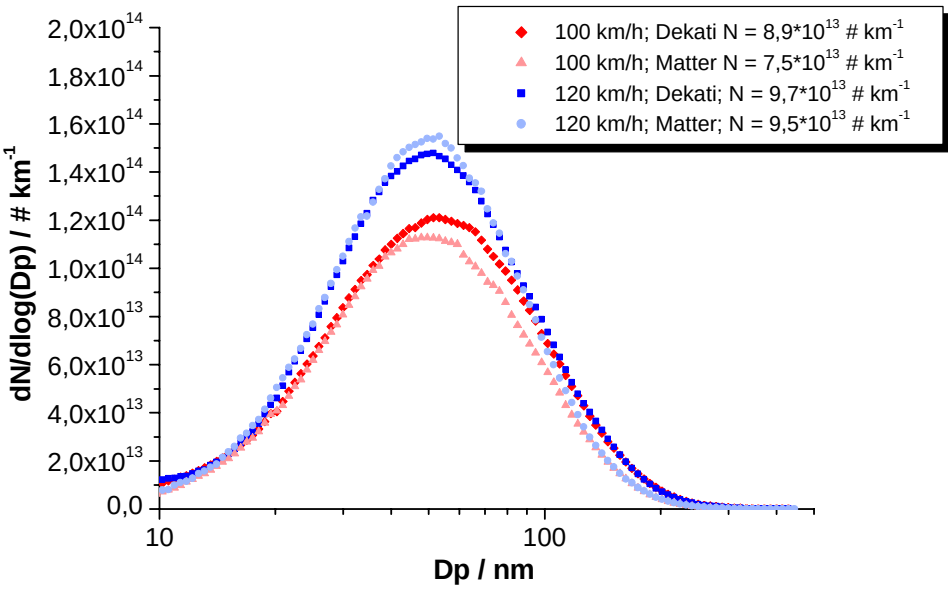

Fig. 1. Comparison of particle size distribution measured after dilution at the tailpipe of the diesel test vehicle with a rotating disk (Matter) and two ejector type (Dekati) diluters at 100 km h^{-1} and 120 km h^{-1}. The Matter diluter was set to a dilution ratio of DR=1:100; two Dekati diluters were cascaded (DR=1:80), connected via a reservoir volume which inserted 2 s of residence time.

In Fig. 2 size distributions are shown which were measured at three different sampling locations: 1.) directly at the tailpipe, 2.) after 6 m of heated and insulated transfer hose sampled at the tunnel middle at 3.5 m, and 3.) after 6 m of heated and insulated transfer hose sampled at the tunnel end at 15.5 m. Depending on the residence time of the particles in the transfer line and dilution tunnel the maximum of the size distribution is shifted towards larger particle diameters. Due to coagulation the integrated particle number decreases with increasing residence time in the dilution system.

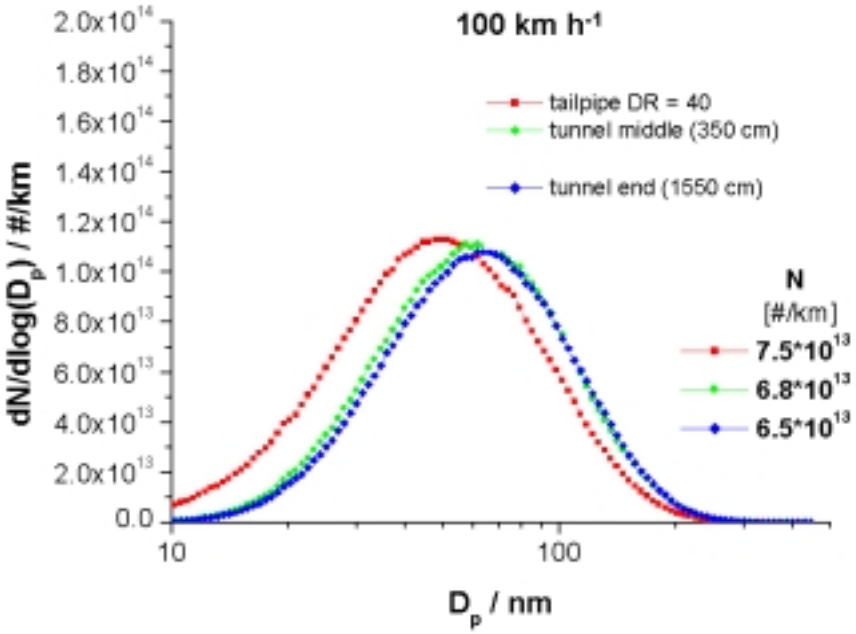

Fig. 2. Comparison of particle size distribution measured at three sampling location with the Matter diluter. The diesel vehicle was running at constant speed of 100 km h^{-1}. The Matter diluter was set to a dilution ratio of 1:40. At the tunnel the total dilution ratio was 1:440.

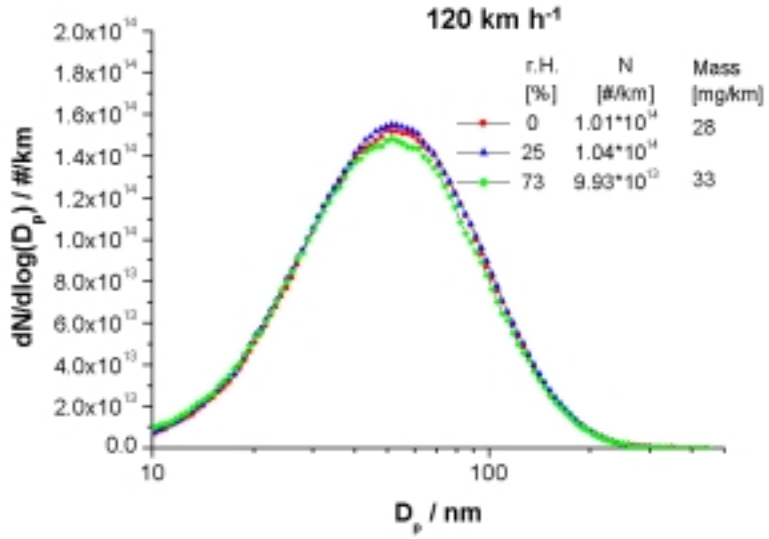

Fig. 3. Comparison of particle size distribution measured with the Matter diluter at the tailpipe of the diesel vehicle. The short sampling line was heated and the exhaust was diluted with humidified synthetic air at the given relative humidity (r.H.) values.

A dilution parameter which may have an impact on the measured exhaust particle size distribution is the relative humidity of the dilution air. Higher relative humidity could lead to particle growth, or restructuring (Weingartner et al. (1997)), or could enable particle nucleation and subsequent growth to a detectable size range. A dilution air humidifier was constructed and connected to the Matter diluter which was applied to the tailpipe. The diesel test car was operated at 120 km h^{-1}. Independent of the relative humidity all size distributions were alike and had the maximum around 50-60 nm. No particle mode around 10-20 nm was observed which would have indicated formation of secondary particles (Fig. 3).

3.2. Real world particle emissions

The Ford Mobile Laboratory (FML) was utilized to measure the particle size distribution in the exhaust trail of the same diesel vehicle previously tested in the emission lab. The measurements were performed on a high speed test track at 14 to 100 m distance to the test vehicle. Clearly, exhaust particles and gases, i.e. NO_x, CO and CO_2 could be measured, if the FML was inside the exhaust plume. From the known NO_x emission of the test vehicle and the measured concentration inside the plume the atmospheric dilution ratio of 1000 to 9000 was calculated. As in the emission laboratory the maximum of the size distribution was found around 50-60 nm. The total amount of particles emitted agrees well with the number determined on the chassis dynamometer. No second mode of smaller particles was observed at 50 km h^{-1} and 70 km h^{-1} (Fig. 4). However, at 100 km h^{-1} and 120 km h^{-1} additional 10 - 20 nm particles became apparent, which is in contrast to the observations at tailpipe dilution, or in the dilution tunnel. The bimodal size distribution indicated the presence of nucleation particles in addition to the soot mode. If the chasing distance was increased from 14 m (0.5 s) to 100 m (3.7 s) the bimodal shape was not effected.

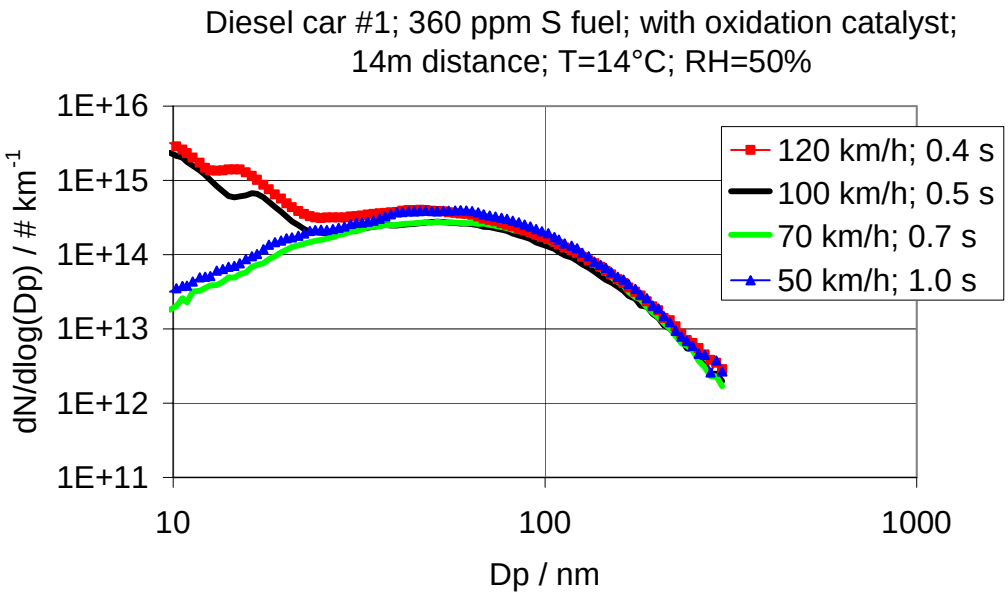

Fig. 4. Size distributions measured at different speeds in the exhaust plume of the test vehicle. running on 360 ppm S fuel and oxidation catalyst.

3.3. Fuel sulfur and oxidation catalyst effect

To further explore the formation conditions of the nucleation mode and the role of fuel sulfur the diesel passenger car was operated on low (10 ppm S) sulfur fuel and the particle size distribution measured with the FML chasing the exhaust plume. As shown in Fig. 5 even at 120 km h^{-1} a uni-modal size distribution and no nucleation mode particles were observed.

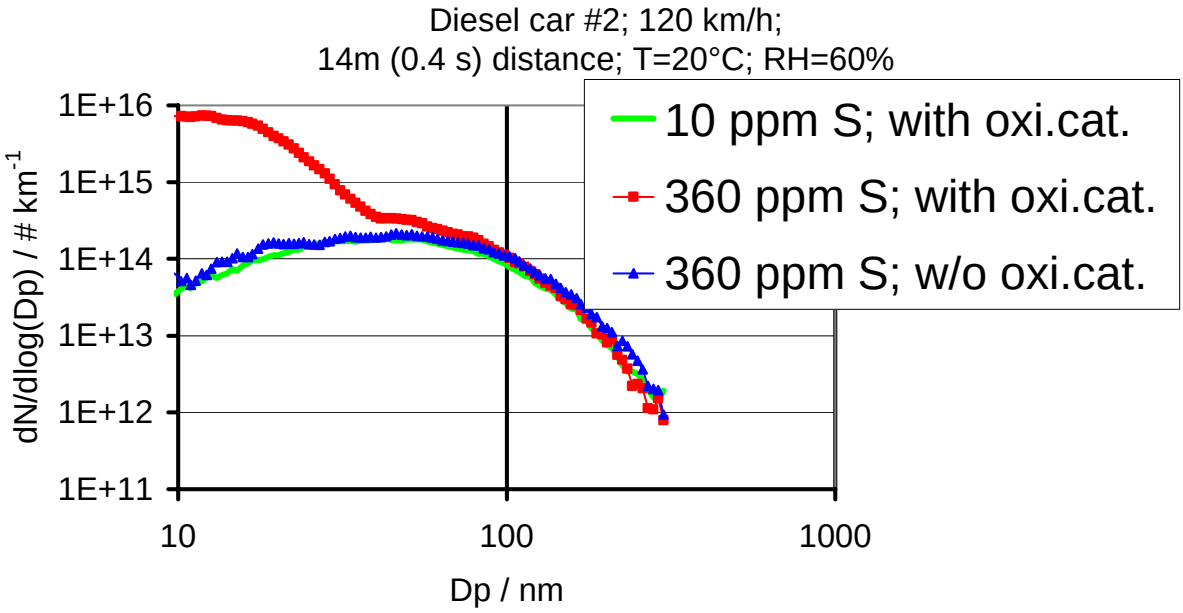

Fig. 5. PM size distributions measured in the exhaust plume of a test vehicle with different S fuel, with and w/o oxidation catalyst.

In the next experiment the fuel was changed back to regular sulfur content (360 ppm S), and a similar bimodal size distribution was observed as shown in Fig. 4. If the oxidation catalyst was removed the nucleation mode was absent and a size distribution very similar to the experiment with the 10 ppm S fuel and oxidation catalyst present.

These experiments show that the presence of fuel sulfur and of the oxidation catalyst are necessary to produce nucleation mode particles. It is likely that the fuel sulfur is oxidized to sulfuric acid which would form nucleation droplets in the exhaust plume. If the bulk of the 10-20 nm particle is made of sulfuric acid/water, or if hydrocarbons condense on the sulfuric acid nuclei (Tobias et al. (2001)) remains open.

Conclusions

In this work the effects of exhaust dilution method, sampling location and dilution parameters were investigated under carefully controlled conditions. The emphasis of the work is to better understand dilution processes and to define laboratory 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; 340 ppm fuel sulfur content) under laboratory conditions were uni-modal with a maximum of the particle mobility diameter around 50 to 70 nm. Depending on the sampling position (tailpipe versus different positions at the dilution tunnel) and on the residence time the maximum of the size distribution shifted to a larger particle diameter and the total number decreased. This is consistent with particle coagulation occurring during the residence in the sampling line and dilution tunnel.

The different tailpipe dilution systems were in reasonable agreement; no nucleation mode was observed despite introducing a residence time between primary and secondary dilution, or dilution with humidified air.

Particle size distributions were measured in the exhaust plume of the same diesel passenger car at a high speed test track using a Mobile Laboratory. The measurements showed good agreement of the size and number of the soot mode particles. However, at 100 and 120 km h^{-1}, using 360 ppm sulfur fuel and the regular oxidation catalyst mounted, an additional nucleation mode at 10-20 nm was observed. Using low sulfur fuel (S<10 ppm) this nucleation mode disappeared which is strong evidence for the fact that fuel sulfur is oxidized to sulfuric acid which forms efficiently particle nuclei.

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