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**The effects of the catalyst and fuel sulfur on PM emissions -
wind tunnel and dynamometer measurements**

The effects of the catalyst and fuel sulfur on PM emissions – wind tunnel and dynamometer measurements

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Introduction

There are a number of popular conceptions about motor vehicle PM emissions that are not consistent with many recent dynamometer measurements. These include "Although gasoline vehicle PM mass emissions are lower than those of diesel vehicles, their particle number emissions are comparable", "New direct injection diesel vehicles emit more particles than older technology vehicles", and "Real world emissions include more nanoparticles than are measured in dynamometer tests". Actually, chassis dynamometer tests on current model gasoline vehicles indicate them to have much lower particle number emissions than their light duty diesel counterparts. And recent reports on direct injection diesel vehicles show them to have equal or lower particle number emissions than indirect injection engines. Nuclei mode particles likely play an important part in these inconsistencies. Nuclei particles observed in urban areas are often attributed to diesel vehicle emissions, specifically to the sulfur compounds contained in the fuel. To complicate matters, the nuclei mode is very sensitive to the manner in which the vehicle exhaust is diluted and cooled. Therefore, the aim of the present work is to examine in a systematic way how fuel sulfur, the catalytic converter, and the manner of exhaust dilution affect PM emissions.

Gasoline Vehicle PM emissions

Because the catalyst efficiently removes hydrocarbons from the exhaust gas, it is a common conception that it can also oxidize soot. However, as Figure 1 illustrates, this is not the case. The PM emissions integrated over the US06 drive cycle are nearly identical irrespective of whether or not an active catalyst is present. Tests of 2 vehicles over the FTP and US06 drive cycles show the catalyst to have less than a 50% effect on particle number emissions, usually much less, and a negligible effect on the mean diameter.

In fact, consideration of the flow through a typical catalyst suggests that it should not affect particles. At 15 cm long and composed of 1 mm x 1 mm channels, the flow ranges from ~4 – 16 cm³/s per channel at 250 – 450 C for the exhaust flow of a light duty vehicle. Under these conditions the flow is laminar, with a transit time of 10 – 40 ms. This implies Brownian displacements of < 0.01 mm for 100 nm particles and < 0.1 mm for 10 nm particles, implying that the overwhelming number of particles never contact the catalyst wall. Hence, soot removal by the catalyst is inefficient.

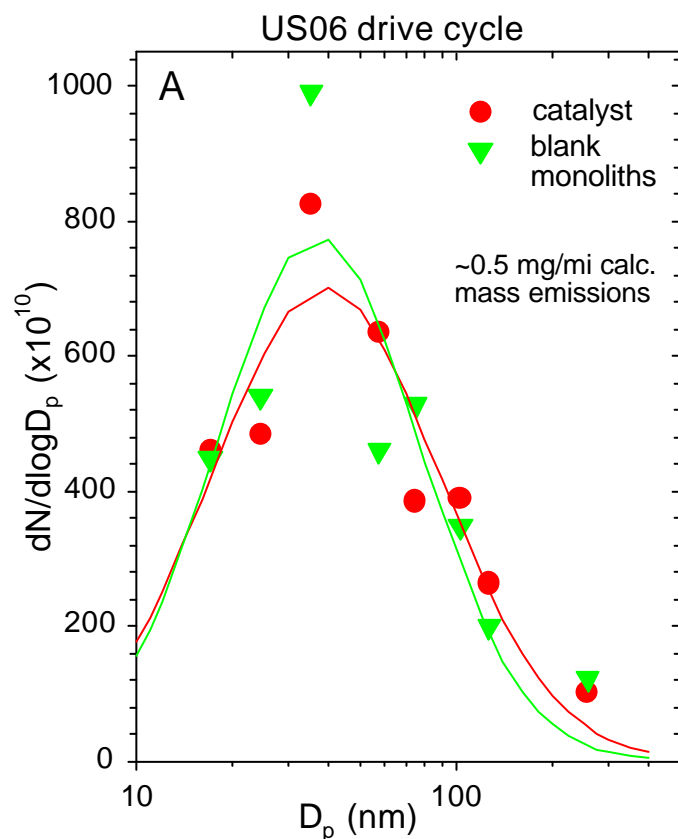


Figure 1. Catalyst effect on gasoline vehicle PM

Although particle number measurements show the catalyst to have a small effect if any, filter measurements apparently show otherwise. Figure 2 compares gravimetric determinations of PM mass to the mass calculated from the corresponding size distributions. For a catalyst equipped vehicle, the filter and size distribution measurements are in agreement within the measurement uncertainties. However, when a blank substrate replaces the catalyst, the filter measurements increase about five fold, whereas the calculated masses show no change.

This inconsistency can be explained by the adsorption onto the filter of gaseous hydrocarbons that are present in much higher concentrations when the active catalyst is not present. Shauer and Cass have reported similar gas phase adsorption in the case of diesel vehicle tests. FID measurements by Hochgreb and Kayes show a step decrease from in front of to behind the filter, supporting this explanation.

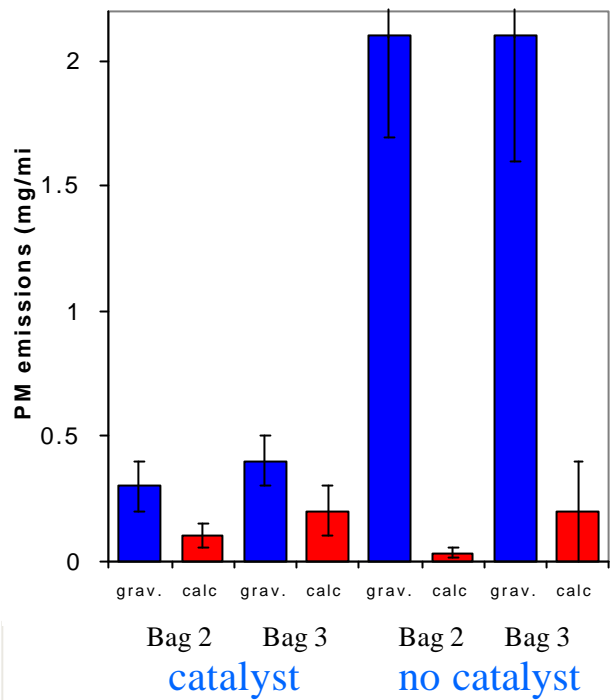


Figure 2. Effect of catalyst on PM mass measurement

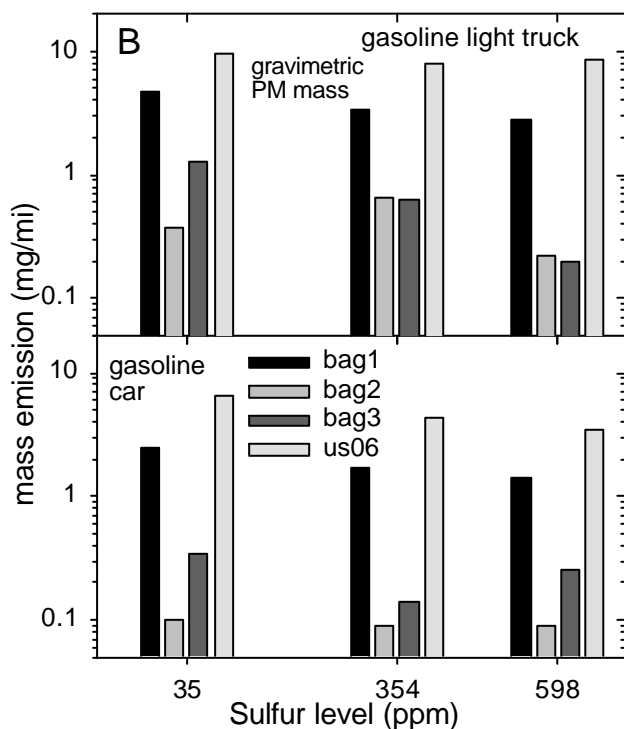
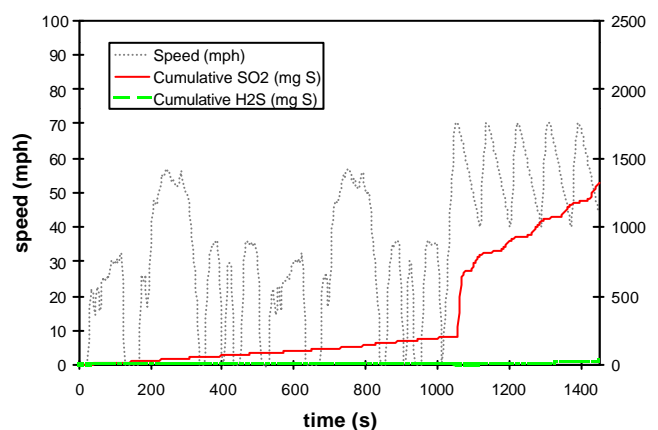


Figure 3. Sulfur effect on PM mass emissions

Three vehicles were tested over the FTP and US06 drive cycles for three levels of fuel sulfur ranging from 35 ppm to 600 ppm S. These dilution tunnel measurements show the sulfur level to have no effect on PM mass, particle number, and average particle size. Figure 3 illustrates this for the gravimetric PM mass measurements for two of the test vehicles.

A comparison of sulfur emissions to fuel consumption shows that the three way catalysts of these test vehicles store sulfur, and then release it during high speed / load conditions, as illustrated in Figure 4. The sulfur is emitted almost entirely as SO₂.

Figure 4. (right) Cumulative SO₂ & H₂S emissions over bags 1&3 of the FTP and high speed accelerations



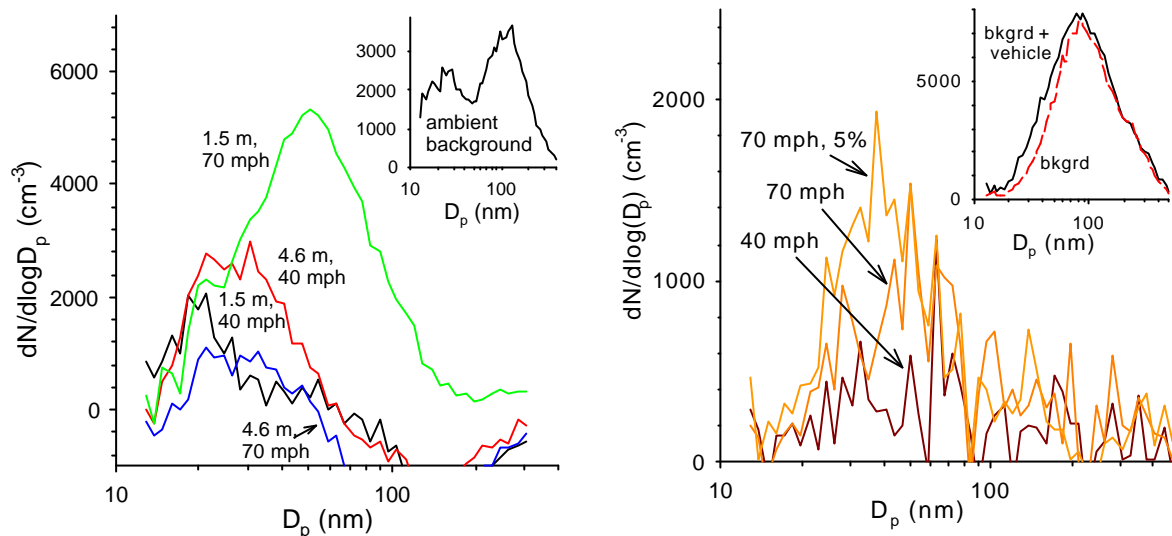


Figure 5. Wind tunnel measurements of gasoline vehicle particle emissions at steady state operation

Figures 5 and 6 illustrate gasoline vehicle PM emissions measured in a wind tunnel. To ensure that emissions from one portion of the test do not interfere with other portions, the wind tunnel was constantly supplied by fresh (ambient) air. Steady state particle emissions are barely visible above the ambient background, as illustrated by the insets in Figure 5. Subtraction of the background shows particle emissions to lie in the 10 – 100 nm range, but no significant nuclei mode is observed.

As the inset to Figure 6 demonstrates, particle emissions from gasoline vehicles primarily occur during transient operation, in this case repeated accelerations from 40 mph to 70 mph. The size distribution of the transient particles is similar to the steady state versions in Figure 5. While the particle concentration during the transient is roughly 5 times the steady state concentration, the PM emissions are still very low, consistent with the dilution tunnel gravimetric measurements of < 2 mg/mi.

Finally, Figure 6 demonstrates that the wind tunnel measurements also show the particle emissions from recent model gasoline vehicles to be independent of fuel sulfur level over the range of 30 – 990 ppm S (at least for the production 3way catalyst of the test vehicles).

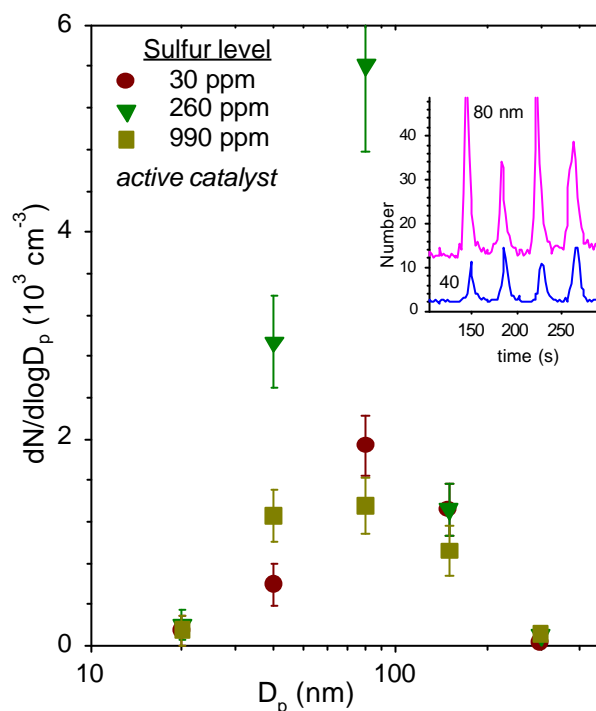


Figure 6. Wind tunnel measurements of transient PM emissions at various fuel sulfur levels

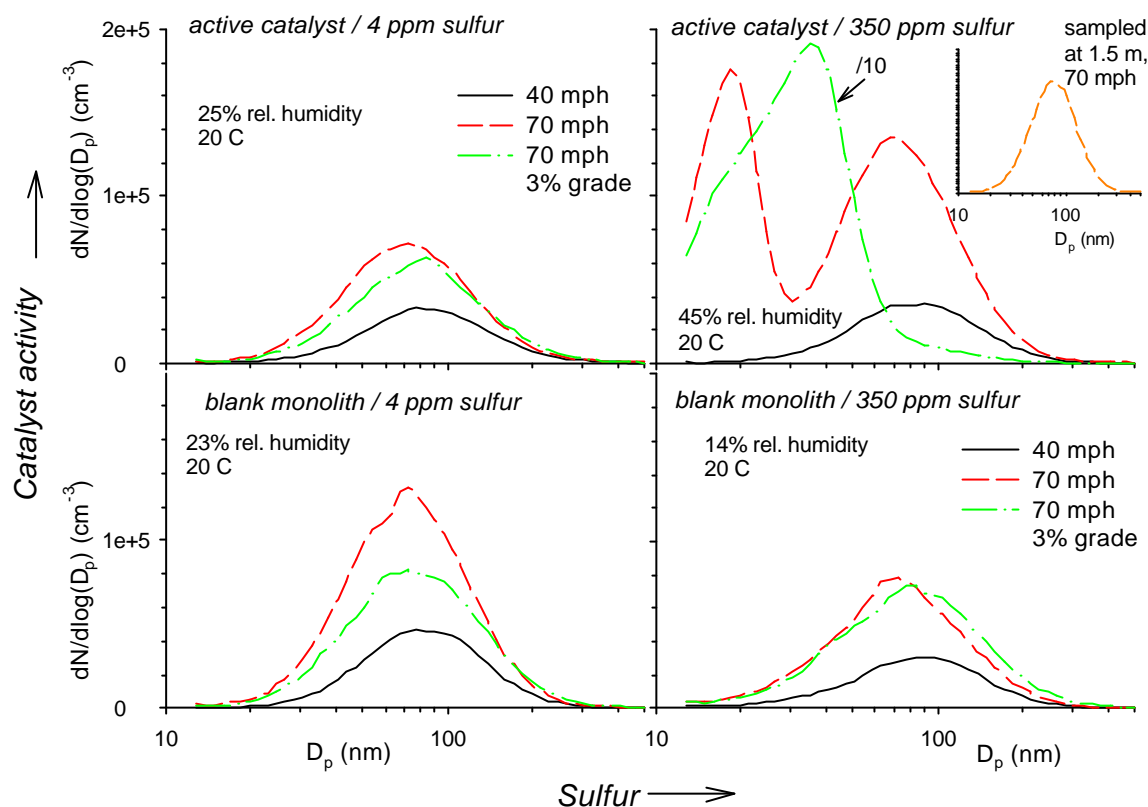


Figure 7. Light duty diesel truck PM size distributions recorded in a wind tunnel as a function of fuel sulfur level and catalyst activity.

Light duty diesel vehicles

A systematic study of the influence of fuel sulfur and the catalyst on PM emissions was conducted by identical tests of a light duty, direct injection, turbocharged, diesel truck run using blank substrate / 4 ppm sulfur fuel, blank substrate / 350 ppm sulfur fuel, active catalyst / 4 ppm sulfur fuel, and active catalyst / 350 ppm sulfur fuel. In each case, the vehicle was run in a wind tunnel (continually supplied with fresh air) at steady state at 40 mph, 70 mph, and at 70 mph with a 3% grade. Emissions during repeated 40 – 70 mph accelerations were also recorded.

As Figure 7 demonstrates, when the vehicle is operated with 3 of the 4 combinations, namely those in which the high sulfur fuel and active catalyst are not simultaneously present, single mode lognormal size distributions characteristic of soot are observed. Tailpipe measurements indicate the particle number concentrations to peak at 10^8 particles/cm³, so that the dilution ratio at the measurement point 5.5 m behind the vehicle is roughly 1000:1. In these tests the vehicle and wind speeds are equal. The tailpipe measurements indicate that the particle concentration in the exhaust varies very little between the three steady state operating conditions, although the mean particle size shifts to smaller diameter, by ~10 nm, as the speed and load increase. The increase in particle emissions in Figure 7 with increased speed and load is, therefore, due to the fact that the exhaust flow increases more rapidly with vehicle speed and load than does the wind speed; thus, effectively the dilution ratio decreases.

When high sulfur fuel is used and an oxidation catalyst is simultaneously present, then a nuclei mode is observed above a threshold speed / load level. In these tests, only the soot mode is present at 40 mph, whereas a nuclei mode is present at the 70 mph and 70 mph with 3% grade operating conditions. However, it is likely that for other vehicles and catalyst formulations the threshold point can change.

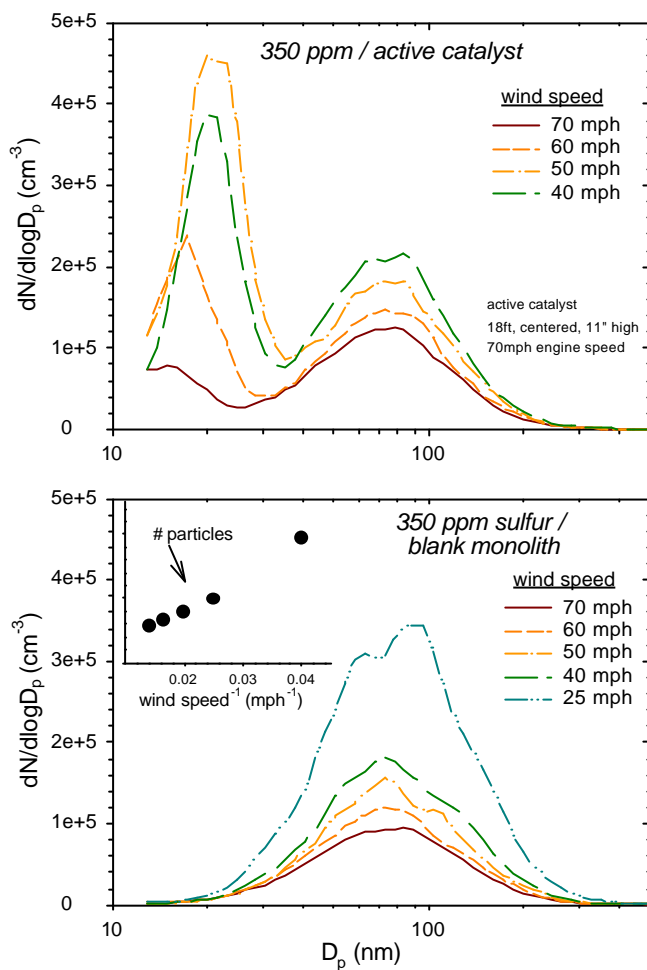


Figure 8. Effect of wind speed on PM size distributions.

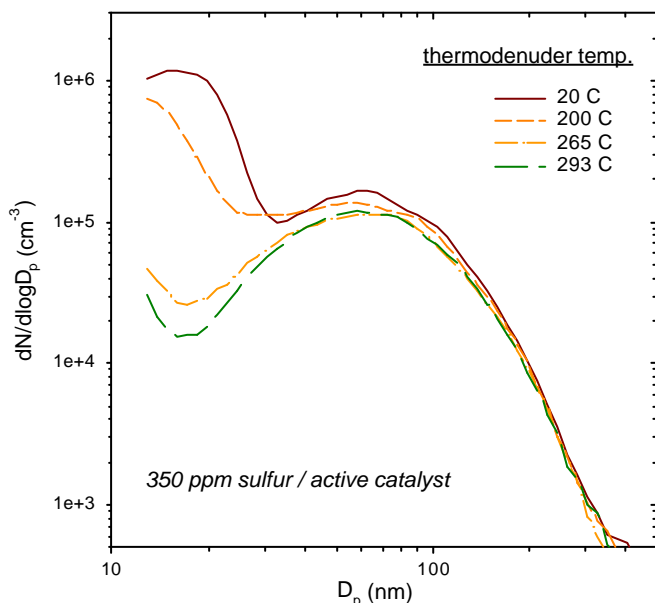


Figure 9. Effect of thermodenuder on PM size distributions.

The inset in Figure 7 indicates that as one moves the sampling point closer to the tailpipe, from 5.5 m to 1.5 m, the nuclei mode disappears. Figure 8 shows this from a different perspective, namely by varying the wind speed while maintaining a constant vehicle speed of 70 mph. The soot mode scales linearly with the inverse wind speed, as demonstrated in the inset to the lower graph, which depicts data for the 350 ppm sulfur / blank monolith combination. The soot mode in the 350 ppm sulfur fuel / active catalyst case exhibits the same dilution effect; however the nuclei mode shows a steeper dependence on wind speed. Furthermore the size distribution also moves to larger particle diameter as the wind speed is lowered. This demonstrates how the rate of dilution and exhaust cooling can promote or suppress nucleation.

The fact that the nuclei mode appears only when the vehicle is tested with the 350 ppm sulfur fuel / active catalyst combination suggests that this mode arises from sulfate nucleation. The dependence of this mode on the wind speed also corroborates this. Additional evidence is provided by the thermodenuder data presented in Figure 9. Here the aerosol sampled from behind the test vehicle is first heated to evaporate the semivolatile components, and then passed through a diffusion adsorber to remove the gaseous material so that it does not renucleate or condense onto the soot. The soot mode exhibits only a minor dependence on denuder temperature (due to thermophoretic losses). However, the nuclei mode disappears above ~200 C indicating that these particles are semivolatile liquid droplets.

PM emissions measurements made via direct tailpipe sampling, using a two stage ejector pump diluter, also exhibit a nuclei mode, but typically above a higher threshold speed / load than in the wind tunnel testing. This is likely due to the sensitivity of the nuclei mode to sampling conditions. Usually the first stage of dilution is carried out with heated dilution air during ejector pump dilution, which might explain the higher threshold that is required. But for reasons that are not clear, the use of room temperature

dilution air for the first stage of dilution did not increase the presence of the nuclei mode.

Conclusions – gasoline vehicles

In the case of recent model, conventional, gasoline vehicles the catalyst does not significantly remove engine out soot – the very low PM emissions, of ~ 2 mg/mi over the FTP drive cycle, are due the engines operating at stoichiometric air/fuel ratios. Gasoline engines can have high soot emissions if operated rich. Increased soot formation is also possible upon engine design changes, if these are not carefully made, such as with direct injection gasoline engines operated with stratified charge.

For the 3-way catalysts tested and at light duty vehicle exhaust flows, there appears to be insufficient sulfate formation for nucleation to occur under the "real world" conditions of the wind tunnel, even up to 1000 ppm. This could change, however, if catalyst formulation is modified to make it more active and perhaps with lean burn engine strategies where more oxygen is available, or during low temperature starts. Although the sulfur is not efficiently converted to sulfate, it does adsorb on the catalyst and decreases catalyst performance. A nucleation mode originating from semivolatiles hydrocarbons is also not noted, likely due to the efficient removal of the precursors by the catalyst. Nanoparticle emissions are sometimes observed, but at high load operation and with insufficient ventilation, e.g., at 70 mph with a 5% grade, and with the wind speed reduced to only 25 mph. These are likely due to organic material volatilized and /or pyrolyzed from the exhaust system, or even the underbody of the vehicle.

Conclusions – light duty diesel vehicles

The diesel soot mode is essentially independent of fuel sulfur level and the presence of an oxidation catalyst. These particles exhibit a lognormal size distribution that is nearly the same at the tailpipe as it is after being sampled from behind the vehicle during wind tunnel testing. A nucleation mode not ordinarily observed with low sulfur fuel (either with or without a catalyst) or for high sulfur fuel when the catalyst is absent. As with the gasoline vehicles, if the vehicle is run sufficiently hot and with insufficient ventilation then it may be possible to observe a nuclei mode from heat released organic material collected in the exhaust system.

When high sulfur fuel is used in conjunction with an oxidation catalyst then a nuclei mode is formed above a speed / load threshold that likely varies from one vehicle and catalyst formulation to another. This nanoparticle mode is formed after the exhaust gases exit the tailpipe and while the exhaust is diluted and cools. This is indicated by the fact that the nuclei mode disappears as the PM measurements are brought closer to the tailpipe, and as the wind speed past the vehicle is increased. Thermodenuder experiments indicate these particles to be semivolatile liquid droplets. These observations, and the requirement that the oxidation catalyst and high sulfur fuel both be present suggests that the nuclei mode consists of a sulfate aerosol, which might be coated with additional hydrocarbons.

This study demonstrates that measurement of the nuclei mode is difficult and depends significantly on the type of exhaust sampling that is used. Elimination of the nuclei mode from vehicle emissions, however, is simply a matter of removing the sulfur from the fuel. Finally, while light duty and heavy duty diesel vehicles both exhibit nuclei mode particles, the conditions under which they emit these particles are likely sufficiently different as to preclude extrapolating from one vehicle class to another.