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INFLUENCE OF THE DIESEL FUEL SULPHUR CONTENT ON THE NANOPARTICLE EMISSIONS FROM A FLEET OF CITY BUSES

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Abstract

Particle emissions from twelve buses, aged 1 to 19 years, operating alternatively on low sulphur (LS; 500 ppm) and ultra-low sulphur (ULS; 50 ppm) diesel fuel were monitored at four steady-state operating modes on a chassis dynamometer. The mean particle number emission rate using ULS diesel was lower than the rate using LS diesel in each of the four modes. The fractional reduction was highest in the newest buses and decreased with mileage up to about 500,000 km, at which stage a bus was about 8 years old. No further decrease was apparent as the mileage increased thereafter. However, the mean total suspended particle (TSP) mass emission rate did not show a systematic difference between the two fuel types. When the fuel was changed from LS to ULS diesel, the reduction in particle number was mainly in the nanoparticle size range, with occurrences of the nuclei mode being significantly restricted. Overall, 58% of the particles were smaller than 50 nm with LS fuel as opposed to just 45% with ULS fuel, suggesting that sulphur in diesel fuel was playing a major role in the formation of nanoparticles. The greatest influence of the fuel sulphur level was observed at the highest engine load, where 74% of the particles were smaller than 50 nm with LS diesel compared to 43% with ULS diesel.

KEYWORDS: Diesel, sulphur, nanoparticle, vehicle emission

INTRODUCTION

Ultra-fine particles in the ambient atmosphere are of current interest because of their association with adverse health effects and their impact on the earth's radiation balance, visibility impairment, and atmospheric chemistry. Diesel emissions are a major source of fine particles in the environment. Diesel emission particles range from about 3 nm to 1 μm in diameter and exhibit a characteristic bimodal size distribution with two distinctive modes. In some cases as much as 90% of the particles are smaller than 50 nm in diameter (1). These so-called 'nanoparticles' comprise the nuclei mode. They are primarily semivolatile and consist mainly of hydrocarbons and hydrated sulphuric acid condensates formed during the cooling and dilution of the exhaust emissions. A small number of nuclei mode particles may contain a solid core such as carbon or metallic ash originating from lubrication oil additives (1,2,3). Particles larger than 50 nm form the accumulation mode. These are mainly agglomerated solid carbon particles mixed with condensed heavy hydrocarbons with some metallic ash and sulphur species (1,4). Most of the particulate matter (PM) mass, typically over 90%, occurs in the accumulation mode. Abdul-Khalek et al. (5) found that, for nearly all operating conditions, more than 50% of the particle number but less than 1% of the particle mass was found in the nuclei mode.

In order to minimize the associated adverse effects, there are strong pressures to reduce the level of sulphur in diesel fuels worldwide. Until the early 1990's, the sulphur level in diesel fuel was not subject to environmental regulations. However, fuel specifications have shown that the maximum sulphur level in good quality diesel was about 0.5% (5000 ppm = 5000 mg/kg). Subsequently, environmental regulations have limited the maximum sulphur level to about 500 ppm, the fuel being typically referred to as "low sulphur (LS) diesel". Further pressures from the increasingly stringent diesel emission standards, such as the Euro 4 and US2007, will require the use of after treatment devices such as diesel particulate filters (DPF) in the future. In order to implement these technologies, the maximum sulphur levels will have to be limited to 50 or 10 ppm. Diesel fuels consisting of typically 15 ppm (but not more than 50 ppm) sulphur are commonly referred to as "ultra low sulphur (ULS) diesel". In Europe, diesel (and gasoline) of maximum sulphur content of 10 ppm is termed "sulphur-free" fuels. In Australia, the maximum sulphur level of 5000 ppm was reduced to 500 ppm (LS) in 2002. It is proposed to reduce the sulphur content to 50 ppm (ULS) by the year 2006, in order to bring the fuel into compatibility with Euro 4 emission standards. During combustion, the amount of fuel sulphur converted to sulphate is about 2% and rarely exceeds 4% (6). Because sulphates form a small fraction of the PM emissions, studies have shown that lowering fuel sulphur levels has only a limited potential as a means of PM control (7,8). However, it may have a significant effect on the particle number emissions. There is only a very limited body of

knowledge on the influence of the fuel sulphur level on particle number emissions (7-13). In all of these studies, increasing fuel sulphur levels resulted in an increase of nanoparticles. In one study, the number concentration produced by the low sulphur fuel was nearly seven times higher than that by the ultra-low sulphur fuel (12). In another study (13), no significant nuclei modes were observed with lower sulphur fuels but the nanoparticle emissions increased with increasing fuel sulphur level, especially at high load. Heating the emissions with a thermal denuder removed most of the nuclei mode, suggesting that the nanoparticles were largely composed of semivolatile material (14).

The majority of studies carried out to investigate the influence of fuel sulphur level on particle emissions have been conducted on engine dynamometers, and on a limited number of engines. To-date, there has been no detailed investigation covering a large number of heavy-duty vehicles over a range of different specifications. The present study was carried out with the aim of determining the influence of two types of fuel, LS and ULS diesel, on the particle mass and number emission rates from a bus fleet consisting of buses of different classes (pre EURO I, EURO I, and II) and in particular to investigate how this influence may vary with the odometer mileage of the buses.

EXPERIMENTAL AND STATISTICAL METHODS

Twelve in-service buses operating on low sulphur (LS) diesel fuel were tested on a chassis dynamometer over a period of seven days in June 2001. The fleet included two MAN SL200 buses each 19 years old (pre EURO I), seven Volvo B10M buses ranging from 6 to 12 years old (EURO I) and three B10L buses each 1 year old (EURO II). The specifications of the buses are shown in Table 1. None of the tested buses was equipped with a catalytic converter. Exhaust emissions were monitored at each of four steady-state operating modes as defined by engine power at 0% (Idle; mode7), 25%(mode 11), 50% (mode 10) and 100% (mode 8) rated full power. These four modes were selected from the standard thirteen mode ECE-R49 diesel emission test cycle for heavy duty vehicles. The buses were then run for about three months on ultra-low sulphur (ULS) diesel fuel and tested in exactly the same manner during a second round of measurements carried out over seven days in October 2001.

The tail pipe of the vehicle exhaust was attached to the primary segment of the sampling line. A small portion of the exhaust flow was drawn out, through a short (0.75m) thermally isolated connecting tube, into the dilution tunnel and diluted with clean ambient air drawn through a HEPA filter. As the connecting tubing was reasonably short, the temperature drop over its length was small and therefore there was no need for additional heating. The flow rate through the dilution tunnel was maintained constant. This resulted in a variation of the primary dilution ratio from about 5 at the 100% power mode to about 20 in the idle mode. However, within a given mode, the dilution ratios remained fairly constant between buses and fuels. The primary dilution ratio values are provided as supplementary material to this paper (Table 3). The residence time in the dilution tunnel was maintained between 1 and 2 s.

Carbon dioxide concentrations were sampled directly from the primary exhaust and the dilution tunnel. The primary dilution ratio was calculated as the ratio of the concentration of CO_2 in the primary exhaust to that in the dilution tunnel.

The total suspended particulate (TSP) mass concentration was measured by drawing a sample of air from the dilution tunnel, through conductive tubing, by means of an air pump at known velocity and collecting particulate matter on teflon-coated glass fibre filters. The filter diameter was 47 mm and they were obtained from Pall Corporation with specification P/N 66143, TF200. The flow rates through the filter were held constant during sampling. The sample mass was determined by weighing the filters on a Mettler AE 240, model Toledo A6 balance of sensitivity 0.01 mg.

A Dekati diluter (model L7) was used to dilute a small portion of the air-exhaust mix from the dilution tunnel by a further factor of 10. The Dekati diluter was connected directly to the dilution tunnel by a short stainless steel tube of 0.5 inch diameter and length 10cm. In this way, the primary exhaust was diluted by clean air in a ratio of between 50 and 200 for sampling with a Scanning Mobility Particle Sizer (SMPS). The outlet of the Dekati diluter was attached to the inlet of the SMPS by flexible conductive tubing. The SMPS used in this study (model 3934) consisted of a 3071A electrostatic classifier and a 3022 Condensation Particle Counter (CPC). The flow rates were set to 0.7 and 7 lpm for the polydisperse and sheath flow respectively and the up and down scanning times were 120 s and 45 s respectively. For these measurements, a window of 0.008 to 0.4 μm was selected as the optimum to cover the number-size distribution spectra for most of the tests and most of the operational modes. At least three number-size distribution scans were obtained at each of the four operational modes for each bus, using each of the two fuels. All temperatures and

flow rates were monitored continuously. In each experiment, the engine was first allowed to run at the required rate until the exhaust temperature and flow rates had attained steady values. These conditions were then maintained for measuring periods of 30 min in mode 7, 20 min in modes 10 and 11, and 10 min in mode 8. These time intervals were selected, as they were the minimum times required for the TSP filters to collect a measurable mass of particles for analysis in each mode. Longer sampling periods were avoided in order to prevent engine overheating, especially at full power in mode 8. All the elements of the sampling line were made of stainless steel.

The volumetric flow rate of the exhaust gas was calculated by measuring the pressure difference across a restriction orifice in the primary sampling segment and the temperature of the primary exhaust air. This flow rate was than multiplied by the measured concentrations, which were corrected for dilution, to calculate the emissions per second. No correction was made for diffusion losses.

The mean values and standard deviation of the particle number and mass emission rates of the twelve buses were calculated for each mode and fuel type. Thus, two sets of twelve paired measurements of the emission rate of each parameter – number and mass, were available with each fuel type in each mode. The corresponding mean values for each fuel-type group were computed and compared. This statistical comparison was performed through a two-sample students paired two-tailed t-test to determine significant differences between the group means. The test statistic, distributed as t on number of degrees of freedom df, was determined from

$$t = \frac{\bar{x} - \bar{y}}{\sqrt{\frac{s_1^{\,2}}{m} + \frac{s_2^{\,2}}{n}}}$$

$$df = \frac{\left(\frac{s_1^{\,2}}{m} + \frac{s_2^{\,2}}{n}\right)^2}{\frac{\left(s_1^{\,2}/m\right)^2}{(m-1)} + \frac{\left(s_2^{\,2}/n\right)^2}{(n-1)}}$$

where $\bar{x}$ and $\bar{y}$ are the sample means, s_1 and s_2 are the sample standard deviations and m and n are the number of observations in each of the two groups.

From the test statistic, a confidence level was calculated for the two distributions to be significantly different. A confidence level greater than or equal to 95% was taken to indicate that the means of the two distributions were significantly different from each other.

RESULTS AND DISCUSSION

The TSP mass emission rates were calculated for each bus and operational mode. Figure 1 shows the values obtained with the buses operating on LS diesel plotted against the corresponding values with the buses operating on ULS diesel. The graph is an *x*-*y* plot of the emission rates using LS diesel versus ULS diesel, with each point corresponding to a particular mode and bus. The straight line represents equality of the parameters on the two axes. The overall mean TSP emission rate was greater with the buses operating on LS diesel than on ULS diesel in modes 11, 10 and 8 while in mode 7 – the idling mode, it was lower. However, the differences in emissions using the two types of fuel were not statistically significant in any of the modes investigated.

Figure 2 shows the corresponding graph for the particle number emission rates. Here, note that most of the points lie above the line of equality, suggesting that the particle emission rate was higher with LS diesel than with ULS diesel. This was true in each of the four modes. The reduction of mean particle emission rates with ULS over LS diesel in modes 7, 11, 10 and 8 were approximately 40%, 31%, 44% and 59% respectively. A statistical analysis using a paired *t*-test showed that the emission rates were different at a confidence level exceeding 95% in modes 8, 10 and 11 but not in mode 7 (idle).

The mean size of the particles emitted was greater with the buses operating on ULS diesel fuel than on LS diesel fuel in each of the four modes, the difference being statistically significant in modes 11, 10 and 8 but not in the idle mode (a summary of particle size data has been supplied as supplementary material – Figure 6).

The observed differences in total particle number and mass emission rates between the two types of fuel suggest that the difference in particle number was in the nuclei mode (smaller than 50 nm). This is also supported by the observed smaller mean particle size with the LS fuel. The majority of the particle mass occurs in the accumulation mode and any reduction in particle number there would certainly have been reflected in a corresponding decrease of the total particle mass.

Further, analysis of the size spectra showed that the bimodal structure with both the nuclei and accumulation modes present was more readily observed with the LS fuel than with the ULS fuel. In order to define the presence or absence of a nuclei mode we used the assumption that the SMPS resolution of a size classification was sufficient to distinguish between the two modes as suggested by Burtscher (15). Particle number-size distributions obtained by the SMPS were observed on a log-log scale. As this involved 12 buses, four modes and two types of fuel with three to six SMPS scans per combination, the total number of distributions analysed amounted to nearly 400. If a unimodal distribution showed a peak number concentration in the nanoparticle range (particle size of less than 50 nm), we classified that distribution as having a nuclei mode. If the peak concentration occurred at a size greater than 50 nm, we classified that distribution as accumulation mode only. Similarly, in a bimodal distribution, we looked for the presence of a mode below 50 nm and, if found, we defined it as a nuclei mode. Nuclei modes were clearly more likely to occur in the emissions from buses operating on LS fuel than with ULS fuel in each of the four modes. The bimodal structure, although not present in every SMPS scan, was predominant with the LS fuel in all four tested modes. This was most obvious in the 100% power mode and the idle mode. With LS fuel, 8 out of the 12 buses showed nuclei modes in at least three of the four operational modes, while with ULS fuel only 3 buses exhibited this trend. Overall, 57% of the scans with LS fuel showed nuclei modes compared to just 33% with ULS fuel. There were a significantly large number of scans where the LS diesel showed a nuclei mode but the ULS diesel did not. One such example is shown in Figure 3. The converse of this – a nuclei mode with ULS diesel together with no such mode with LS diesel was very rare and was observed in just two out of the 48 bus/mode combinations – and they were both observed with the same bus.

Next, we determined the mean percentage of particle numbers below the size of 50 nm in each of the four operational modes with each of the two fuels. The corresponding percentage numbers in the four modes are plotted against each other in Figure 4. Again, the straight line shows equality between the axes. There is a strong bias towards LS fuel, with all four points lying well above the line of equality and the strongest differences being observed in mode 8 (100% power) and mode 7 (idle). In mode 8, on average, 74% of the particles were smaller than 50 nm with LS fuel, while the corresponding figure with ULS fuel was only 43%. Overall, 58% of the particles with LS fuel were smaller than 50 nm, compared to just 45% with ULS fuel. A t-test analysis, considering all buses, showed that the percentage of particles smaller than 50 nm with LS fuel was significantly greater than the corresponding percentage with ULS fuel at a confidence level exceeding 99% in mode 8 and at a confidence level exceeding 95% in each of modes 7 and 11. In mode 10, the difference was not statistically significant.

At this point, it is pertinent to question the precise role of the fuel type on the particle number emission rate. In particular, if the fuel type has an impact on the particles in the nanoparticle range, it will have a profound effect on the total particle number emission rate. We have shown that LS diesel fuel produces more nanoparticles than ULS diesel fuel (Fig 4). It also appears that the difference is most marked in the idle mode and the highest power mode. Diesel emissions include considerable amounts of vapour phase semivolatile hydrocarbons and sulphuric acid. Most of the

particulate mass occurs as black carbon in the accumulation mode and act as a 'sponge' for the condensation and/or adsorption of the semivolatile materials (5). In the absence of that 'sponge', provided that the conditions allow the nucleating species to exceed its supersaturation ratio, gas species will nucleate homogeneously to form large numbers of liquid nanoparticles. The driving force for the gas to particle conversion is the saturation ratio, defined as the ratio of the partial pressure of a species to its saturated vapour pressure. For sulphuric acid, the maximum saturation ratios occur during dilution and cooling of the exhaust and are typically achieved at dilution ratios between 5 and 30 (5). These were the primary dilution ratios achieved in the present experiments. A reduction of the fuel sulphur level lowers the partial pressure of sulphuric acid, hindering homogeneous nucleation of that species. Thus, this may provide an explanation for the reduced number of nanoparticles and nuclei modes when the fuel was changed from LS to ULS diesel. However, separating the effects of sulphuric acid and the semivolatile hydrocarbons is not straightforward. In Table 2, we present some of the basic specifications of the two fuels. Note that as the sulphur content is reduced from 500 ppm to 50 ppm, the aromatic hydrocarbon content is also reduced from 14% to 9% by mass. Thus, the nanoparticles may well consist of a combination of sulphuric acid and PAH's. In the past, it has been suggested that the semivolatile particle precursors responsible for the formation of the nuclei mode are a combination of unburnt hydrocarbons and sulphuric acid (5,9,12).

If there is a large mass of particles in the accumulation mode, as in the case of older engines, the available surface area would be larger and the process of absorption of vapour on to accumulation mode particles may dominate over the process of nucleation, partially suppressing the formation of the nuclei mode (5). In the newer types of engines the mass of particles in the accumulation mode, and therefore the available surface for absorption, is lower than in the older engines. We may then hypothesize that in newer engines the process of nucleation would become dominant and lead to an increase in the number fraction of particles in the nuclei mode.

Influence of the vehicle mileage on nanoparticle emissions. In order to verify this hypothesis, we investigated the effect of the mileage of the buses on the particle number emission rates with the two fuels. The odometer readings or mileage (in km) was considered to be a more relevant parameter than the age itself. It was also decided to class the buses into five distinct groups according to their odometer readings. In order to also investigate the effect of the fuel, the ratios of the total particle number emission rates with LS to ULS diesel for each bus were calculated for all four operational modes and are shown as a function of the odometer reading class in Figure 5. The histograms show the mean LS/ULS emission ratios for the various mileage groups. Note that, as hypothesized, the mean values of the ratio are highest for the newest buses. In other words, the fractional reduction of particle number emissions when the fuel is changed from LS diesel to ULS diesel is greater for newer buses. A t-test analysis showed that the mean LS/ULS emission ratio of buses in the two groups with a mileage of over 500,000 km was significantly greater than the mean of the buses in the groups with greater mileages at a confidence level of 90%. The difference due to the fuels became less effective with increasing mileage up to about 500,000 km, when the buses were about 8 years old, after which it did not change significantly with further increase in mileage.

As modern technology succeeds in achieving more complete combustion, engines of newer design generally exhibit lower particle mass emission and therefore a lower particle surface area in the accumulation mode. This may give rise to increased homogeneous nucleation and the production of large numbers of nanoparticles. In older engines, the larger number of accumulation mode particles offer a more effective sink for the vapours and restrict the formation of nanoparticles. Therefore, the consequent reduction of the total particle and nanoparticle numbers as the sulphur and aromatics content is reduced would be much more prominent in the newer engines than in the older engines. On the other hand, one half of the bus/mode combinations in the two oldest buses showed nuclei modes with ULS fuel. If we assume that most or all of the nanoparticles are composed of sulphuric acid (2, 12), we would expect a drastic reduction in nuclei mode occurrence when we switch from LS fuel to ULS fuel. So, why are there such a high proportion of bus/mode combinations with nuclei modes and why is it more likely to occur in the older buses? This observation suggests that an alternative mechanism may be playing an important role in the older buses. We know that as a bus gets older, the exhaust emissions contain more unburned lubrication oil due to leakage or higher consumption (2,3). We suggest that, in addition to sulphuric acid, nuclei mode particles may also be formed by the process of homogeneous nucleation of organic components either from the lubricating oil or the fuel. The presence of sulphuric acid may provide nucleating seeds for the organic components and further enhance the formation of nanoparticles as has been suggested in other studies (2, 5). For example, with the two oldest buses, a nuclei mode was present in all but one of the eight possible bus/mode combinations with LS diesel. Unfortunately, not much is known about the chemical composition of nanoparticles. So, we have to rely on our knowledge of particle mass measurements. It has been shown that, in the emissions from a vehicle operating on LS diesel with 450 ppm of sulphur, just 0.7 to 5.3% of the nuclei mode particulate mass is constituted of sulphuric acid (2). Therefore, when the fuel sulphur content is reduced tenfold, as from LS to ULS diesel, the contribution of the sulphuric acid to the nuclei mode mass would become much less than 1%. Although it was suggested that it is unlikely that organic compounds alone are nucleating (2), once the sulphur in the fuel is reduced from 500 ppm to 50 ppm, we do not see any other likely candidate that will initiate nucleation except organic components. This is also in accordance with the recent results by Vaarslahti et al. (16) who have observed nuclei modes with diesel fuel containing a sulphur content of less than 2ppm. They also indicate that, depending on the conditions, two different types of nuclei modes can be formed from the same diesel engine; one mainly due to the sulphur in the fuel, and the other presumably from hydrocarbons. In further support of these observations, Mathis et al. (17) have observed that nanoparticles contain at least two compounds of different volatility. They also suggest that sulphuric acid seeds are more likely to be coated by less volatile hydrocarbon compounds.

Influence of engine load. Figure 4 shows that engine power is also of some importance in determining the presence of nanoparticles and nuclei modes. The largest influence of the fuel sulphur level was observed in the highest load mode 8 where 74% of the particles were smaller than 50 nm with LS compared to 43% with ULS. The lower load modes 10 and 11 did not show a significant influence of the fuel sulfur level on the percentage of particles smaller than 50nm as nucleation was not readily observed in these modes. A similar observation was made by Vaaraslahti et al (16), although they used a fuel of much lower sulphur content. In the present study, a large number of nuclei modes were also observed in mode 7 (idle) with both types of fuel. However, the influence of the fuel sulphur level was not as readily observable as in mode 8.

Tobias et al. (2) showed that there is more complete burning of the semivolatile fuel components as the engine load increases. Therefore in mode 7 (idle) there would be an abundance of semivolatile fuel components that could even initiate homogenous nucleation without a strong influence of the sulfuric acid and therefore the fuel sulfur level. As engine load increases, the fuel to

air ratio increases and reaches a peak in mode 8. Consequently, the engine-out sulphur dioxide (SO_2) concentration and production rate of SO_3 would also be highest in this mode over all other modes. Therefore, the nanoparticles found in mode 8 are likely to be from the condensation of sulphuric acid and water rather than from unburnt hydrocarbons from the fuel, thus justifying the observed high influence of the fuel sulphur level on nanoparticles emissions observed in this mode.

These results further confirm previous observations based on vehicle age, that there is a possibility of two separate mechanisms being responsible for the formation of nuclei mode particles in diesel emissions. The first occurs mainly in the idle mode and appears to be a result of semivolatile organic compounds and sulphuric acid. The second occurs at the high loads and is dominated by sulphuric acid and water nucleation.

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Table 1: Specifications of the buses.

Bus No	Type of Bus	Date of Entry to Service	Mean Mileage ($x10^3$ km)	Max Power (Hp)	No of Cyls	Engine Capacity (L)
1	Volvo B10M	18-7-89	757	160	6	10
2	Volvo B10L	29-3-00	116	160	6	10
3	Volvo B10M	20-4-95	547	140	6	10
4	Volvo B10L	14-3-00	126	180	6	10
5	Volvo B10L	6-4-00	117	178	6	10
6	Volvo B10M	21-6-93	584	172	6	10
7	Volvo B10M	5-5-93	545	161	6	10
8	Volvo B10M	10-5-95	401	180	6	10
9	Volvo B10M	11-5-95	362	172	6	10
10	Volvo B10M	5-8-93	421	168	6	10
11	MAN SL200	2-6-82	912	115	6	9
12	MAN SL200	18-8-82	930	46	6	9

Table 2:Some basic specifications of the two types of fuel used in this study.

Property	Test Method	Unit	LS BP G32	ULS BP G50
Density (at 15ºC)	ASTM D4052	kg L^{-1}	0.82 - 0.86	0.830 - 0.855
Cetane Index (min)	ASTM D4737		46	51
Viscosity (at 40ºC)	ASTM D445	cSt	2.0 - 4.5	2.0 - 4.5
Distillation 95% recovered	ASTM D86	ºC	371	350
Sulphur Total (max)	ASTM D4294	mg kg^{-1}	500	50
Aromatics Total	IP 391	% mass	14	9

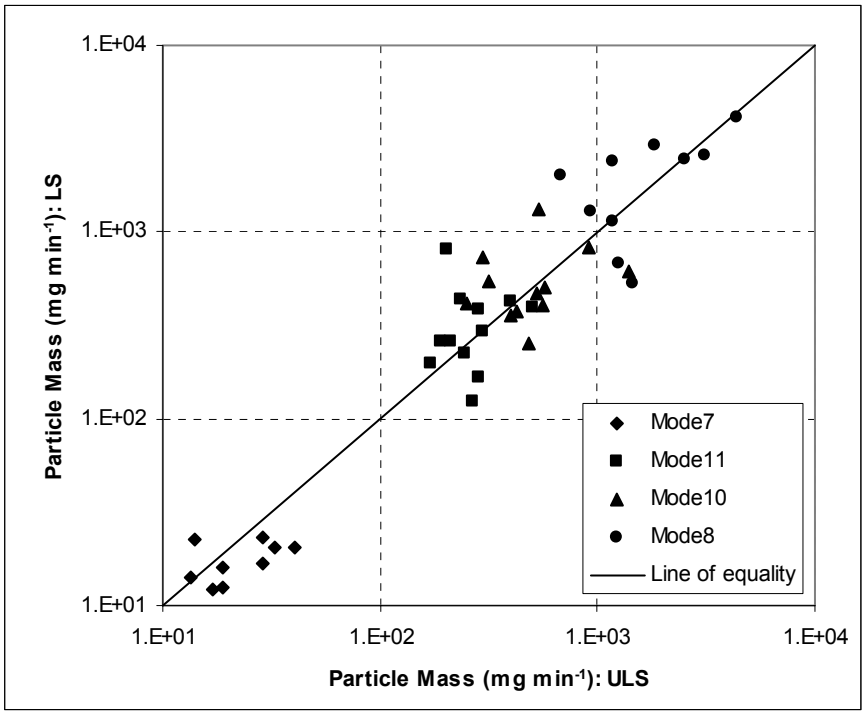


Figure 1 : Particle mass emission rates with LS diesel vs ULS diesel fuel. Each point represents a given mode and bus. The symbols differentiate the four operational modes and the straight line represents equality.

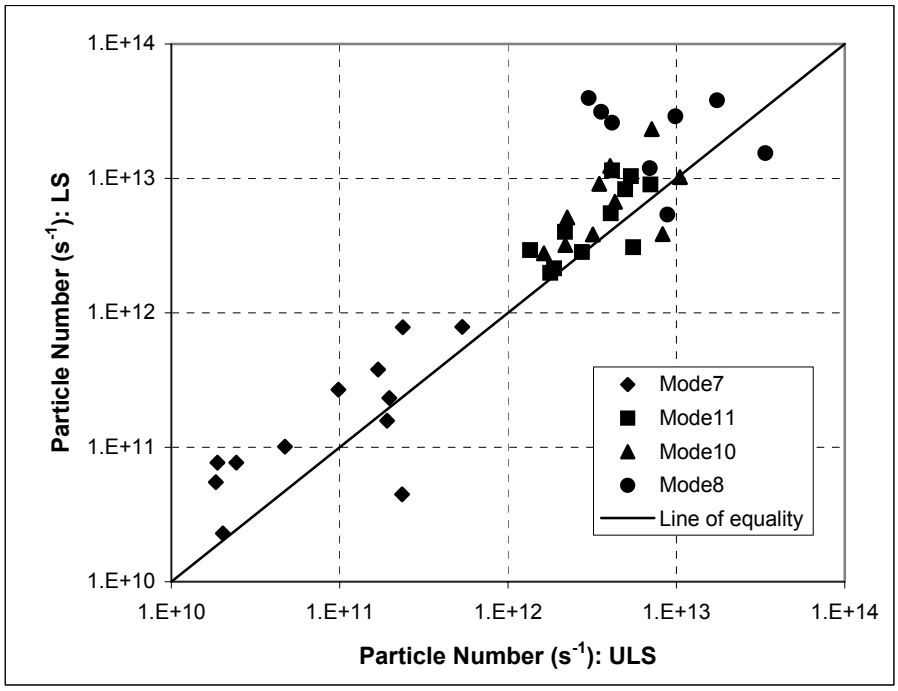


Figure 2 : Particle number emission rates with LS fuel vs ULS fuel. Each point represents a given mode and bus. The symbols differentiate the four operational modes and the straight line represents equality. particle number concentrations are in the size range 8 to 400 nm.

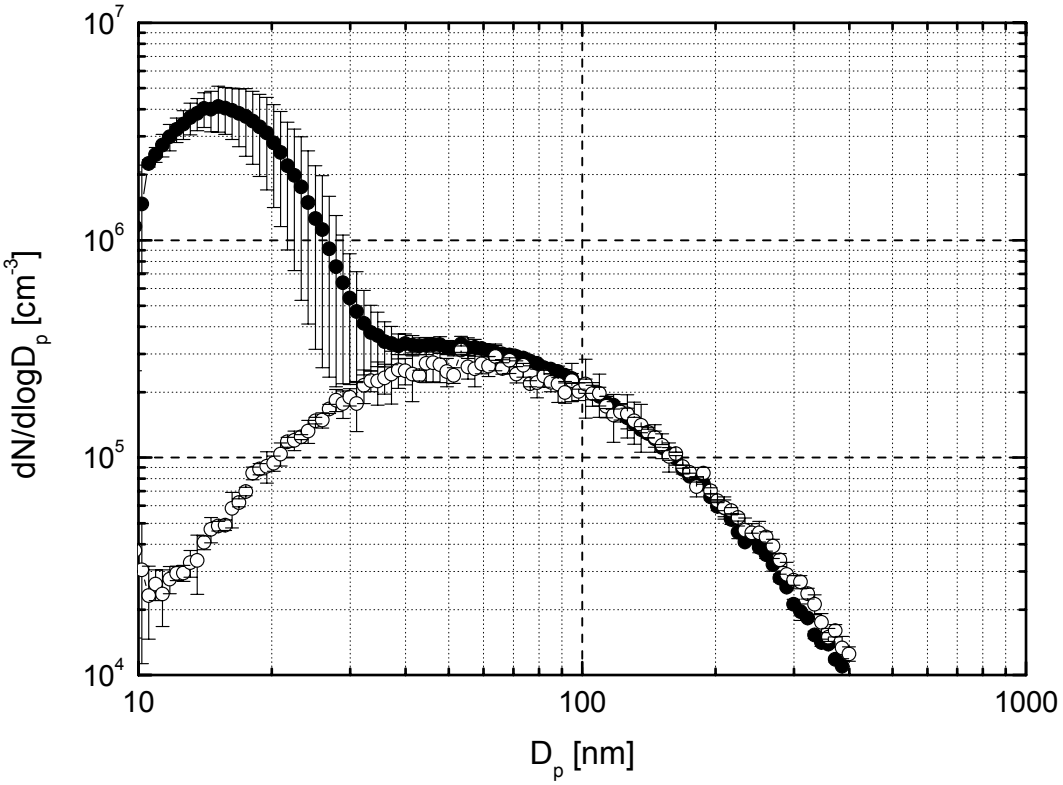


Figure 3: A typical SMPS number-size distribution spectra where a nuclei mode was observed with LS diesel (full circles) and no nuclei mode was observed with ULS diesel (open circles). Each distribution represents the mean of three SMPS scans under the same conditions with the error bars as shown. This example is for Bus 5 in Mode 8. Both distributions have been corrected for dilution.

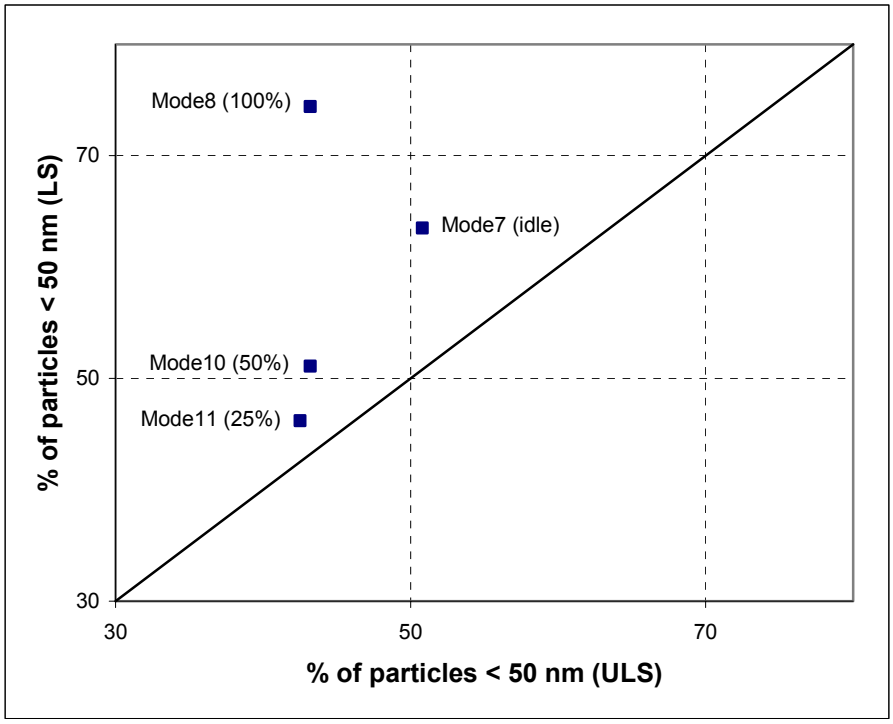
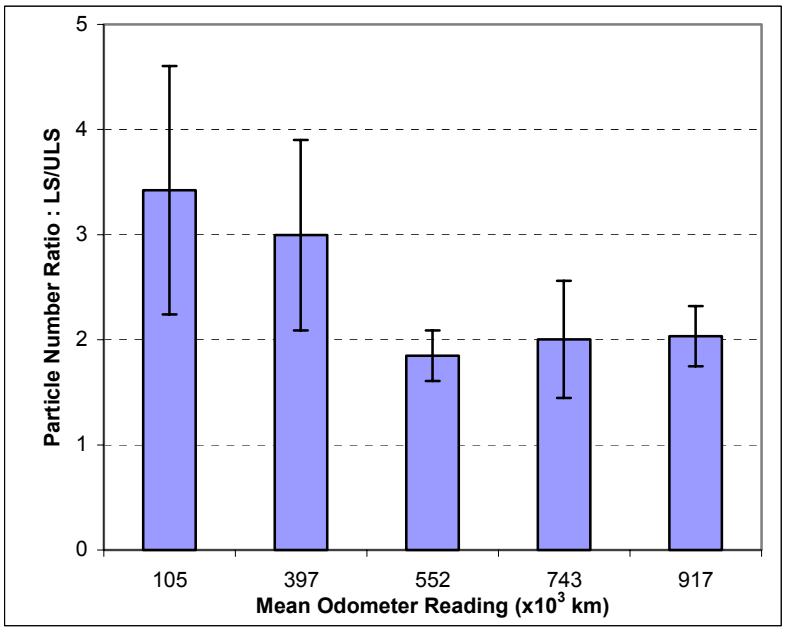


Figure 4 : Mean percentage of particles smaller than 50 nm in the SMPS number-size scans at each operational mode with LS diesel fuel plotted against the same quantity with ULS diesel fuel.



.Figure 5 : Ratios of total particle number emission rates with LS and ULS diesel fuel in all four operational modes as a function of the odometer readings of the buses. The buses have been classed into five groups according to the odometer readings and the histograms show the mean ratios for each group.