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Influence of Diesel Fuel Sulfur on Nanoparticle Emissions from City Buses

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Particle emissions from twelve buses, operating alternately on low sulfur (LS; 500 ppm) and ultralow sulfur (ULS; 50 ppm) diesel fuel, were monitored. The buses were 1−19 years old and had no after-treatment devices fitted. Measurements were carried out at four steady-state operational modes on a chassis dynamometer using a mini dilution tunnel (PM mass measurement) and a Dekati ejector diluter as a secondary diluter (SMPS particle number). The mean particle number emission rate (s^{-1}) of the buses, in the size range 8−400 nm, using ULS diesel was 31% to 59% lower than the rate using LS diesel in all four modes. The fractional reduction was highest in the newest buses and decreased with mileage up to about 500 000 km, after which no further decrease was apparent. 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. Over all operational modes, 58% of the particles were smaller than 50 nm with LS fuel as opposed to just 45% with ULS fuel, suggesting that sulfur in diesel fuel was playing a major role in the formation of nanoparticles. The greatest influence of the fuel sulfur content 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.

Introduction

Ultrafine 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 vehicles are a major source of fine particles in the environment. Diesel particle emissions range from about 3 nm to 1 μm in diameter and exhibit a characteristic bimodal size distribution with two distinctive modes. Very often, as many as 90% of these particles are smaller than 50 nm in diameter. These particles are known as "nanoparticles" and occur predominantly in the nuclei mode (*1*). They are primarily semivolatile and consist mainly of hydrocarbons and hydrated sulfuric acid condensates formed during the cooling and dilution of the exhaust (*1*, *2*). A small number of nanoparticles may contain a solid core such as carbon or metallic ash originating from lubrication oil additives (*1*, *3*, *4*). Particles larger than 50 nm are mainly agglomerated solid carbon particles mixed with condensed heavy hydrocarbons with some metallic ash and sulfur species (*1*, *5*). Most of the particulate matter (PM) mass, typically over 90%, occurs in the accumulation mode. Abdul-Khalek et al. (*6*) found that, for nearly all operating conditions, more than 50% of the total particle number but less than 1% of the particle mass occurred in the nuclei mode.

To minimize the adverse health effects associated with vehicle emissions, there are strong pressures to reduce the sulfur content in fuels worldwide. Until the early 1990s, the sulfur content in diesel fuel was not subject to environmental regulations. However, fuel specifications have shown that the maximum sulfur content in good quality diesel was about 0.5% (5000 ppm = 5000 mg/kg). Subsequently, environmental regulations have limited the maximum sulfur content to about 500 ppm, with the fuel being typically referred to as "low sulfur (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. To implement these technologies, the maximum sulfur contents will need to be limited to 50 ppm. In Europe, diesel and gasoline fuels with maximum sulfur contents of 10 ppm are termed "sulfur-free" fuels. In Australia, the maximum sulfur content of 5000 ppm was reduced to 500 ppm (LS) in 2002. It is proposed to reduce the sulfur content to 50 ppm, commonly referred to as "ultralow sulfur (ULS) diesel" by the year 2006, to bring the fuel into compatibility with Euro 4 emission standards. During combustion, the amount of fuel sulfur converted to sulfate is about 2% and rarely exceeds 4% (*7*). Because sulfates form a small fraction of the particulate mass (PM) emissions, studies have shown that lowering fuel sulfur levels has only a limited potential as a means of PM control (*8*, *9*). However, it may have a significant effect on the particle number emissions. Although interpretation of results of studies on the influence of the fuel sulfur content on particle number emissions are complicated by differences in testing procedures such as dilution, type of cycle, and vehicles used, they have all shown that increasing fuel sulfur content generally results in an increase of nanoparticles (*2*, *8*). In one study, the number concentration produced by the low sulfur fuel was nearly seven times higher than that produced by the ultralow sulfur fuel (*10*). In another study (*2*), no significant nuclei modes were observed with lower sulfur fuels but the nanoparticle emissions increased with increasing fuel sulfur content, 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 (*11*).

The majority of studies carried out to investigate the influence of fuel sulfur content on particle emissions have been conducted on engine dynamometers, and on a limited number of vehicles. 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 test fleet consisting of buses of different classes (pre EURO I, EURO I, and EURO 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 sulfur (LS) diesel fuel were tested on a chassis dynamometer over a period of

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TABLE 1. Specifications of the Buses

bus no.	engine type	emission cert std (Euro)	max power (Hp)	engine capacity (L)	chassis type	date of entry to service	mean mileage ($\times 10^3$ km)	odometer group[a]
1	THD101GC	Pre-E	160	9.6	Volvo B10M	18−7−89	757	4
2	D10HA	Euro II	160	9.6	Volvo B10L	29−3−00	116	1
3	THD101GC	Euro I	140	9.6	Volvo B10M	20−4−95	547	3
4	D10HA	Euro II	180	9.6	Volvo B10L	14−3−00	126	1
5	D10HA	Euro II	178	9.6	Volvo B10L	6−4−00	117	1
6	THD101GC	Euro I	172	9.6	Volvo B10M	21−6−93	584	3
7	THD101GC	Euro I	161	9.6	Volvo B10M	5−5−93	545	3
8	THD101GC	Euro I	180	9.6	Volvo B10M	10−5−95	401	2
9	THD101GC	Euro I	172	9.6	Volvo B10M	11−5−95	362	2
10	THD101GC	Euro I	168	9.6	Volvo B10M	5−8−93	421	2
11	D2566MUH	Pre Euro	115	11.4	MAN SL200	2−6−82	912	5
12	D2566MUH	Pre Euro	46	11.4	MAN SL200	18−8−82	930	5

[a] The odometer group refers to the classification used to group the buses by mileage.

TABLE 2. Some Basic Specifications of the Two Types of Fuel Used in This Study

property	test method	unit	LS BP G32	ULS BP G32
density (at 15 °C)	ASTM D4052	kg L^{-1}	0.82−0.86	0.830−0.855
cetane index (min)	ASTM D4737		46	51
viscosity (at 40 °C)	ASTM D445	cSt	2.0−4.5	2.0−4.5
distillation 95% recovered	ASTM D86	°C	371	350
sulfur total (max)	ASTM D4294	mg kg^{-1}	500	50
aromatics total	IP 391	% mass	14	9

7 days in June 2001. The test fleet included two D2566MUH buses each 19 years old (pre EURO I), seven Volvo THD101GC buses ranging from 6 to 12 years old (EURO I), and three D10HA 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 operational 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 (*12*). The buses were then run for about 3 months on ultralow sulfur (ULS) diesel fuel and tested in exactly the same manner during a second round of measurements carried out over 7 days in October 2001. The mean environmental temperatures between the two sets of measurements differed by no more than about 10 °C. The basic specifications of the two fuels are given in Table 2.

The tail pipe of the vehicle exhaust was attached to the primary segment of the sampling line. All the elements of the primary sampling line were constructed of stainless steel. A small portion of the exhaust flow (0.5−1%) was drawn out, through a short (0.75 m) thermally insulated connecting tube, into the dilution tunnel, and diluted with clean ambient air drawn through a HEPA filter. The temperature in the dilution tunnel was maintained below 52 °C. The total volumetric flow rate of the diluted primary exhaust through the dilution tunnel was maintained constant throughout each experiment for a given bus and operational mode. As the exhaust flow rate into the dilution tunnel increased with load, 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 operational mode, the dilution ratios remained fairly constant between buses and fuels. The primary dilution ratio values are provided as Supporting Information to this paper (Table 3). The residence time in the dilution tunnel was maintained between 1 and 2 s. The flow rate through the dilution tunnel was maintained above a value that provided good mixing. The minimum flow rate was calculated from the required critical Reynolds number of the flow in the tunnel.

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 a steady flow rate and collecting particulate matter on Teflon-coated glass fiber filters (47 mm, Pall Corp., P/N 66143, TF200). Sampling was carried out over a known period of between 10 and 30 min, depending on operational mode, and the flow rate through the filter was held constant throughout this time at a value between 10 and 15 L min^{-1}. The maximum sampling air temperature was maintained below 52 °C in accordance with USEPA gravimetric analysis standards (*13*). 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 in. diameter and 10 cm length. 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 a flexible conductive tube 30 cm long. 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 L/min for the polydisperse and sheath flow, respectively, and the up and down scanning times were 120 and 45 s, respectively. For these measurements, a window of 0.008−0.4 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. Some subsidiary experiments were carried out to compare the particle number concentrations measured by the SMPS in the Dekati diluter and in the dilution tunnel. Within error of measurement, the concentrations measured in the diluter were a factor of 10 lower than that measured in the dilution tunnel, suggesting that no new particles were being formed in the second stage of dilution. This is in agreement with Kittelson et al. (*2*) who also found that particle production by homogeneous nucleation occurs in the first stage of dilution and is not affected by further dilution.

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 because 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.

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. The pressure difference and the temperature remained stable over time throughout each measurement under a given set of conditions. The flow rate was then multiplied by the measured concentrations, which were corrected for dilution, to calculate the emissions per second. No correction was made for diffusion losses. Exhaust gas temperatures varied by between 75 and 100 °C in mode 7 (idle) to between 400 and 450 °C in mode 8 (full power), irrespective of fuel type.

The mean particle number emission rate and particle mass emission rate of the twelve buses were calculated for each mode and fuel type. A statistical comparison was performed through a two-sample Student's paired two-tailed *t*-test to determine significant differences between the mean values using the two types of fuel. 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. Each point corresponds to a particular mode and bus. The results suggested that 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 particle mass 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 average reduction in mean particle number emission rates of the 12 buses with ULS compared to 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 mean particle number emission rates using the two fuels were significantly different in modes 8, 10, and 11. There was no significant difference in mode 7 (idle).

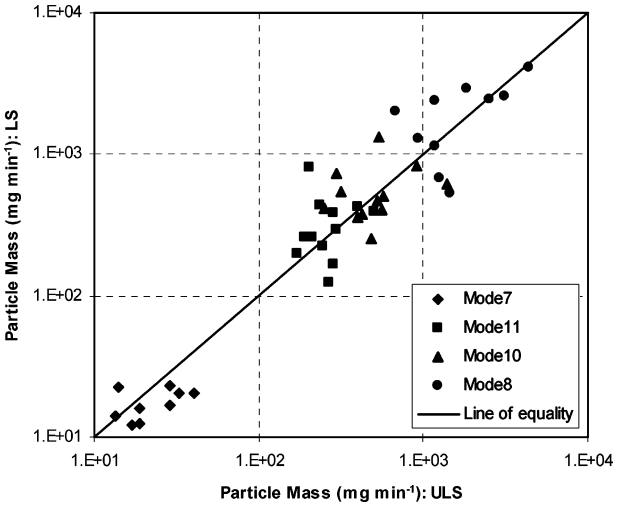

FIGURE 1. Particle mass emission rates with LS diesel vs ULS diesel fuel. Each point represents a given mode and bus. The symbols differentiate the four operational modes and the straight line represents equality. The engine air out flow rate remained constant throughout the duration of each measurement period.

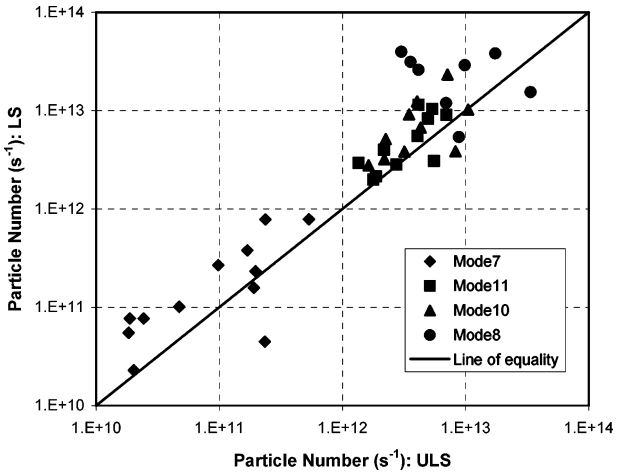

FIGURE 2. Particle number emission rates with LS fuel vs ULS fuel. Each point represents a given mode and bus. The symbols differentiate the four operational modes and the straight line represents equality. Particle number concentrations are in the size range 8 to 400 nm.

The mean count median diameter (CMD) 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 (Figure 3). The difference was statistically significant in modes 8, 10, and 11. The difference was not statistically significant in mode 7 (the idle mode) (Figure 3).

Although in many instances they dominate the total particle number, nanoparticles contribute very little to the total particle mass (*6*). The observed difference in total particle number and the absence of a significant difference in mass emission rates between the two types of fuel suggest that the difference in particle number was in the nanoparticle size range. This is also supported by the observed smaller mean particle sizes with the LS fuel over the ULS fuel in Figure 3. 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. Such a decrease was not observed.

Further, analysis of the SMPS data showed that many of the size distributions were bimodal with both the nuclei and accumulation modes clearly visible. However, a number of

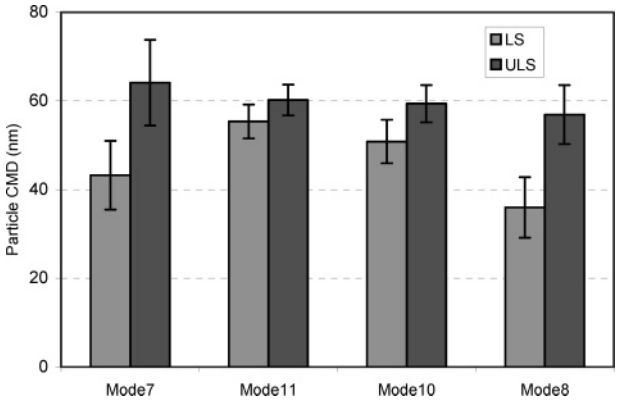

FIGURE 3. Mean count median diameters of the particles using the two fuels in the four operational modes.

distributions were unimodal and it was not easy to ascertain whether they contained a nuclei mode. To define the presence or absence of a nuclei mode we assumed that the SMPS resolution of a size classification was sufficient to distinguish between the two modes as suggested by Burtscher (*14*). Particle number−size distributions obtained by the SMPS were plotted on a log−log scale. As this involved 12 buses, 4 modes, and 2 types of fuel with 3−6 SMPS scans per combination, the total number of distributions analyzed amounted to nearly 400. A unimodal distribution with a peak number concentration in the nanoparticle range (particle size of less than 50 nm) is strongly indicative of the presence of a nuclei mode. Thermal conditioning of the exhaust gas exhibiting such particle size distributions generally shows that most of the particles are volatile and smaller than 50 nm in diameter (*15*). Thus, we classified such distributions as having a nuclei mode. If the unimodal distribution 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 peak below 50 nm and, if found, we could clearly define it as a nuclei mode. This classification was accomplished by visual observation of the SMPS size distributions. Although this arbitrary definition was not perfect, it provided a good indication of the presence or absence of a nuclei mode. Size distributions classified as containing a nuclei mode generally showed a significantly higher proportion of nanoparticles than those distributions classified as not containing a nuclei mode. It should also be noted that peaks due to large particle numbers below 10 nm were sometimes observed as a result of down scans of the SMPS. The contribution of these artifacts to the nanoparticle number concentration was found to be less than 1%. Observations of peaks below 10 nm were not considered when assigning nuclei modes.

In the present study, nuclei modes were more readily observed in the emissions from buses operating on LS fuel than with ULS fuel in each of the four modes. One such example is shown in Figure 4. The bimodal distribution, 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 3 of the 4 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 (Figure 4). 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 (modes 7 and 8, bus no. 1).

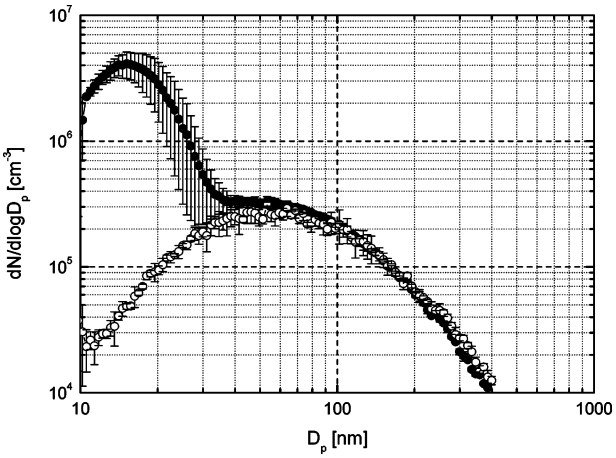

FIGURE 4. Typical SMPS number−size distribution spectra where a nuclei mode was observed with LS diesel (full circles) and no nuclei mode was observed with ULS diesel (open circles). Each distribution represents the mean of three SMPS scans under the same conditions with the error bars as shown. This example is for Bus 5 in Mode 8. Both distributions have been corrected for dilution.

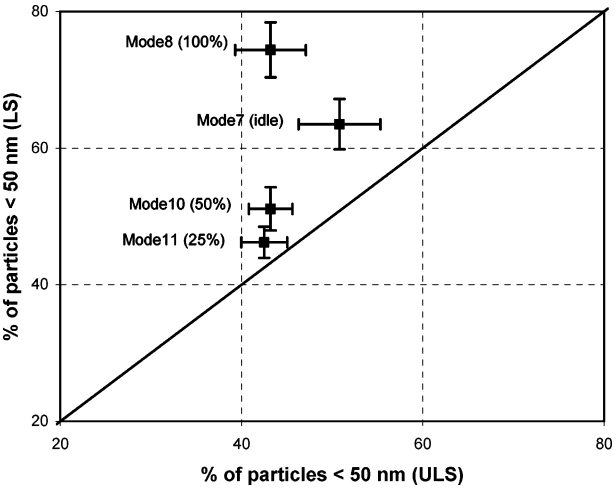

FIGURE 5. Mean percentage of particles smaller than 50 nm in the SMPS number-size scans at each operational mode with LS diesel fuel plotted against the same quantity with ULS diesel fuel. The error bars show the corresponding standard errors.

Next, we determined the mean percentage of particle numbers within the measurement range 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 5. Each point is the average of 30−36 readings, i.e., 12 buses × 3 SMPS scans in each mode. The error bars show the corresponding standard errors of the means. Again, the straight line shows equality between the axes. There is a strong bias toward 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 (Figure 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 vapor phase semivolatile hydrocarbons and sulfuric acid (*1*, *3*). Most of the particulate mass occurs as black carbon in the accumulation mode and acts as a "sponge" for the condensation and/or adsorption of the semivolatile materials (*6*). 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 vapor pressure. For sulfuric acid, the maximum saturation ratios occur during dilution and cooling of the exhaust and are typically achieved at dilution ratios between 5 and 30 (*6*). These were the primary dilution ratios achieved in the present experiments. A reduction of the fuel sulfur content lowers the partial pressure of sulfuric 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 sulfuric 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 sulfur content is reduced from 500 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 sulfuric acid and PAH's. In the recent past, several other workers have suggested that the semivolatile particle precursors responsible for the formation of the nuclei mode are a combination of unburnt hydrocarbons and sulfuric acid (*6*, *10*, *16*).

Influence of Vehicle Mileage on Nanoparticle Emissions. Emissions from older engines typically contain more particle mass in the accumulation mode than those from more modern engines. This is due to two reasons: (i) older engines were designed under less stringent emission standards than newer engines, and (ii) with increased mileage, wear, and tear, engines tend to emit more unburned soot (*2*, *8*). In the present study, there was a direct link between the mileage of the buses and the engine certification standards (see Table 1). Considering the small sample of buses investigated in this study (5 mileage groups, 3 certification standards), it was virtually impossible to separate the two effects. However, in combination, these two effects contribute to a large particle surface area in the accumulation mode for the adsorption of vapor emitted by older engines. The resulting drop in saturation ratio may hinder homogeneous nucleation, partially suppressing the formation of nuclei modes (*6*). Conversely, we may hypothesize that nuclei modes are more likely to occur in emissions from newer engines than from older engines.

To test this hypothesis, we investigated the effect of the age of the buses on the particle number emission rates with the two fuels. The odometer reading or mileage (in km) was used as a measure of the age and emission standard certification of a bus. Thus, it was decided to class the buses into five distinct groups according to their odometer readings (Table 1). To investigate the effect of changing the fuel, the ratios of the total particle number emission rates with LS to ULS diesel for each bus were calculated as averages over all four operational modes and are shown as a function of the odometer reading class in Figure 6. Note that, as hypothesized, the mean values of the ratio are highest for the newest group of 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 under 500 000 km was significantly greater than the mean of the buses in the groups with higher mileages at a confidence level of 90%. The difference due to the fuels became less obvious 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.

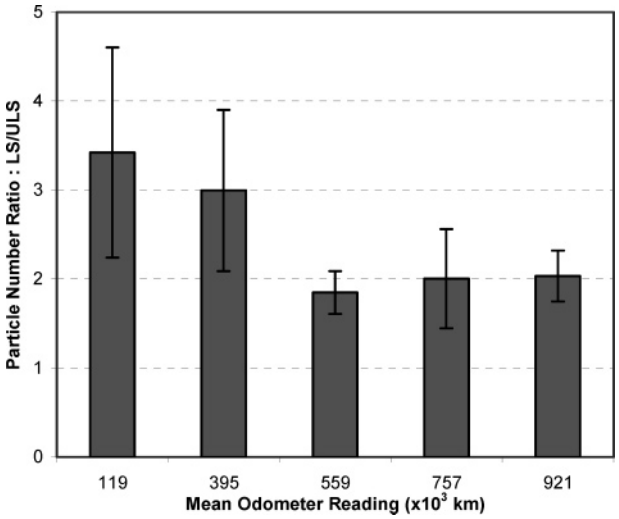

FIGURE 6. Ratios of total particle number emission rates with LS and ULS diesel fuel in all four operational modes as a function of the odometer readings of the buses. The buses have been classed into five groups according to the odometer readings and the histograms show the mean ratios for each group. The bus numbers of the groups are as follows: Group 1 (105) 2, 4, 5; Group 2 (397) 8, 9, 10; Group 3 (552) 3, 6, 7; Group 4 (743) 1; Group 5 (917) 11, 12. The error bars show the standard errors.

As explained earlier, in older engines the larger number of accumulation mode particles, in the form of soot, offers a more effective sink for the vapors and restricts the formation of nanoparticles. Therefore, the consequent reduction of the total particle and nanoparticle numbers as the sulfur and aromatics content is reduced is expected to be much more prominent in the newer engines than in the older engines. However, with the ULS fuel, surprisingly, the two oldest buses (bus nos. 11 and 12; 19 yrs old) showed nuclei modes for many operating modes. For example, using ULS fuel, of the 8 possible combinations of these two oldest buses, 4 showed nuclei modes, while of the 12 possible combinations with the group of 3 newest buses (bus nos. 2, 4, and 5) only one showed a nuclei mode. If we assume that most or all of the nanoparticles are composed of sulfuric acid (*3*, *10*), we would expect a drastic reduction in nuclei mode occurrence when the fuel is changed from LS to ULS diesel. So, with the lower sulfur content ULS fuel, why do a number of buses still show nuclei modes and why were they observed more frequently with the older buses? These observations suggest that an alternative mechanism, unrelated to the sulfur content of the fuel, 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 (*3*, *4*). We suggest that, in addition to sulfuric 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 sulfuric acid may provide nucleating seeds for the organic components and further enhance the formation of nano-

particles as has been suggested in other studies (*3*, *6*). For example, with the two oldest buses (nos. 11 and 12) operating on LS fuel, nuclei modes were observed in the majority of bus/mode combinations. Bus no. 12 overheated in mode 8 and no data were available for this rated power. Thus, the number of bus/mode combinations for the two oldest buses include 4 for Bus no. 11 and 3 for Bus no. 12. Of these 7 combinations, 6 showed nuclei modes. 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 sulfur, just 0.7−5.3% of the nuclei mode particulate mass is constituted of sulfuric acid (*3*). Therefore, when the fuel sulfur content is reduced 10-fold, as from LS to ULS diesel, the contribution of the sulfuric 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 (*3*), once the sulfur in the fuel is reduced from 500 to 50 ppm, we do not see any other likely candidate that may initiate nucleation except organic components. This is also in accordance with the recent results by Vaarslahti et al. (*17*) who have observed nuclei modes with diesel fuel containing a sulfur content of less than 2 ppm. 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 sulfur in the fuel, and the other presumably from hydrocarbons. In further support of these observations, Mathis et al. (*18*) have observed that nanoparticles contain at least two compounds of different volatility. They also suggest that sulfuric acid seeds are more likely to be coated by less volatile hydrocarbon compounds.

Influence of Engine Load. Figure 5 shows that engine power is also of some importance in determining the presence of nanoparticles and nuclei modes. The largest influence of the fuel sulfur 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 50 nm as nucleation was not readily observed in these modes. Vaaraslahti et al. (*17*) reported a similar observation, although they used a fuel of much lower sulfur content. In the present study, although not as readily observable as in mode 8, a relatively large number of nuclei modes were also observed in mode 7 (idle) with both types of fuel. Recent work suggests that the cooling temperature difference between the engine out and the environment may play a role in the generation of nanoparticles (*14*, *19*, *20*). In the present study, it was noted that the temperature of the exhaust air entering the primary dilution tunnel was 250−300 °C in mode 11, and 300−350 °C in mode 10. In the idle mode, this temperature rarely exceeded 100 °C. The higher exhaust gas supersaturation due to this lower temperature may offer a possible explanation for our observation of more nanoparticles and nuclei modes in the idle mode over the two intermediate modes, 10 and 11.

Tobias et al. (*3*) suggested that there is more complete burning of semivolatile fuel components as the fuel-to-air ratio increases with engine load. Consequently, the engine-out sulfur dioxide (SO_2) concentration and production rate of SO_3 would be highest in mode 8, the maximum power mode. Therefore, the large number of nanoparticles found in mode 8 in the present study are likely to be from the condensation of sulfuric acid and water rather than from unburned hydrocarbons from the fuel. This may also explain the observed high influence of the fuel sulfur level on nanoparticles emissions observed in this mode.

Finally, it is important to assess the possible effects of sulfur in lubrication oil on the particle emissions. It has been suggested that this effect may be significant when using low sulfur fuels (*17*). In the present study, the sulfur content of the lubrication oil used by all the buses was 6000 ppm. However, the consumption rate of oil in relation to fuel is very small. We assess that the contribution of lubrication oil sulfur to particle emissions is negligible when compared to that from the fuel sulfur. Moreover, the buses used the same type of oil with both types of diesel fuel. Therefore, in the present study, the sulfur content of the oil could not have been responsible for any differences observed in the nature of the emissions using the two types of fuel.

The results of this study, using fuels of two different sulfur contents confirm previous observations 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 sulfuric acid. The second occurs at the high loads and is dominated by sulfuric acid and water nucleation.

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Supporting Information Available

Table of primary dilution ratios and particle size distributions by bus. This material is available free of charge via the Internet at http://pubs.acs.org.

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