

Effect of Lube Oil on the Physicochemical Characteristics of Particulate Matter Emitted from a Euro 4 Light Duty Diesel Vehicle

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ABSTRACT

This paper investigates the effect of lubrication oil on the physical and chemical characteristics of the particulate matter (PM) emitted from a Euro 4 diesel vehicle. Two different lubrication oils were examined. A fully synthetic ACEA grade B3 service-fill oil of low sulfur content (1760 ppm wt.) falling into the 0W-40 SAE viscosity grade and a mineral ACEA B2-98 motor oil of high sulfur (8890 ppm wt.), falling into the 15W-40 SAE viscosity grade. To exclude interferences from the fuel derived sulfur, a rather sulfur-free fuel (< 10 ppm wt.) was used in the experiments. The experiments included steady state tests, the certification cycle and real-world high-speed transient driving conditions. The properties measured included total particle mass collected on Teflon-coated filters, total particle number measured by a condensation particle counter, size distributions determined by a scanning mobility particle sizer. Chemical analysis was performed to investigate the metallic and the ionic character of the particulate matter for the different lubes. Results showed that the vehicle complies with the Euro 4 emission limits when tested over the type-approval NEDC regardless of the lubrication oil used. Both PM mass and number were drastically reduced with particle filter.

INTRODUCTION

Due to the substantial fuel economy benefit over its gasoline counterpart, diesel car is the key measure for reducing carbon dioxide and, thus, lowering the risk of dangerous climate changes. As a consequence, they are expected to overtake gasoline car sales in Europe and to form an emerging passenger car market in the US.

However, diesel vehicles continue to be higher emitters of particulate matter (PM) and nitrogen oxides (NO_x)

than gasoline ones fulfilling the equivalent emission standard. PM emissions have been significantly reduced over the last years and new vehicles complying with the Euro 4 standards emit below 25 mg/km, compared to ~100 mg/km 10 years ago. Future Euro 5 emission standards though (recently proposed at 3 mg/km) will be difficult to reach without the introduction of diesel particle filters (DPFs), which typically result to PM levels even below 1 mg/km [1]. In some instances DPFs have been seen to lead to the formation of a large number of volatile nanoparticles, especially at high loads [2-6]. The high nucleation rate has been attributed to the reduction in solid particle surface by the DPF, which enhances the homogeneous nucleation of sulfuric acid vapor [6]. Elimination of these particles will require strict control of the sulfur in both the fuel and the lube oil [7-9].

Fuel sulfur content in the near future is going to decrease into very low levels (as low as 1 ppm). When using very low sulfur fuels, the effect of the sulfur in lubricating oil may become dominating. Several studies have shown that lubricating oil contributes significantly to the engine-out PM yield accounting for 25% of the total PM mass emission in heavy – duty applications and somewhat lower in light – duty applications [10-11]. In this framework, the present work investigates the effect of two lubricating oils of different origin (synthetic vs. mineral oil base) and sulfur content on NO_x and PM emissions from a current technology (Euro 4) diesel passenger car. The study includes measurements of gaseous pollutants, the NO₂/NO_x split, particle size and number concentration and particle chemistry. To minimize any fuel effect we used an ultra-low sulfur fuel. The same vehicle is then retrofitted with a catalyzed DPF (CDPF) to examine the effect of this technology to all emission parameters studied. It is expected that the results of this study will provide useful experimental support to all discussions related to future emission standard formulation.

EXPERIMENTAL

VEHICLE CONFIGURATIONS

The vehicle tested in this study was a diesel Honda Accord 2.2 i-CTDi, with initial mileage of 23000 km, which complies with Euro 4 passenger car emission regulations in Europe. This vehicle in its original configuration (OAC) is equipped with an oxidation pre-catalyst and a two-stage oxidation underfloor catalyst with DeNO_x characteristics (the so-called "4-way catalyst"). More information about the engine and the vehicle aftertreatment can be found in the literature [12]. The vehicle was also tested in an alternative configuration, where its underfloor catalyst was replaced by a SiC catalyzed diesel particle filter (CDPF; Ø 5.66"×10", 300 cpsi, 52% porosity). This retrofitted vehicle is expected to fulfill the upcoming Euro 5 PM emission standards in Europe.

FUELS AND LUBRICATION OILS

In order to increase the efficiency of aftertreatment devices and to be able to distinguish the contribution of lube oil originating sulfate particulates, low sulfur fuel was used in the experiments. The fuel, which was provided by Shell Hellas, had a nominal sulfur content of less than 10 ppm wt. and fulfilled Directive 2003/17/EC (EN590:2004) in all other properties. Two different lubrication oils were tested. The first was a fully synthetic ACEA grade B3 service-fill oil of low sulfur content falling into the 0W-40 SAE viscosity grade (from this point on denoted as Low Sulfur Lube – LSL). The second one was a mineral ACEA B2-98 motor oil falling into the 15W-40 SAE viscosity grade and having about 5 times higher sulfur content (from this point on denoted as High Sulfur Lube – HSL). The synthetic oil was replaced at the middle of the measurement campaign and the vehicle was subjected to 500 km conditioning with the mineral lubrication oil. Additional details and the chemical analysis of the lube oils are given in Table 1.

CONDITIONING AND TESTING PROTOCOL

The emission measurement tests comprised both transient cycles and steady-state tests. Each measurement day started with a cold-start New European Driving Cycle (NEDC) which was followed by three real-world driving cycles, developed in the framework of the European "Artemis" Project [13]. NEDC is a combination of a (cold-start) urban driving test (UDC) and an extra-urban test (EUDC). The "Artemis" driving cycles are all hot-start and include an Urban, a Road and a Motorway part. Finally, two steady-state tests at constant speeds of 50 and 120 kph (road load) were conducted. The daily test sequence is summarized in Table 2. At the end of each daily test, the vehicle was driven by running three additional EUDCs and was soaked overnight, as a preconditioning for the following measurement day. The measurement campaign consisted of 8 test days in total (2×LSL×OAC, 2×HSL×CDPF).

Table 1: Properties and composition in trace elements (ppm) of the lubrication oils used in this study

Property/Element	Low Sulfur Oil	High Sulfur Oil
Base Stock	Synthetic	Mineral
Viscosity Grade	0W - 40	15W - 40
KV100 (cSt)	12.8	14.94
KV40 (cSt)	74.48	105.94
Viscosity Index	174	148
Barium (Ba)	0.066±0.002	0.067±0.002
Cadmium (Cd)	0.01±0.001	0.32±0.003
Cobalt (Co)	NA ^(*)	NA
Chromium (Cr)	3.9±0.1	1.76±0.1
Copper (Cu)	0.062±0.002	0.063±0.002
Iron (Fe)	19±0.3	13.5±0.1
Manganese (Mn)	0.41±0.01	0.035±0.01
Nickel (Ni)	2.72±0.1	1.344±0.05
Phosphorus (P)	605±40	883±45
Antimony (Sb)	0±<0.4	0±<0.4
Selenium (Se)	0±<0.1	0±<0.1
Silicon (Si)	0±<0.1	0±<0.1
Tin (Sn)	0±<0.4	0±<0.4
Strontium (Sr)	0.54±0.05	0.072±0.004
Calcium (Ca)	1540	NA ^(*)
Zinc (%)	662±	NA
Sulfur (%)	0.176	0.889

^(*) Not Available

Table 2: Test sequence of the daily measurement procedure

Order	Driving Cycle / Test	Engine operation
1	Cold start NEDC	Transient
3	Urban Artemis	Transient
4	Road Artemis	Transient
5	Motorway Artemis	Transient
6	50 kph	Steady-state
7	120 kph	Steady-state
8	3×EUDC, preconditioning for next measurement day	Transient

EMISSION SAMPLING AND ANALYSIS

Dynamometer/Constant volume sampling

The vehicle was run on a transient vehicle dynamometer, simulating drag, inertia and rolling resistances, as specified by Directive 98/69/EC. The exhaust was primarily diluted and conditioned following Constant Volume Sampling (CVS), as shown in Figure 1. A 6 m long corrugated stainless steel tube transferred the exhaust from the vehicle to the CVS tunnel inlet. The tube was insulated to minimize heat losses and particle thermophoresis and was clamped onto the vehicle with a metal-to-metal connection to avoid interference with synthetic material connectors. A flowrate of 500 Nm³/h (calculated at 0°C and 1 atm) was maintained in the CVS tunnel by a positive displacement pump. The dilution air was filtered with a HEPA class H13/EN1822 filter at the inlet of the dilution tunnel.

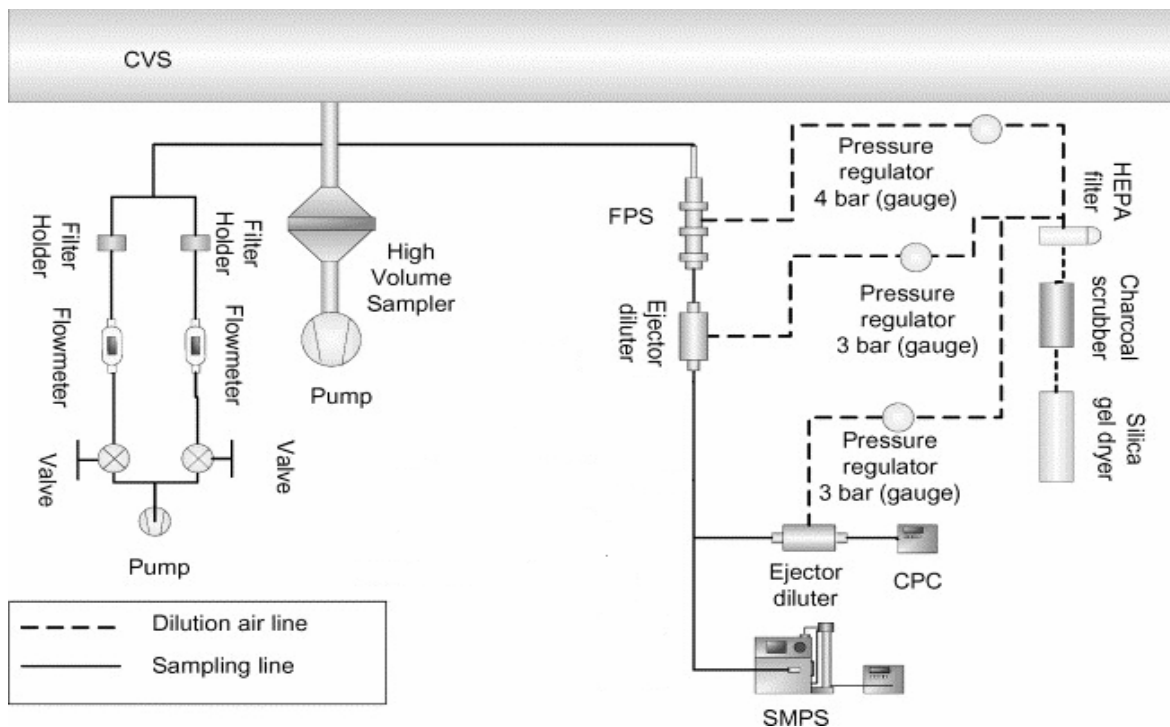


Figure 1: Experimental setup schematic

Gaseous pollutants sampling

Gaseous emissions were determined following the regulations. Hydrocarbon emissions were measured by a heated-line flame ionization detector (FID), nitrogen oxides by a chemiluminescence (CLD) analyzer, and carbon monoxide and carbon dioxide using Non-Dispersive Infra-Red (NDIR) analyzers. Fuel consumption was determined using the carbon content of the exhaust gas. In addition to the above the NO_2/NO_x ratio was measured using a two-channel fast response chemiluminescence analyzer (Cambustion Ltd, model fNOx400). Sample was taken with heated probes from the raw exhaust about 3 m from the end of the exhaust pipe. NO_2 concentration was derived from simultaneous measurement of NO and NO_x .

Collection and Chemical Analysis of Particulate Matter

PM was collected on 47 mm PTFE-coated fiber filters (Pallflex TX40H120-WW) to determine PM mass, following the regulations. Each filter was ultrasonically extracted using deionized-distilled water with a small amount of isopropyl alcohol to reduce the hydrophobicity of PTFE coating. Water-soluble ions were determined by ion-chromatography (IC) according to Mouratidou et al. [14]. Ions were recovered almost quantitatively, while the percent recoveries of PAHs ranged between 76 % - 106 % for individual compounds. The estimated precision of quantification by IC was better than $\pm 10\%$. Finally, PM samples were also collected on high-volume 8.5×10^7 cellulose filters, which were subsequently analyzed for heavy metals and trace elements by Energy Dispersive X-Ray Fluorescence Analysis (ED-XRF) according to Arditoglou et al. [15]. Detection limits of individual elements ranged between 1-

100 ng cm^{-2} . The estimated precision of XRF analysis ranged between 0.1% and 30% for individual elements, being $< 5\%$ for most of them. One single filter for each type of chemical analysis was used over all driving cycles in the CDPF configuration to increase the total mass collected on the filters. Thus, PM chemical analyses are a composite of all driving cycles in the CDPF case

Airborne Particle Measuring System

A Fine Particle Sampler (Model FPS-4000, Dekati, Ltd., Tampere, Finland) was used to sample and further dilute exhaust from the CVS tunnel, for airborne particle characterization. Depending on the particle emission concentration (use of the CDPF in the exhaust line) one or two additional, ejector-type dilution stages were installed to bring the aerosol concentrations within the measuring range of the particle analysis instrumentation. The FPS dilution ratio was monitored daily for drifts using CO_2 as a trace gas while the ejector diluters were calibrated at the start of the measurement campaign [16].

A Condensation Particle Counter (CPC, Model 3010, TSI Inc., Shoreview, MN) monitored the number concentration of the total particle population in real time. A Scanning Mobility Particle Sizer (SMPS, Model 3936L, TSI Inc., Shoreview, MN) was applied for the measurement of the number weighted size distributions over steady-state tests. The sheath air flowrate was set at 10 lpm and the monodisperse flowrate at 1 lpm, giving a size spectrum of 7.64-289 nm.

RESULTS AND DISCUSSION

TRANSIENT CYCLE TESTS

Regulated emissions

The regulated emission data obtained with the two lubrication oils at different aftertreatment configurations over the various driving cycles are summarized in Figures 2-5. In all figures, error bars correspond to the maximum and minimum of the measurement. The levels of the Euro 4 and the proposed Euro 5 emission standards are also shown [17]. When tested over the type-approval NEDC, the vehicle complied with the Euro 4 emission limits in all configurations and by some margin, especially for CO (Figure 2), which practically disappears over the hot-start “Artemis” cycles.

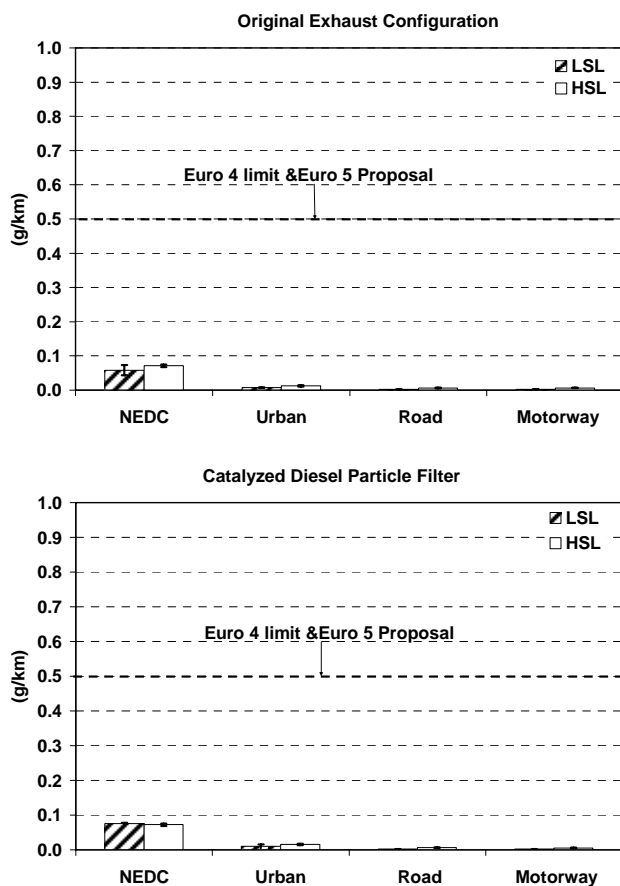


Figure 2: Carbon Monoxide (CO) emissions as a function of driving cycle for the original (top) and CDPF (bottom) configurations.

The NO_x emission rate (Figure 3) was found significantly above the NEDC-based NO_x emission standard over the non regulated cycles. The emission rates measured for OAC and HSL were 3.7, 2.1 and 2.6 times higher than the Euro 4 limit over the urban, road and motorway Artemis cycles respectively; the corresponding values measured for CDPF and HSL were 3.4, 2.1 and 2.6 whereas for LSL were 3.3, 2.0 and 2.1 both for the OAC and CDPF configurations.

No significant differences were seen between the two lubrication oils, although, in most cases, HSL tended to lead slightly higher NO_x emissions. In addition, the NO_x emission rate was somewhat higher for the CDPF exhaust configuration. These results further support our previous observation that the low NO_x emission profile of the vehicle over the NEDC is rather due to engine calibration. Finally, as expected, the $\text{HC}+\text{NO}_x$ emission profile was almost identical with that of NO_x (Figure 4).

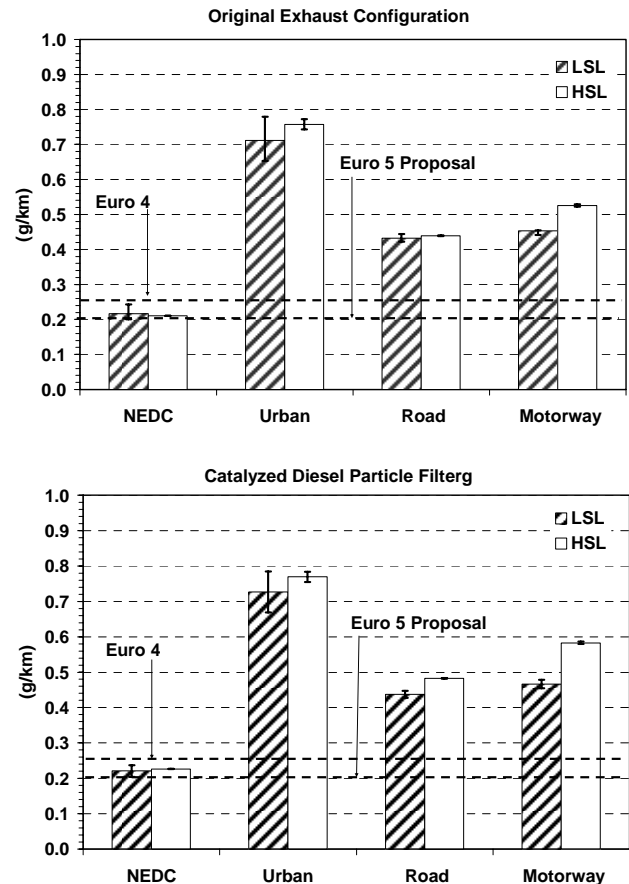


Figure 3: Nitrogen Oxides (NO_x) emissions as a function of driving cycle for the original (top) and CDPF (bottom) configurations.

The mean PM emission rate over the NEDC was at the Euro 4 emission standard with OAC and LSL and it was increased by 12% for HSL. PM emission rate for LSL was reduced over the non-regulated cycles as well (by 14% over the Road cycle and by 21% over the Motorway cycle) with the exception of the Urban cycle where it was increased by about 10% (opposite to fuel consumption – see below). As shown, the PM emission rate over this cycle was in general increased.

As expected, the CDPF results in significant reduction of PM emission rate. With LSL use the reduction was about 96% over the NEDC and motorway cycles and about 93% over the urban and road cycles. For HSL the reduction was 97% over the NEDC, 88% over the urban, 95% over the road, and 81% over the motorway cycles,

respectively. At CDPF configuration, the LSL showed better performance than HSL especially in urban and motorway cycles.

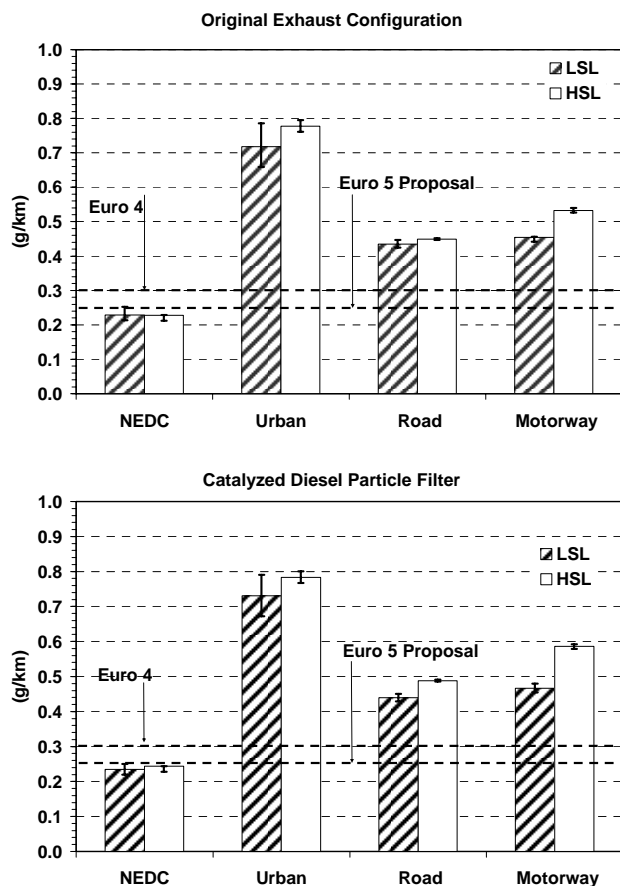


Figure 4: Sum of Nitrogen Oxides (NO_x) and total hydrocarbon (HC) emissions as a function of driving cycle for the original (top) and CDPF (bottom) configurations.

The PM emissions were generally found to follow the fuel consumption (FC) pattern (Figure 6) over the different cycles. FC, as calculated from the carbon balance based on exhaust measurements, was found significantly lower when using the LSL. The difference between the two lubricant oils was about 10% for the NEDC and the Artemis urban cycle and about 7% for the Artemis Road and Motorway cycles. Better lubricity of the synthetic fuel may be partly responsible for this. However, a fuel consumption difference of up to 10% is beyond the range one would normally expect for a lube oil effect. However, no other obvious reason could be identified for this difference.

Non-regulated pollutants

The high NO₂/NO_x ratios usually observed in modern diesel engines [18, 19, 20] were also observed in this study. In all tests, this ratio exceeded 50% (Figure 7). The OAC configuration leads to 5-8% higher NO conversion when HSL is used. On the other side, CDPF produces slightly higher NO conversion (2-5%) with LSL

(except for the case of motorway cycle). In both aftertreatment configurations (including the oxidation pre-catalyst), the catalytic formulation probably promotes high NO₂/NO_x ratios to enhance oxidation of PM even under relatively low exhaust temperatures. This fact in conjunction with the low sulfur fuel effects (the low exhaust SO_x content and its limited adsorption on the active catalytic centers), provide a reasonable explanation of the high NO₂/NO_x ratio observed.

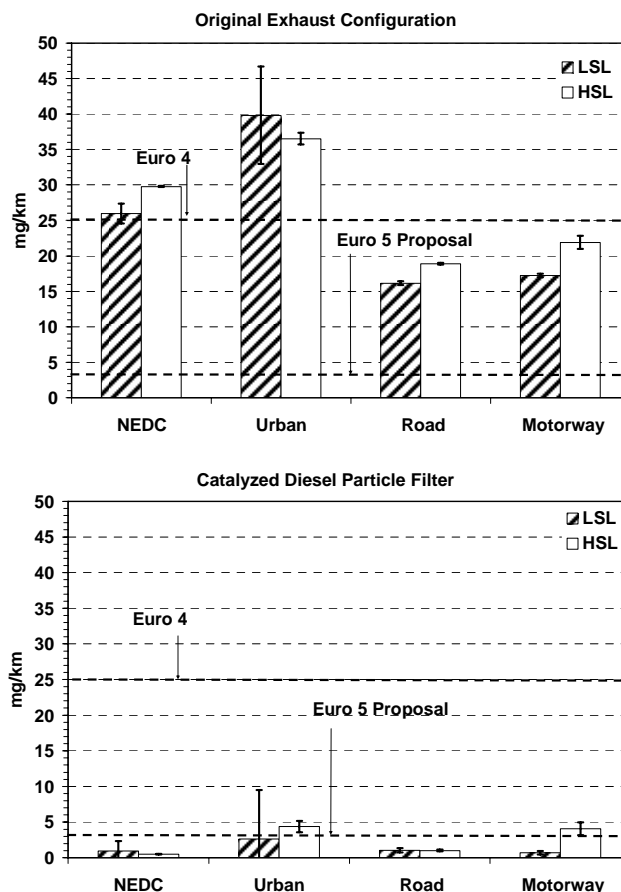


Figure 5: Particulate matter (PM) emissions as a function of driving cycle for the original (top) and CDPF (bottom) configurations.

The effect of the driving cycle on the NO₂ over NO_x ratio is not clear although some rough trends could be identified. The high temperature motorway cycle produced the lowest ratio when using LSL, whereas the lowest ratio was measured over the cold start NEDC when using the HSL. In the first case, the high temperature thermodynamic equilibrium limitation of NO to NO₂ seems to control the conversion. In the second case, the lower ratio mainly comes from the initial, cold-start operation of the catalyst, since the NO₂/NO_x ratio was found 50-60% over the cold UDC and 70-77% over the EUDC part.

Figure 8 summarizes the results for the total particle number emission rate. The total number emission rate in the OAC/LSL configuration was $5.6-7.5 \times 10^{13} \text{ km}^{-1}$,

over the different driving cycles. The corresponding result in the OAC/HSL configuration was $7.3\text{-}9.9 \times 10^{13} \text{ km}^{-1}$, that is, on average higher by about 20%. When the CDPF was installed, the reduction was dramatic (two to three orders of magnitude) with the exception of CDPF/HSL configuration over the Artemis Motorway cycle. In this case, the total number emission rate was about three orders of magnitude higher than that produced by CDPF/LSL configuration, about 1.3 times higher than that produced by OAC/HLS and about 2.1 times higher than that produced by OAC/LSL configuration.

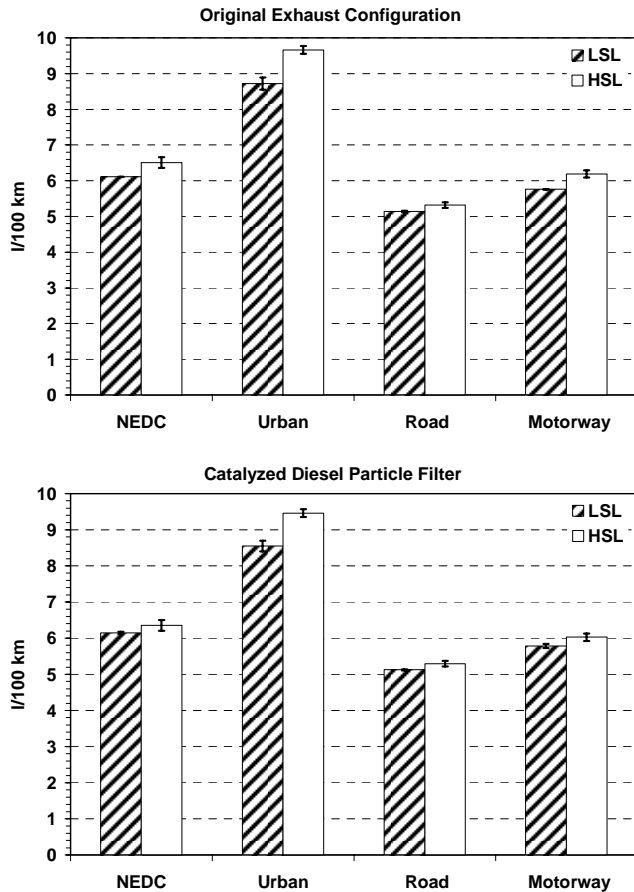


Figure 6: Fuel consumption (derived from carbon balance calculations) as a function of driving cycle for the original (top) and CDPF (bottom) configurations.

This result may be attributed to the nucleation-condensation of species present in the exhaust (mainly condensable sulfur species) at relative high concentrations due to the increased oxidative performance of the catalyst. This fact, in conjunction with the reduced surface area imposed by the CDPF, favors the process of nucleation-condensation which commences during or/and after the dilution-cooling of the exhaust and leads to the formation of a distinct nucleation mode of high number concentration (see below in the steady state tests). Further, a significant increase is observed in the CDPF particle number over the cold-start NEDC, compared to the urban and road Artemis cycles. Again, volatile nucleation mode

nanoparticles may explain this higher particle number. In addition, any shake-out of loose solid particle depositions, as the filter is exposed to this highly transient operation with respect to the thermal and flow conditions, may also contribute to the increase in particle number.

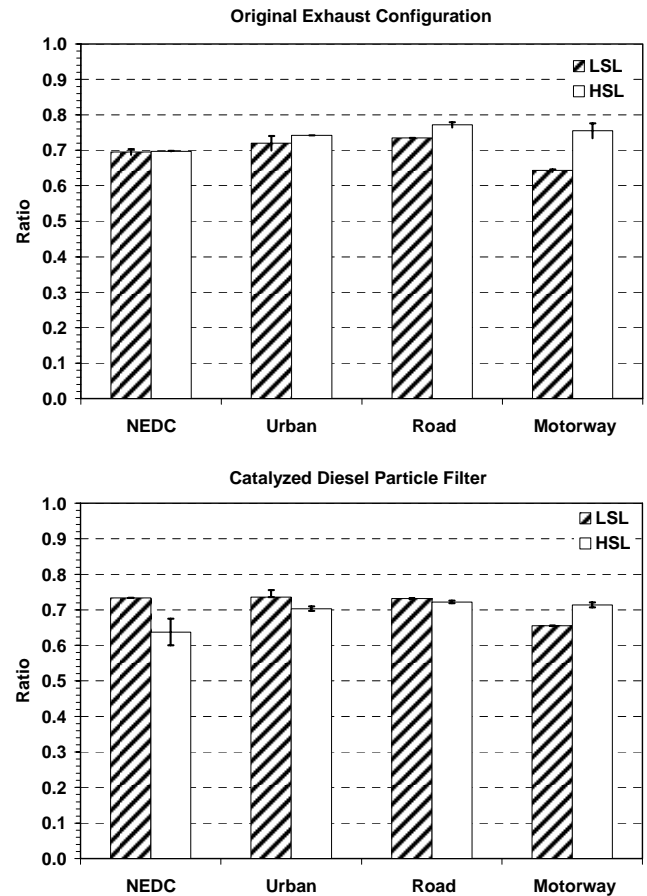


Figure 7: NO_2/NO_x mass ratio as a function of driving cycle for the original (top) and CDPF (bottom) configurations.

In this case, it is believed that they are formed by the nucleation-condensation of semi-volatile material earlier stored within the substrate and/or the particulate layer and released during the cold-start cycle as the CDPF heats up. This can be clearly seen in Figure 9 which shows the elevated particle number that was produced during the first ~300 s of the driving cycle. The extent of this phenomenon is lower in the OAC configuration, probably because the particle exhaust concentration is high enough to mask such effects.

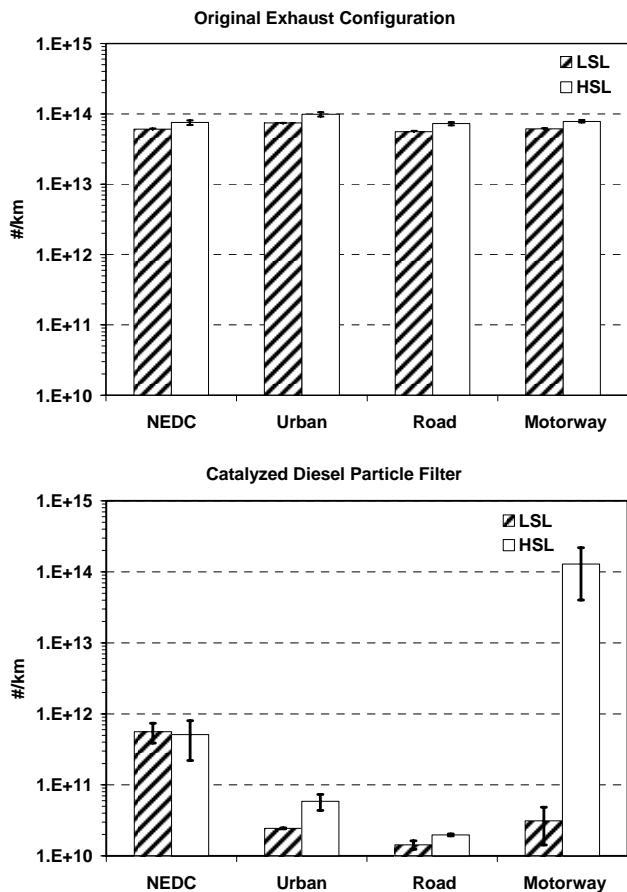


Figure 8: Total particle number as a function of driving cycle for the original (top) and CDPF (bottom) configurations.

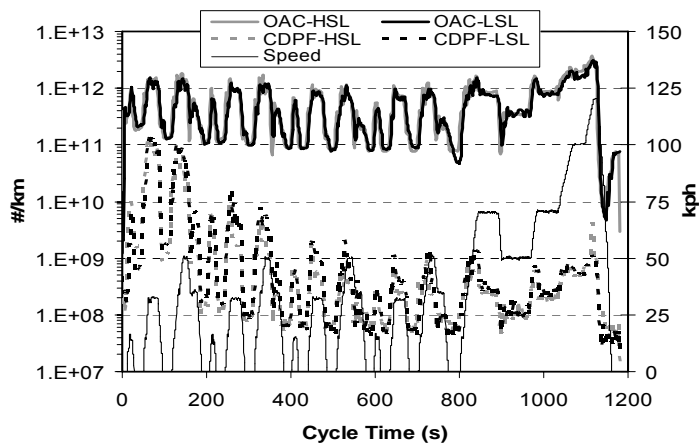


Figure 9: Particle number emission flux over the NEDC driving cycle for different aftertreatment configurations and lubrication oils (OAC: original exhaust configuration, CDPF: catalyzed diesel particle filter, LSL: low sulfur oil, HSL: high sulfur oil).

STEADY STATE TESTS

Figure 10 and Figure 11 show the number-weighted particle size distributions at 50 kph and 120 kph, respectively. At 50 kph and OAC configuration, the two lubrication oils exhibited almost the same lognormal

distributions with a geometric mean diameter in the range of 55-60 nm (59 nm for HSL and 55 nm for LSL). When the CDPF was installed, the number concentration dropped by 3 orders of magnitude. The distributions remained lognormal and the geometric mean diameter was about 54 nm for both lubrication oils.

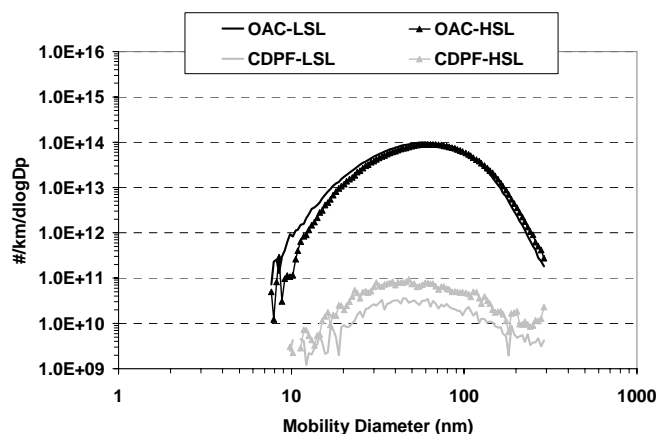


Figure 10: Number-weighted particle size distributions over 50 kph for different aftertreatment configurations and lubrication oils (OAC: original exhaust configuration, CDPF: catalyzed diesel particle filter, LSL: low sulfur oil, HSL: high sulfur oil)

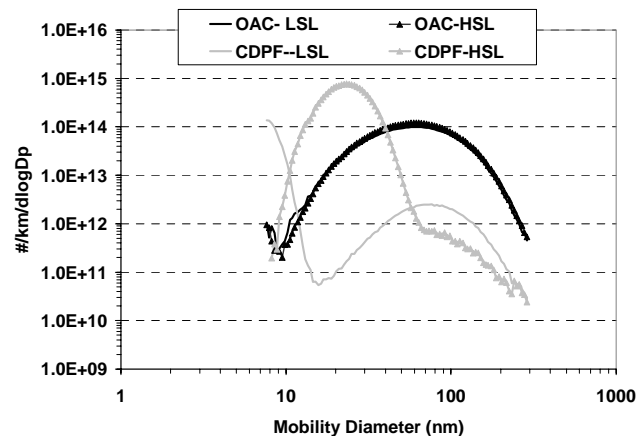


Figure 11: Number-weighted particle size distributions over 120 kph for different aftertreatment configurations and lubrication oils (OAC: original exhaust configuration, CDPF: catalyzed diesel particle filter, LSL: low sulfur oil, HSL: high sulfur oil)

The particle size distributions obtained at 120 kph and at OAC configurations were almost identical between the two oils, i.e. lognormal in shape with a geometric mean diameter of 58 nm. When the CDPF was installed, the number concentration of the accumulation mode particles dropped by almost 2 orders of magnitude. At the same time, a distinct nucleation mode formed. This result is considered as a consequence of sulfuric acid nucleation, a phenomenon that is favored in the absence of the solid fraction. The high oxidation rate of sulfur oxides over the aftertreatment configurations at high

exhaust temperature leads to sulfuric acid concentrations which are high enough to initiate nucleation, even with the ultra low sulfur fuel. These tests seem to be the most appropriate to compare the two lubrication oils. In the case of HSL, the nucleation mode has been completely developed having a geometric mean diameter of 23 nm. In the case of LSL, the nucleation mode is shifted to smaller particle sizes and it is not fully recorded due to instrument detection limitations. However, it can be easily deduced that its geometric mean diameter is in the range of 10 nm. Simulation of the recorded nucleation mode distribution suggests a geometric mean diameter of 8 nm.

At the CDPF configuration, the total number concentration with HSL use was about 20 times higher than LSL, whereas the mass concentration was about 8.5 times higher. The latter exceeds the sulfur mass ratio of the oils ($0.889/0.176 = \sim 5.1$) indicating that sulfur cannot be the only reason of higher PM emissions. Rather, a combination of reasons, including the increased sulfur oxidation rate, storage/release of condensable material, and possible differences in oil consumption induced by the different lubrication oil characteristics seem responsible for the higher emissions in case of the HSL. Further, the increased hydrocarbon material measured with HSL (possibly due to the mineral base of HSL) may account for the increased particle mass concentration.

PM CHEMICAL ANALYSIS

Emission of trace elements

The XRF analysis performed on the Hi-Vol cellulose filters provided the emission rate of a number of trace elements for the two lube oils measured (Table 3). HSL showed significantly higher total metallic emission rate than LSL, regardless the aftertreatment configuration applied: about 4.5 times higher over NEDC, road, and motorway cycles and 3.2 times over the urban cycle.

Generally, most of Table 3 elements were also identified in the chemical analysis of the lube oils (Table 1). For both oils, the most abundant elements in the exhaust were Ba, Sn, Zn, Cd, Cu, Cr, and Fe. Fe, Zn, and Cr were detected in relatively significant amounts in both lube oils, although this was not the case for other metals. Fe is regularly one of the most abundant elements in diesel vehicle exhaust [21, 22], while high Zn and Cr were also reported by other investigators in the exhaust of a diesel passenger car [23]. Combustion has been also identified as a significant emitter of Cd [24]. Other sources of trace elements include engine attrition and elements not filtered by the engine intake filter or present in the fuel [25].

The high (and variable) Ba levels measured in the vehicle exhaust require some further attention. Ba compounds have been used as smoke-suppressants in the fuel [25, 26]. Although these have been rather phased-out in recent years, one cannot exclude high Ba

emissions due to fuel additives. When an engine is operated at relatively cold conditions Ba additives can lead to white deposits (barium carbonate) formation on the exhaust valves and nozzles. Later, these deposits can be destroyed under higher load conditions and may explain the variable Ba abundance in the exhaust. Another possible source of Ba may be the oxidation catalyst washcoat attrition, where Ba is used as a stabilizer. Ba is known of its NO_x storage properties and it is expected in relatively high abundance in the 4-way catalyst used in this car [3].

The effect of driving cycle is significant on the emission rate of all elements. Their emission rate generally follows the total PM emission rate shown in Figure 5. Therefore, the highest emission rates for both lube oils is appear over the Artemis urban cycle and the lowest over the Artemis motorway cycle. The most significant effect was however observed when the DPF was installed in the exhaust line. The total elemental emission was reduced by a factor of 5.2 for LSL and of 4.4 for HSL. Specific emission was also significantly reduced except for Cr and Sn in the case of HSL. Only Fe and Sn are in comparable levels with the non-DPF emission rate.

Ion emission rate

The ionic species determined by the IC-analysis included nitrate, sulfate and ammonium species (Table 4). For the OAC configuration, HSL showed by far higher ion emission than LSL except from the case of sulfates measured over the urban cycle. The nitrate emission rate of both lubricants follows the NO_x emission rate presented in Figure 3. For both lubricating oils, the absolute emission rate and the effect of aftertreatment configuration is a function of the driving cycle. Thus, ion emission increases over the Artemis cycles and over the urban cycle in particular.

The effect of CDPF on ion emissions can be compared to the non-DPF cases by calculating the “average” OAC emissions for LSL and HSL, similarly to trace elements. On this basis and for HSL, CDPF reduces nitrate and ammonium emissions by a factor of 35 and sulfates by a factor of 5. For LSL, CDPF reduced ion emission by a factor of 1.6 for nitrate, of 6.5 for sulfate and of 4.2 for ammonium.

CONCLUSIONS

A measurement campaign was carried out to investigate the effect of lubrication oil chemical composition on the emission profile of a Euro 4 diesel passenger vehicle operating on ultra low sulfur fuel. The vehicle was configured in two aftertreatment setups, the original one with an oxidation pre-catalyst and a two-stage oxidation underfloor catalyst and an alternative one where the underfloor catalyst was replaced by a SiC catalyzed diesel particle filter. The lubricants tested included a fully synthetic service-fill oil of low sulfur content and a mineral service-fill oil of higher sulfur content. An extended measurement protocol included determination

of regulated gaseous pollutants and PM, NO₂/NO_x ratio, particle number and size distribution, as well as metal and ion determination of the particulate emitted. The

following conclusions can be drawn from the measurement results:

Table 3: Average emission rate (µg/km) and standard deviations of trace elements detected by XRF-analysis on PM samples

Trace Element	NEDC		Urban		Road		Motorway		CDPF ^a	
	LSL	HSL	LSL	HSL	LSL	HSL	LSL	HSL	LSL	HSL
Ba	64.6±62.6	371.5	111±16	650	12.3±2.4	236.8	32.6±21.5	233	9.4	75.8
Cd	18.8±2.4	30.4	61.4±19.4	76.2	20.2±2.19	21.5	10.6±0.1	18.1	3.0±1.9	8.8
Co	3.0±2.0	4.6	10.9±8	45.7	1.5±0.4	2.8	1.5±1.1	8.6	1.16	2.5
Cr	16.4±7.6	1.5	28.8±8.8	4.0	8.9±2.2	0.6	5.6±0.7	0.6	3.4±0.9	6.4
Cu	8.7±8.6	17.5	16.8±2.5	89.2	4.1±0.6	21.5	3.8±0.2	24.8	2.5±0.9	7.5
Fe	12.5±6.7	167.7	62.3±49.6	390	6.6±0.7	108.8	9.2±4.4	84.5	21.2±9.4	46.0
Mn	3.4±0.4	19.5	7.4±2.3	48.7	ND	6.5	2.4±1.3	10.9	ND	3.9
Ni	3.8±2.3	9.3	27.7±10.7	19.5	4.6±1.1	3.6	3.2±1.0	3.7	2.3±0.3	1.9
P	ND	2.9	57.6±2.9	6.6	8.8±0.8	9.9	ND	1.3	ND	0.6
Pb	5.7±1.9	41.2	6.9±2.1	56.7	2.7±0.3	20.6	2.6±2.5	10.2	ND	7.2
Sb	2.2±0.6	81.0	39.0±12.5	308	9.9±5.8	34.6	ND	46.7	ND	10.2
Se	2.7±1.6	5.3	12.4±4.2	19.2	1.8±0.4	11.7	2.9±0.2	1.7	1.1±0.1	0.5
Sn	27±16.8	11.2	63.8±38.5	32.5	16.7±6.2	7.4	18.3±2.1	6.1	3.6±2.1	38.2
Sr	6.0	22.6	4.2±1.8	43.7	0.3±0.1	18.9	2.0±1.6	13.9	ND	5.6
Ti	ND	33.1	24.1±4.2	33.1	6.2±0.6	14.0	4.5±0.1	6.5	ND	2.8
Zn	25.6±0.2	83.6	87.9±53.2	163	26.3±10.2	67.4	24.4±4.1	70.6	4.2±0.2	9.2

^a Emission derived as a composite from all driving cycles
 ND: Not Detectable (below the limit of detection)

Table 4: Average emission rate (µg/km) and standard deviations of ions measured by IC-analysis on PM samples

Ion	OAC-NEDC		OAC-Urban		OAC-Road		OAC-Motorway		CDPF	
	LSL	HSL	LSL	HSL	LSL	HSL	LSL	HSL	LSL	HSL
NO ₃ ⁻	617±298	5940	2220±794	8660	1350±764	18500	1207±838	17650	841 ±7.9	360
SO ₄ ⁻	293±11.6	2800	1555±1095	1272	281±157	4380	380±213	12580	96.3±68.6	1010
NH ₄ ⁺	81.5 ±2.1	1460	437±76.2	3780	120±69.2	1563	79.9±20.2	564	47.4±19	52.5

- NO_x emissions largely depend on the driving cycle. Over non regulated cycles NO_x emission was found significantly higher than the NEDC-based one, indicating that engine and aftertreatment are not tuned outside the legislative operation window for them to provide effective NO_x control. Significant differences between the two lubrication oils were not found, although, in most cases, mineral oil tended to emit slightly higher.
- The vehicle complied with Euro 4 PM emission limit over the NEDC with the synthetic oil but not with the mineral one.
- The particle filter effectively reduces PM mass emission (96-97% over the original aftertreatment configuration) regardless of the oil used.
- The particle filter drastically reduces number emission as well (by 2-3 orders of magnitude) over the NEDC and driving cycles up to moderate speeds.
- Volatile nanoparticles were measured downstream of the filter under specific conditions (cold-start and high loads) and may mask the number emission reduction. Use of mineral oil with high sulfur content seems to intensify the nucleation effect.
- Metallic emission rate was reduced by a factor of 4.5 over the NEDC when synthetic oil was used and showed similar reductions over the non-regulated Artemis cycles.
- The particle filter reduces metallic emission over the original aftertreatment configuration by a factor of 5.2 for the synthetic oil and by a factor 4.4 for the mineral oil. The most abundant trace elements found in the exhaust were Ba possibly originating from catalyst washcoats and/or fuel additives. Synthetic oil showed significantly decreased specific metallic emission rate relative to mineral oil regardless of the aftertreatment configuration applied.

8. Nitrates were found to be the most abundant ion group and correlated with NO_x emissions. Compared with the original configuration, the particle filter reduces ion emission by a factor of 1.6 for nitrate, of 6.5 for sulfate and of 4.2 for ammonium when the synthetic oil was used. The corresponding reductions for the mineral oil were by a factor of 35 for nitrate and ammonium emissions and by a factor of 5 for sulfate emissions.
9. In almost all cases tested, the vehicle exhibited better emission performance with the use of the synthetic oil over the mineral one.

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DEFINITIONS, ACRONYMS, ABBREVIATIONS

CDPF:	Catalyzed Diesel Particle Filter (configuration)
CLD:	Chemiluminescence Detector
CPC:	Condensation Particle Counter
CVS:	Constant Volume Particle Sampling
DOC:	Diesel Oxidation Catalyst
CDPF:	Catalyzed Diesel Particle Filter
EUDC:	Extra Urban Driving Cycle
FID:	Flame Ionization Detector
FPS:	Fine Particle Samples
HSL:	High sulfur Lubricant
HPLC:	High-Pressure Liquid Chromatography
IC:	Ion Chromatography
LSL:	Low sulfur Lubricant
NDIR:	Non-Dispersive Infrared Detector
NEDC:	New European Driving Cycle
OAC:	Original Configuration
PM:	Particulate Matter
SMPS:	Scanning Mobility Particle Sizer
UDC:	Urban Driving Cycle
XRF:	X-Ray Fluorescence Analysis

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