

Effect of a DPF and Low Sulfur Lube Oil on PM Physicochemical Characteristics from a Euro 4 Light Duty Diesel Vehicle

Elias Vouitsis, Leonidas Ntziachristos, Zissis Samaras

Lab of Applied Thermodynamics, Aristotle University Thessaloniki, GR 54124 Thessaloniki, Greece

Theodoros Grigoratos, Constantini Samara

Environmental Pollution Control Lab, Aristotle University Thessaloniki, GR 54124 Thessaloniki, Greece

George Miltsios

Mechanical Engineering Dept., Technological Educational Institute of Serres, GR 62124 Serres, Greece

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ABSTRACT

This paper studies the effect of a Catalyzed Diesel Particle Filter (CDPF) on the emission profile of a Euro 4 diesel vehicle operated on low sulfur fuel and lubrication oil. The vehicle was tested in its original configuration and with the CDPF retrofitted in place of its main underbody catalyst. Experiments included steady state tests, the certification cycle and real-world high speed transient driving conditions. Measurements 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 and chemical analysis of the mass collected for elemental and organic carbon, ions, PAHs, and trace elements. Results showed that the vehicle complies with the Euro 4 emission limits when tested over the type-approval NEDC, but it emits more nitrogen oxides and, in some cases, more particulate matter when tested over real-world test cycles. The CDPF reduces PM mass emission up to 90-95% and particle number by 2-3 orders of magnitude. However, nucleation of volatile species may occur under specific conditions of the engine exhaust dilution and sampling system and may mask this reduction. Emissions of chemical elements, elemental and organic carbon were also substantially reduced by the CDPF, while moderate reductions of ionic species and PAHs were observed.

INTRODUCTION

European member states have committed themselves in reducing greenhouse gases from road transportation, in the framework of their obligations to the Kyoto protocol. In this direction, they have negotiated a commitment from the automakers to reduce greenhouse emissions from the fleet of new cars by 25% in 2008, compared to

the 1995 levels. Amongst several measures that automakers took to reduce fleet average emissions, the promotion of diesel cars has been a fundamental one, due to the substantial fuel economy benefit of diesel cars over their gasoline counterparts. As a consequence, several diesel passenger cars are now offered in the European market, exhibiting desirable torque and drivability characteristics combined with a 20-30% improved fuel economy over gasoline ones. A recent survey showed that diesels accounted for 49% of the total European car market at the end of 2005 and they are expected to overtake gasoline car sales in Europe during 2006 [1]. At the same time, an emerging diesel passenger car market has been forming in US as well [2], in addition to the established market for diesel sport utility vehicles and pickups, which are commonly used as passenger vehicles.

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 by introducing engine related measures, such as high-pressure fuel injection and electronic control of the injection timing, and open-flow aftertreatment (diesel oxidation catalysts – DOCs). 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 (expected at 5 mg/km) will be difficult to reach without the introduction of diesel particle filters (DPFs), which result to PM levels even below 1 mg/km [3]. In some instances DPFs have been seen to lead to the formation of a large number of volatile nanoparticles, especially at high loads [4-8]. 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 [8].

Elimination of these particles will require strict control of the sulfur in both the fuel and the lube oil [9-11].

NO_x emission standards for diesels have been also becoming more stringent. Although the diesel NO_x emission standard was halved in the transition from Euro 3 to Euro 4 (2005), this still remains more than three times higher than the equivalent gasoline one. Aftertreatment devices are also considered for future NO_x emission standards, ranging from selective catalytic reduction, using an external agent to chemically reduce NO_x to N₂, and NO_x adsorbers, where NO_x adsorbs on the catalyst during lean operation and is later reduced to N₂ by forcing a rich environment over the catalyst. For the time being, manufacturers make use of the "conventional" formulation for diesel catalysts to reduce NO_x, by taking advantage of the limited NO_x reduction by HC over Platinum (Pt). At the same time, specific interest has been raised concerning the primary (direct) NO₂ emissions, produced in the exhaust of vehicles equipped with DOCs. NO₂ is by far more toxic than NO and recent studies [12, 13] indicate that NO₂ time-series do not decline with time as effectively as NO ones. Primary NO₂ emissions are mainly considered responsible for these persistent concentrations in urban areas [12-15]. It is believed that the increased use of certain types of DPFs in buses is likely one of the reasons for the increasing trends in the NO₂/NO_x ratio [15]. Other reasons include the increased penetration of diesel cars in the passenger car fleet and the new light- and heavy-duty engine and control technologies.

The various parameters that define the PM and NO_x pollution problem from diesel vehicles have initiated a number of discussions within each member state, involving the industry, the authorities, the academia and the community. As a result, several countries ask for an accelerated scheme for the introduction of diesel particle filters, specific measures which will guarantee fuel-neutral emission standards [16], PM emission standards based on the particle number in addition to total mass (the Particulate Measurement Programme [17]), NO₂ specific standards [12], while in Greece diesel cars are still banned from the two major cities until DPFs become mandatory, due to the elevated PM concentrations. In this framework, the current study aims at the detail characterization of NO_x and PM emissions from a current technology (Euro 4) diesel passenger car, including gaseous pollutants, the NO₂/NO_x split, particle size and number concentration information and particle chemistry. The maximum reduction potential of the car is sought by using ultra-low sulfur fuel and lube oil. The same vehicle is then retrofitted with a DPF 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 6 000 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 [18]. The vehicle was also tested in an alternative configuration, where its underfloor catalyst was replaced by a SiC catalyzed diesel particle filter (CDPF; \varnothing 5.66"×10", 300 cpsi, 52% porosity). This retrofitted vehicle is expected to fulfill the upcoming Euro 5 PM emission standards in Europe. In addition, a series of measurements with the vehicle equipped only with the oxidation pre-catalyst (PCT) were made to estimate the effect of the underfloor catalyst on the emissions.

FUELS AND LUBRICATION OILS

In order to increase the efficiency of aftertreatment devices and to minimize the contribution of sulfate particulates, low sulfur fuel and lubrication oil were 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. In the course of the experiments, two low sulfur lubrication oils were used. The first was the initial-fill oil used by the vehicle manufacturer, a fully synthetic ACEA grade B3 oil, falling into the 0W-40 SAE viscosity grade. The second, a regular service oil provided by BP, was also a fully synthetic ACEA grade B3 oil falling into the 0W-40 viscosity grade. The oil was changed in the middle of the measurement campaign and the vehicle was subjected to 500 km conditioning to the service fill lubricating oil. Additional details and the chemical analysis of the lubrication oils are given in Table 1. The data of Table 1 indicate that the two lubricating oils are largely similar as regards their properties and in particular their sulfur content. A preliminary analysis indicated that there was no relation of any statistical significance between the oils and the measurement results and hence it was decided not to differentiate between the two oils.

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 [19]. 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 comprised 9 test days (3×OAC, 2×PCT, 4×CDPF).

Table 1: Properties of the lubrication oils used in this study

Property	Initial Fill Oil	Service Fill Oil
Base Stock	Synthetic	Synthetic
Viscosity Grade	0W - 30	0W - 40
KV100 (cSt)	7.58	12.8
KV40 (cSt)	39.38	74.48
Viscosity Index	164	174
Calcium (%)	0.368	0.154
Zinc (%)	0.090	0.075
Phosphorous (%)	0.075	0.078
Sulfur (%)	0.221	0.176
Iron (ppm)	64	NA ^(*)
Copper (ppm)	41	NA

^(*) 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.

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 NO₂/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. NO₂ 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. After weighing, the PM-laden filters were cut in two equal portions for analysis of ionic species and polycyclic aromatic hydrocarbons (PAHs). One half of 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. [20]. The other half filter was ultrasonically extracted using acetonitrile and cleaned up through C₁₈ solid phase extraction cartridge. PAHs were determined by high pressure liquid chromatography with programmable fluorescence detection (HPLC/FD) according to Kalaitzoglou et al. [21]. The system was calibrated with the NIST 1647a Standard PAH Mixture containing 16 PAHs. The recoveries of ions and PAHs were examined by analyzing filter samples spiked with low and high concentrations of standard compounds. 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 and HPLC was better than ±10% and ±15%, respectively. Parallel to the PTFE-coated filters, 47 mm Quartz filters (Pallflex 2500QAT-UP) were deployed to collect PM for subsequent analysis of elemental (EC) and organic carbon (OC) following a modified Walkley-Black method [22]. Finally, PM samples were also collected on high-volume 8.5×10⁷ 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. [23]. 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.

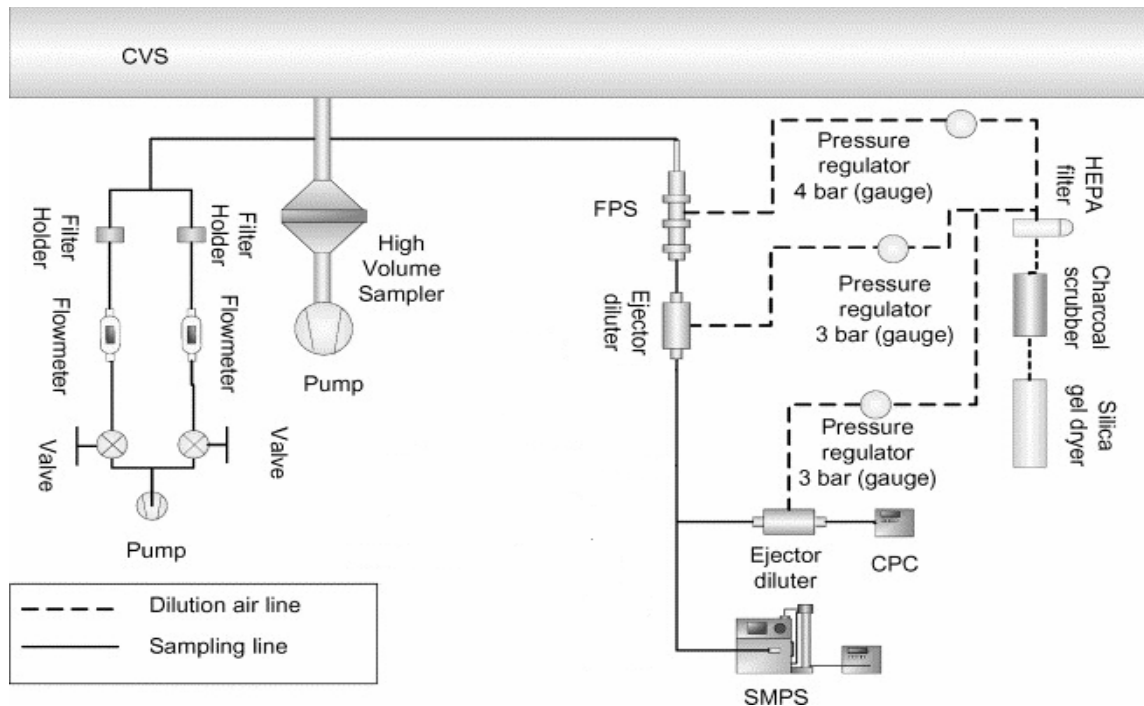


Figure 1: Experimental setup schematic

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 CO₂ as a trace gas while the ejector diluters were calibrated at the start of the measurement campaign [24].

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 different aftertreatment configurations over the various driving cycles are summarized in Figure 2 to 5. The levels of the

Euro 4 and the proposed Euro 5 emission limits are also shown. 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, which practically disappears over the hot-start “Artemis” cycles. Interestingly, the vehicle continued to comply with the NO_x emission standard, even when the two-stage underfloor catalyst was removed. This indicates that the NO_x emission profile of the vehicle over the NEDC is rather due to engine calibration.

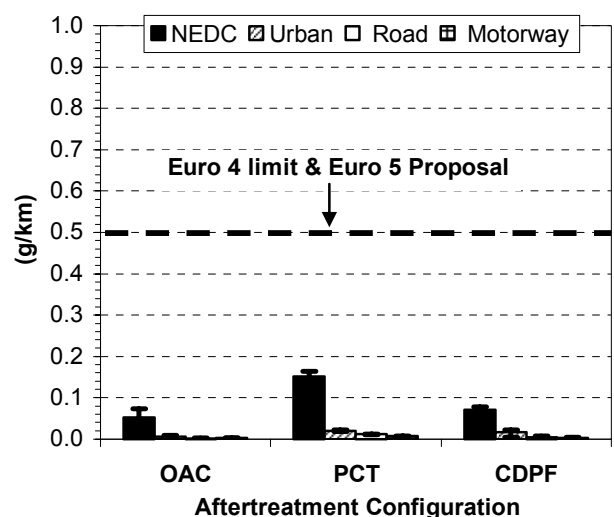


Figure 2: CO emission rate for different aftertreatment configurations and driving cycles

The NO_x emission rate was found significantly above the NEDC-based NO_x emission standard over the non regulated cycles. The emission levels measured were 3.2, 2.0 and 2.1 times higher than Euro 4 limit over the urban, road and motorway Artemis driving cycles respectively, a difference that is important for emission inventorying models. In the high exhaust temperature case of the motorway cycle though, use of the main underfloor catalyst seems to reduce NO_x emissions by 10% (compare OAC and PCT). Another interesting result is the reduction of NO_x emissions when the CDPF is used (compare CDPF and PCT). This reduction probably originates from an exhaust gas recirculation increase due to backpressure built-up in the exhaust line. This implies that appropriate tuning of the engine and aftertreatment devices can lead to NO_x reductions also over off-cycle conditions.

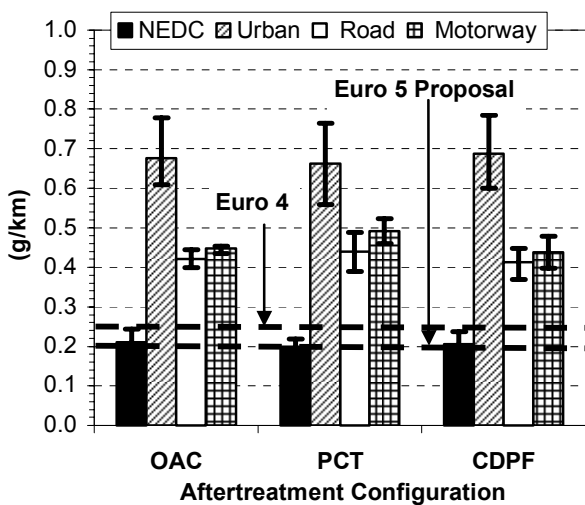


Figure 3: NO_x emission rate for different aftertreatment configurations and driving cycles

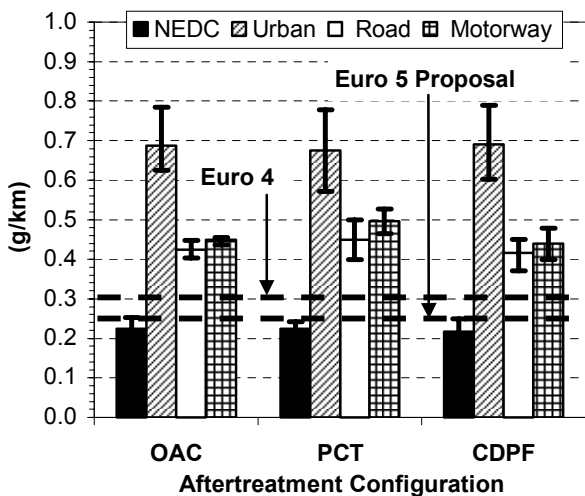


Figure 4: NO_x+HC emission rate for different aftertreatment configurations and driving cycles

PM emissions (Figure 5) were found to generally follow the fuel consumption pattern, shown in Figure 6, over the different cycles. The mean emission rate or the NEDC was at the Euro 4 emission standard for the OAC configuration and increased by about 10% when the main underfloor catalyst was removed. The underfloor catalyst also resulted in a ~10% positive effect on PM in road and motorway cycles. Over the urban cycle, the PCT configuration seems to result in a lower emission level, but this is rather due to an outlier measured at the OAC configuration. Exclusion of this outlier brings the OAC and the PCT measurements at the same level (31 mg/km), implying a minimal effect of the underfloor catalyst at this low temperature condition. This is rather expected, given that when the exhaust gas temperature is low, the effect of the close-coupled pre-catalyst in oxidizing the semivolatile material will be relatively more important than the effect of the main catalyst. Finally, one needs to mention that the variation of PM levels in different driving cycles is low compared to the variation of NO_x, and that off-cycle PM emissions can reach even lower levels than those of the certification cycle.

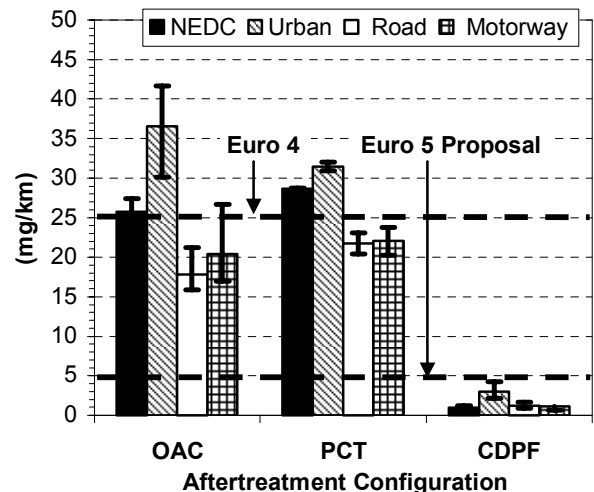


Figure 5: PM emission rate for different aftertreatment configurations and driving cycles

The CDPF results in 90% and 95% PM reductions over the urban cycle and all other cycles respectively. In fact, the Euro 5 emission limits are reached by a significant margin over all driving cycles, when using the DPF. This confirms once again what several studies have shown in the past, i.e. that DPFs can reduce PM emissions even by more than one order of magnitude.

Non-regulated pollutants

The NO₂/NO_x ratio in older technology diesel engines ranged from 0.1 to 0.3 [25-29], but modern engines are associated with higher values, mainly because of the oxidation aftertreatment used [12, 13, 30]. High NO₂/NO_x ratios are also observed for the current vehicle,

exceeding 50% in all configurations and driving cycles tested (Figure 7). The OAC configuration (only one measurement available) leads to 8-15% higher NO conversion than when the main underfloor catalyst is removed (PCT). However, the highest emission rates are recorded when the vehicle is equipped with the catalyzed DPF. This is because the catalytic formulation of CDPF is specifically designed to maintain high NO₂/NO_x ratio, thus efficiently oxidizing PM with NO₂, even under relatively low exhaust temperatures. This result is consistent with earlier observations on CDPF performance [31].

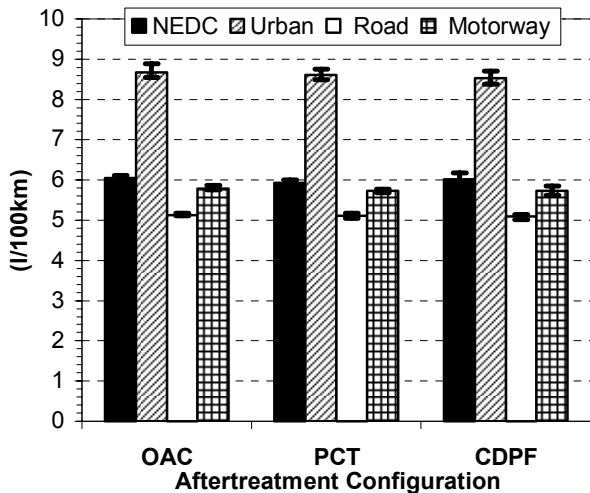


Figure 6: Calculated fuel consumption for different aftertreatment configurations and driving cycles

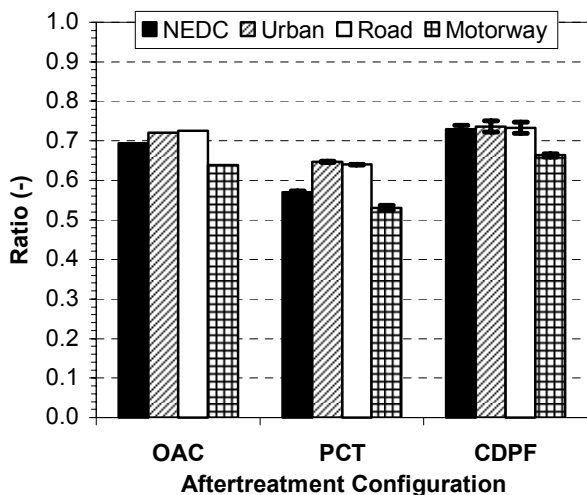


Figure 7: NO₂/NO_x Ratio for different aftertreatment configurations and driving cycles

It is also interesting to note the effect of driving cycle on the NO₂ over NO_x ratio. The lowest ratio was measured over the high temperature motorway cycle in all configurations, a result most likely due to the thermodynamic equilibrium limitation of NO to NO₂ conversion at higher temperatures. The cold-start NEDC also led to a lower ratio. This mainly comes from the initial, cold-start operation of the catalyst, since the NO₂/NO_x ratio was found 55% over the cold UDC and 77% over the EUDC part.

Figure 8 summarizes the results for the total particle number emission over the different driving cycles and aftertreatment configurations tested. The total particle number in the OAC configuration was $6.2-8 \times 10^{13} \text{ km}^{-1}$ for the different driving cycles. The total number emission increased by ~25% on average over all cycles when the underfloor catalyst was removed. When the CDPF was installed, the reduction was dramatic (two to three orders of magnitude). However, a significant increase is observed in the CDPF particle number over the cold-start NEDC, compared to the Artemis cycles. Real-time recordings of the particle number (Figure 9) revealed that the elevated particle number was produced during the first ~300 s of the driving cycle. The increased particle numbers are considered to be volatile nanoparticles, which form as the DPF heats up and gradually releases semi-volatile material, earlier stored within the substrate and/or the particulate layer. The extent of this is lower in the non-DPF configurations both because the particle exhaust concentration is already high therefore masking such effects, but also because the catalysts cannot store as much semi-volatile material as the DPF.

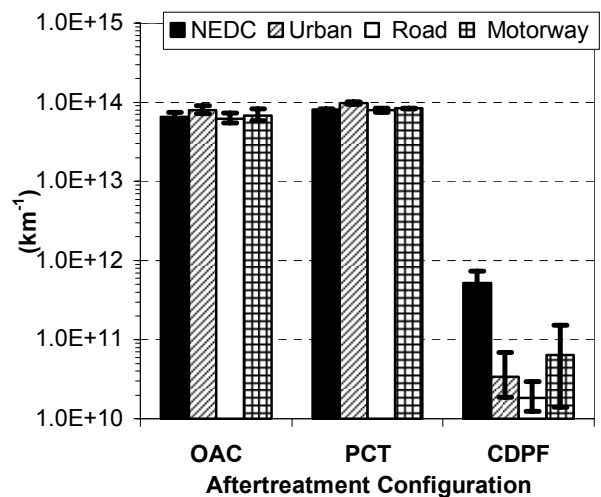


Figure 8: Total particle number emission rate for different aftertreatment configurations and driving cycles

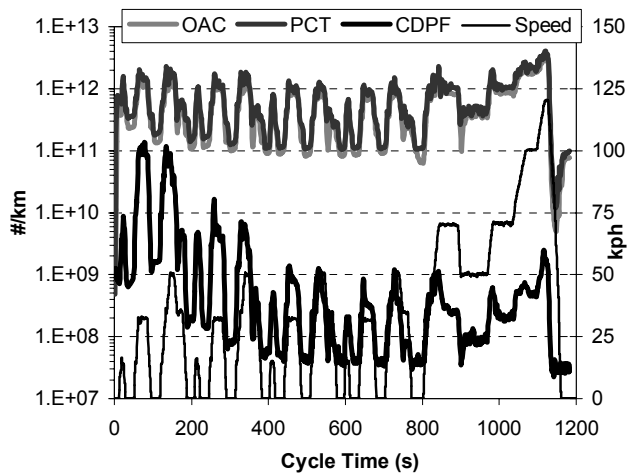


Figure 9: Particle number emission flux over the NEDC driving cycle for different aftertreatment configurations

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 the OAC and PCT configurations exhibited similar lognormal distributions with a geometric mean diameter in the range of 55 nm. When the CDPF was installed, the number concentration dropped by more than 3 orders of magnitude. The distributions remained lognormal and the geometric mean diameter was about 53 nm.

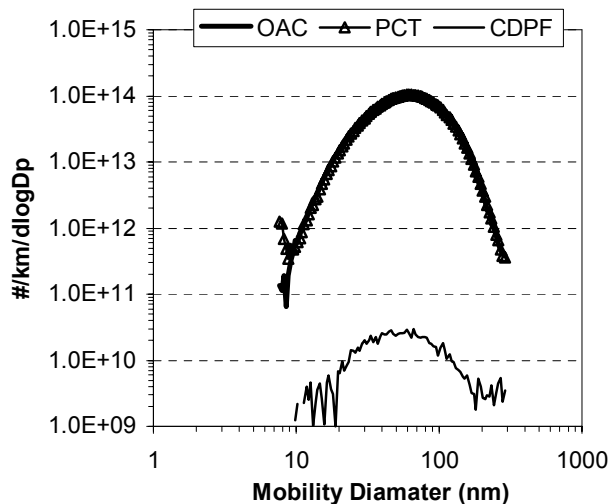


Figure 10: Number-weighted particle size distributions over 50 kph

Again, the particle size distributions obtained at 120 kph with OAC and PCT were rather similar. They were lognormal in shape with a geometric mean diameter in the order of 60 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 catalyzed DPF at high exhaust temperature leads to sulfuric acid concentrations which are high enough to commence nucleation, even with the ultra low sulfur fuel and lubrication oil used in this study. As modeling results indicate [32], this is possible if we assume 90% conversion of fuel sulfur to sulfuric acid and a barrierless nucleation mechanism of the latter.

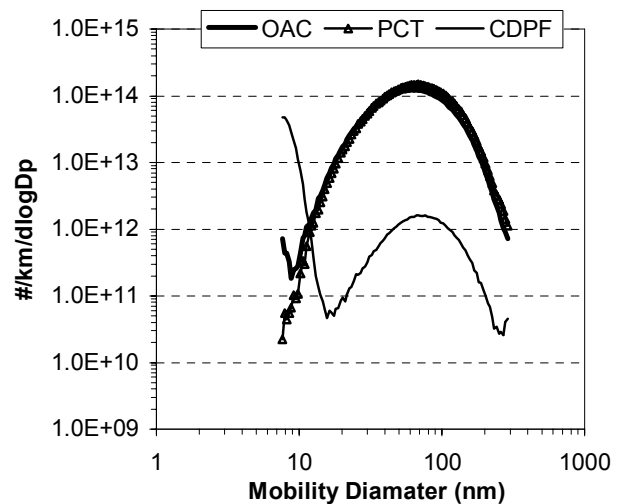


Figure 11: Number-weighted particle size distributions over 120 kph

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 shown in Table 3. Si emissions were also measured but these were highly uncertain and are expected to largely depend on background concentration (crustal material) and, therefore, are not reported. In general, there are small differences between the OAC and PCT cases. This means on one hand that the underfloor catalyst does not have a strong effect on the XRF-detected elements of the PM sample and second, that no single element (of those measured) can be considered as a tracer for DOC. In both OAC and PCT cases, the most abundant elements in the exhaust were Ba, Sn, Zn, Cd, Cr, and Fe. Fe is regularly one of the most abundant elements in diesel vehicle exhaust [33, 34], while high Zn and Cr were also reported by other investigators in the exhaust of a diesel passenger car [35]. Combustion has been also identified as a significant emitter of Cd [36]. In general it is observed that several of Table 3 elements were also identified by the chemical analysis of the lube oil (Table 1). This does not mean that lube oil is the only source of their emission. Engine component attrition, elements not filtered by the engine intake air filter and trace metals in the fuel [37] can be also significant sources of elements measured in the exhaust.

Table 3: Average emission rate ($\mu\text{g}/\text{km}$) and standard deviations of trace elements detected by XRF-analysis on PM samples

Trace Element	NEDC		Urban		Road		Motorway		CDPF ^a
	OAC	PCT	OAC	PCT	OAC	PCT	OAC	PCT	
Ba	64.6±62.6	62.5±8.1	181±121	134±54.7	33.4±30.8	29.5±10.3	22.3±23.7	ND	ND
Cd	18.8±2.7	18.1±1.7	65.8±15.6	69.1±26.9	18.1±3.9	9.0±4.2	10.6±0.1	3.9±1.4	3.0±1.9
Co	3.0±2.3	ND	6.8±6.1	7.9±5	1.5±0.4	ND	1.5±1.1	1.2±0.7	ND
Cr	16.4±5.6	12.9±0.6	30.3±6.7	38.0±14.2	8.6±1.6	ND	5.6±0.7	ND	3.4±0.9
Cu	8.9±8.7	8.8±5.7	17.9±2.6	17.9±5.2	4.0±0.6	6.3±5.8	3.8±0.2	5.0±2.7	2.5±0.9
Fe	12.5±5.6	5.9±1.1	53.7±8.1	69.6±48.7	8.4±3.2	23.8±22.7	9.0±3.1	5.4±3.2	21.2±9.4
Mn	3.4±0.7	ND	10.2±3.9	ND	ND	2.1±0.1	2.4±1.3	ND	ND
Ni	3.8±2.1	3.9±3	17.3±14.8	16.1±8.1	6.2±2.8	6.9±3.2	3.2±0.7	4.0±0.3	2.3±0.3
P	ND	ND	ND	ND	6.2±8	8.1±1.9	ND	ND	ND
Pb	5.7±1.4	ND	4.5±3.5	10.2±6.3	2.7±2	2.3±2.1	2.2±1.8	3.34±1.0	ND
Sb	2.2±0.6	ND	34.9±5.9	24.1±15.3	12.9±6.6	ND	ND	ND	ND
Se	2.7±1.4	3.6±0.6	12.1±3	8.5/1.5	1.7/±.3	3.4±0.4	2.4±0.8	2.4±1.3	1.1±0.1
Sn	27±11.8	29.7/8.5	69.5±29	66.9±2.1	17.6±4.6	16.3±2.7	18.3±2.1	14.1±5.5	3.6±2.1
Sr	ND	0.9±0.6	4.2±1.5	ND	0.4±0.3	ND	2.4±1.6	0.9±0.5	ND
Ti	ND	9.3±0.6	24.1±3.2	ND	6.2±0.6	ND	4.5±0.1	ND	ND
Zn	25.6±8.1	25.1±1.0	69±0.8	9±5.9	30.9±10.7	47±8.6	23.4±3.4	32.4±3.2	4.2±0.2

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

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 [38, 39]. 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 DOC 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. However, this should lead to large differences between the OAC and PCT configurations, which are not evident in the ranges reported in Table 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 appear over the Artemis urban cycle and the lowest over the Artemis motorway. The most significant effect was however observed when the DPF was installed in the exhaust line. The total elemental emission reduction over the OAC condition was 76%. Only Fe seems to be 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). With the exception of sulfates over the motorway cycle, the measured sulfate and nitrate ions were higher in all other cycles, when the underfloor catalyst was in place. This finding is consistent with the higher exhaust oxidation activity expected in the OAC configuration, compared to PCT. It is also important to mention that due to the ultra-low sulfur in the fuel and the lube oil, nitrates are actually higher than sulfates on an absolute scale. It needs to be stressed that nitrate emission rate follows the NO_x emission rate presented in Figure 3.

The absolute emission rate and the effect of aftertreatment configuration on nitrate and sulfate ions is a function of the driving cycle. Over the cold-start NEDC, the underbody catalyst led to an increase of 29% and 58% of sulfates and nitrates respectively, over the PCT case. However, the difference becomes much higher during the hot-start cycles and in particularly for sulfate over the Artemis urban cycle. Actually, during this relatively low temperature cycle, limited sulfate was emitted when the underbody catalyst was removed. The reason for the relatively higher PCT sulfate emission over the motorway cycle is unknown. The effect of storage and release of sulfate in the exhaust and sampling system might be responsible for some of these inconsistencies and the relatively large variation of the

values reported. Such effects can be better controlled only using a partial flow sampling system, instead of a full-flow one.

Table 4: Average emission rate ($\mu\text{g}/\text{km}$) and standard deviations of ions measured by IC-analysis on PM samples

Ion	NEDC		Urban		Road		Motorway		CDPF
	OAC	PCT	OAC	PCT	OAC	PCT	OAC	PCT	
NO_3^-	505 ± 56.9	320 ± 90.5	1908 ± 41	699 ± 50.6	1205 ± 49.6	600 ± 3.2	1116 ± 4.9	436 ± 2.5	841 ± 7.9
$\text{SO}_4^{=}$	203 ± 77.5	157 ± 15.5	1065 ± 108	72 ± 2.8	217 ± 72.8	114 ± 11	289 ± 79.2	423 ± 38.8	96 ± 71.2
NH_4^+	75 ± 15.3	192 ± 24.6	342 ± 50.9	418 ± 15.2	109 ± 48.4	127 ± 6.1	83 ± 18.2	143 ± 19.9	47 ± 40

Ammonium emissions are less important on an absolute scale than nitrates and sulfates. In this case, the main catalyst has a positive effect, by reducing ammonium ions over all driving cycles.

The effect of CDPF on ion emissions can be compared to the non-DPF cases by calculating the composite emission of the latter, similarly to trace elements. On this basis, CDPF reduces ion emissions by 23%, 70% and 57% for nitrate, sulfate and ammonium respectively, compared to the OAC configuration. These reductions are lower than the reductions brought to the total PM mass. This may be the effect of the oxidizing environment in the CDPF which may be effective in the reduction of OC (while EC is retained by filtration) but cannot effectively control ion emissions.

Elemental - organic carbon and PAH speciation

The EC-OC results for OAC and CDPF configurations are given in Table 5. The total (elemental and organic) carbon emissions follow closely the PM mass emission reported in Figure 5, with the exception of motorway emission, with the highest value measured over the urban cycle (33% above the NEDC value). For the rest of the real-world cycles carbon emission was lower than that of NEDC (by 33% for both cycles). EC/OC ratio was higher over NEDC and motorway cycle and decreases significantly over the urban and road cycles. CDPF reduces the total EC and OC emission by more than 90% in accordance to the total PM emission rate.

Sixteen PAH species were determined from the PM samples collected (Table 6). As in several studies looking at PAHs from diesel vehicles, light PAHs ($\text{MW} < 252$) were found at much higher concentrations in the exhaust than heavy ones. The effect of aftertreatment on the emissions is not straightforward. Generally speaking, higher oxidation activity in the exhaust line (OAC, CDPF) leads to lower PAH emission with the exception of fluoranthene. However, light PAHs (such as fluoranthene) are rather volatile and their

partition between gaseous and PM phase may bring significant variations to the measurement.

Table 5: Average emission rate (mg/km) and standard deviations of EC-OC measured by the Walkley-Black method

Carbon Form	OAC				CDPF
	NEDC	Urban	Road	Motorway	
EC	20.1 ± 7.5	19.5 ± 8.5	7.7 ± 4.1	15.2 ± 4.8	1.2 ± 0.0
OC	7.5 ± 2.4	17.1 ± 18.2	10.5 ± 3	3.3 ± 2.4	0.5 ± 0.0
Total	27.5 ± 5.3	36.6 ± 10.3	18.2 ± 8.0	18.5 ± 6.6	1.6 ± 0.0
EC/OC	2.7 ± 1.9	1.1 ± 2.0	0.7 ± 2.0	4.7 ± 4.4	2.4 ± 0.0

It is important to note that unlike its effect on PM mass, the CDPF is associated with moderate reductions of PAHs. Emission rates were generally lower for most of the PAHs when the CDPF was installed compared to the OAC (59%, 58%, 53% and 1% reductions of total PAH over the NEDC, urban road and motorway cycles respectively). The small reduction over the motorway cycle is mainly due to increased emission of fluorene and TBP. The relatively smaller PAH than PM reduction provided by the DPF may be associated with the higher per mass toxicity observed in a similar study for the PM downstream of DPF than downstream of oxidation catalysts [35]. Obviously, conclusions related to exhaust toxicity suffer from large uncertainties in the determination of absolute emission levels of high redox activity species such as PAH and nitroPAHs, but comparisons with different aftertreatment systems, such as the one attempted in this study may lead to useful conclusions related to effective regulation of diesel PM emissions.

CONCLUSIONS

A measurement campaign was carried out to investigate the emission profile of a Euro 4 diesel passenger vehicle operating on ultra low sulfur fuel and low sulfur lubrication oil. A particle filter was also installed in the exhaust line to investigate its emission reduction potential. An extended measurement protocol included determination of regulated gaseous pollutants and PM, NO_2/NO_x ratio, particle number and size distribution, and metal, ion, PAH and EC/OC determination of the particulate emitted. The following conclusions can be drawn from the measurements results:

1. 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 as effective NO_x control.
2. The particle filter effectively reduces PM mass emission (90-95% over the original aftertreatment configuration) satisfying the proposed Euro 5 emission standard as well. Particle number emission

- was also drastically reduced (by 2-3 orders of magnitude).
- Despite the low sulfur fuel and lubrication oil, volatile nanoparticles were also measured downstream of the filter under specific conditions (cold-start and high loads) and may mask the number emission reduction.
 - The particle filter reduces trace elements emission of by 76% over the original aftertreatment configuration. The most abundant trace element found in the exhaust was Ba possibly originating from catalyst washcoats and/or fuel additives.
 - Nitrates were found to be the most abundant ion group and correlated with NO_x emissions. Compared to the original configuration, the particle filter reduces nitrate, sulfate and ammonium emissions by 23%, 70%, and 57%, respectively. These reductions were relatively lower than the reductions brought to the total PM mass.
 - Unlike the case of PM mass, the particle filter is associated with moderate reductions of PAHs, a fact that may lead to higher per mass toxicity observed for the PM downstream of DPF than downstream of oxidation catalysts.

Table 6: Average mission rate (µg/km) and standard deviations of PAHs measured by HPLC.

PAH	NEDC			Urban			Road			Motorway		
	OAC	PCT	CDPF	OAC	PCT	CDPF	OAC	PCT	CDPF	OAC	PCT	CDPF
Acenaphthene	4.8±1.1	6.1	1.9	17.9	26.1±10.8	5.6±3.4	1.76±0.10	13.1±12.4	ND	1.8±1.3	ND	0.41±0.29
Fluoranthene	3.6±1.7	2.3±0.66	1.5±0.09	5.3±0.13	3.0	1.0	1.5±0.26	0.95	ND	1.2±0.45	1.3	0.28±0.20
Phenanthrene	1.9±0.45	4.1±0.68	0.42±0.30	4.1±1.1	7.8±2.3	1.1±0.65	1.7±1.1	4.9±1.6	0.28±0.22	0.86±0.66	3.6±2.3	0.22±0.22
Anthracene	ND	8.1±0.05	1.7±1.3	ND	1.7	ND	ND	0.87±0.28	1.1±0.06	0.088	0.47	0.83
Fluorene	0.8±0.7	4.0±0.74	2.8±0.11	3.1	6.3	5.0±4.4	1.1±0.1	4.7±1.6	1.32	0.38	2.5±0.28	1.3±1.1
Pyrene	5.1±2.2	8.3±0.5	0.92±0.88	2.8±0.9	8.1±2.8	0.89±0.79	0.72±0.26	29.3±0.60	0.36±0.24	0.53±0.16	1.7	0.23±0.17
TBP ^a	1.5±0.44	1.1	ND	2.5	10.9±3.4	ND	0.60	3.8±0.90	ND	0.51±0.31	1.4	2.7±1.9
Benz[a]anthracene	0.84±0.07	1.7±0.2	0.63±0.38	1.1	ND	1.5	0.23±0.03	0.84	0.21±0.18	0.15±0.08	0.47	0.17±0.15
Chrysene	0.96±0.54	1.6	0.27	0.059	ND	0.22	ND	ND	0.12	0.23	ND	0.04
Benzo[e]pyrene	11.8±3.4	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
Benzo[b]fluoranthene	1.1±0.32	ND	0.72±0.31	0.16	ND	0.77±0.76	0.17±0.02	0.55±0.42	0.33	0.09	0.23±0.12	0.1±0.07
Benzo[k]fluoranthene	ND	ND	0.20±0.09	ND	ND	0.33	ND	ND	ND	ND	0.03	ND
Benzo[a]pyrene	ND	ND	0.18	1.07	ND	ND	0.09	0.74±0.10	ND	ND	ND	ND
dBenzo[a,h]anthracene	0.45	ND	0.67	1.0	3.5	0.60±0.54	ND	ND	0.27	0.09±0.04	0.19±0.14	0.08±0.06
Benzo[ghi]perylene	0.39	4.5	ND	0.47	8.2	ND	0.42±0.51	ND	ND	0.09	1.2	ND
Indeno[1,2,3-cd]pyrene	ND	2.2	1.6	1.6	7.0	ND	0.59±0.18	2.0	0.21	0.56	ND	ND

^a Tetrabenzo[a,cd,f,lm]perylene

ND: Not Detectable (below the limit of detection)

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CONTACT

Zisis Samaras, Professor
Laboratory of Applied Thermodynamics
Aristotle University
GR-54124 Thessaloniki Greece
Email: zisis@auth.gr
Web: <http://lat.eng.auth.gr>

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
DPF: Diesel Particle Filter
EUDC: Extra Urban Driving Cycle
FID: Flame Ionization Detector
FPS: Fine Particle Samples
HPLC: High-Pressure Liquid Chromatography
IC: Ion Chromatography
NDIR: Non-Dispersive Infrared Detector
NEDC: New European Driving Cycle
OAC: Original Configuration
PAH: Polycyclic Aromatic Hydrocarbon
PCT: Precatalyst Configuration
PM: Particulate Matter
SMPS: Scanning Mobility Particle Sizer
UDC: Urban Driving Cycle
XRF: X-Ray Fluorescence Analysis