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# Impact of engine warm-up and DPF active regeneration on regulated & unregulated emissions of a Euro 6 Diesel SCR equipped vehicle

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## Abstract

The latest improvements achieved thanks to stringent regulations, Diesel engine design and control developments or after treatment evolutions, contribute to the global reduction of Diesel vehicle emissions. This study proposes an extensive assessment of the gaseous and particulate emissions of a Euro 6b Diesel vehicle equipped with a DOC+SCR+DPF exhaust line, under different transient driving conditions reproduced on a roller test bench. It highlights the negative impact of engine warm-up and DPF active regeneration on the regulated and unregulated gaseous and particulate emissions of this vehicle, in particular:

- Engine cold starts and warm up lead to HCs, CO, $CO_2$, $N_2O$ and $CH_2O$ emissions global increase (the two first however remaining compliant with their related emission limits), as well as higher particle number (also under Euro 6b limit),
- DPF active regenerations lead to more important HCs, CO, $CO_2$ and $CH_2O$ emissions, to dramatic $NH_3$, $SO_2$ and particle number (PN) increase; these procedures are also characterized by significant HCN emission and nucleation particles formation.

It finally tackles the need to further improve the related after-treatment's efficiencies, as well as to consider additional pollutant emission limits for passenger cars for the future standards.

**Keywords:** Selective Catalytic Reduction, Diesel Particulate Filter, regeneration, Hydrogen cyanide, sulfur dioxide, size distribution

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# 1 Introduction

Diesel exhaust emissions are classified by the international agency for research on cancer since 2012 as “carcinogenic to humans” (IARC group 1) and are also related to other health concerns among which lung or heart diseases [7]. The toxicity and environmental diseases of Diesel exhaust are due to the individual substances contained in their gaseous or particulate phases, as well as to the potential combined effects of these numerous substances.

Despite of the improvements achieved, recent Diesel vehicles remain considered as not environmentally friendly and of a public health concern. On the one hand, the particulate and $NO_x$ emissions of their predecessors still tarnished during the last years the improvements achieved thanks to the most recent standards. On the other hand, the recent discovery of defeat devices on brand new Volkswagen group model cars to comply the most stringent standards [15], as well as higher $NO_x$ emissions under real driving conditions [5] [6] [8] [14], highlight the need to carry on improving these after treatment devices and their control strategies to allow a better efficiency, in terms of real driving emissions (RDE).

However, many improvements were achieved thanks to: stringent regulations (regarding to exhaust emissions and fuel quality as well), better Diesel engine design and control, new after treatment devices (such as Diesel particulate filter (DPF) or more recently with $NO_x$ abatement systems such as selective catalytic reduction (SCR) or lean $NO_x$ trap (LNT)) or new formulations of lubricants and additives. Nevertheless, their respective potential benefits remain insufficiently investigated, uncertain and need to be better assessed [2] [11]. This is particularly true in terms of potential side effects or as contribution to secondary organic aerosols (SOA) formation in the atmosphere. A strong interest lies on the latest $NO_x$ emissions control devices (SCR or LNT) considering their growing market penetration [16], their specificities (use of AdBlue for SCR case, rich purges for LNT), as well as their growing contribution to $NO_x$ reduction with a view to the relevant RDE regulation.

The CAPPNOR2 project was launched in 2013, in order to access to a detailed knowledge related to the emissions of Euro 6b compliant vehicles equipped with Diesel engine and to precisely assess their gaseous and particles emissions, the impact of their after treatment devices, as well as their SOA forming potential. The first vehicle studied was equipped with a close-coupled Diesel oxidation catalyst (DOC), an underfloor SCR catalyst and DPF using a fuel borne catalyst (FBC-DPF), the second one with close-coupled LNT and catalyzed DPF (cDPF).

This article focuses on the SCR equipped vehicle emissions. It highlights the negative impact of engine warm-up and DPF’s active regeneration on the regulated and unregulated gaseous and particulate emissions of the vehicle. It also tackles the need to further improve the related after-treatment’s efficiencies, particularly during these specific conditions. It also suggest to consider additional

pollutant emissions limits for passenger cars, as already introduced for heavy-duty vehicles standard.

# 2 Experimental setup

The results presented in this study were obtained during transient tests conducted on a Euro6b compliant chassis dynamometer.
The tested vehicle is a 7 seats people carrier which complies with the latest Euro 6b standard and whose unladen mass is 1430 kg. It is equipped with a 110 kW, 2.0 liter, four-cylinder Diesel engine, with common-rail direct injection, cooled turbocharger, cooled exhaust gases recirculation (EGR) and a 6-speed gearbox.
In order to be fully representative of similar European cars found on the roads, this car was specially hired for the project nearby a specialized company and its mileage was 19700 km at the beginning of the tests. After the implementation of the instrumentation, the main vehicle's parameters where acquired and its emissions analyzed on the chassis dynamometer during approximately 4275 km, under various driving conditions that will be described afterwards.
The fuel used during this study is a European EN 590 compliant Diesel fuel. Its measured cetane number is 52.1 and its measured PCI 42.74 MJ/kg. It contains 4.8% fatty acid methyl ester (FAME), 3.3% poly-aromatic compounds and 8.3mg/kg sulfur. The engine lubricant has been replaced before the beginning of the tests by a low SAPS lubricant, as preconized by the vehicle manufacturer for such engine and after-treatment technologies. Finally, an aqueous solution named AdBlue, containing 32.5 % of urea ($CO(NH_2)_2$) and which complies with international standard ISO 22241-1, was used for the proper SCR catalyst functioning.

## 2.1 Vehicle after-treatment system description

### 2.1.1 Diesel Oxydation Catalyst


Figure 1. Schematic diagram of DOC functioning

The Diesel oxidation catalyst (DOC) mainly allows to oxidize unburnt hydrocarbons and carbon monoxide coming from the engine, since the catalyst temperature is high enough, via the following main chemical reactions:

- **Hydrocarbons oxidation:**

$$C_xH_y + (x+\frac{y}{4}).O_2 \rightarrow x.CO_2 + (\frac{y}{2}).H_2O \quad (1)$$

- **Carbon monoxide oxidation [1]:**

$$CO + ½.O_2 \rightarrow CO_2 \quad (2)$$

The DOC also contributes via the chemical reaction 3, to the oxidation of the nitric oxide (NO) emitted by the engine to nitrogen dioxide ($NO_2$) which then, favors the continuous regeneration of the Diesel particulate filters located downstream, throughout the covered mileage of the vehicle, reducing consequently, the DPF active regeneration frequency.

- **NO conversion to $NO_2$ [1]:**

$$NO + ½.O_2 \rightarrow NO_2 \ (3)$$

### 2.1.2 Selective Catalytic Reduction

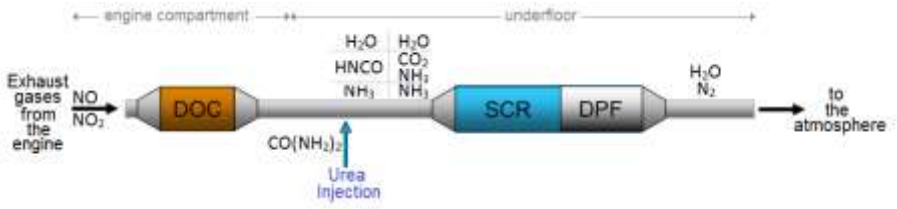


Figure 2. Schematic diagram of SCR catalyst functioning

The SCR catalyst allows to reduce nitrous oxides emissions thanks to the injection in front of the catalyst of AdBlue. As soon as the SCR catalyst and exhaust gases temperatures near the urea injector are high enough (≥ 160°C) to allow the smooth progress of the urea vaporization and decomposition, as well as the NOx reduction by the catalyst, the urea injection can be activated and the following steps occur [9]:

- **AdBlue vaporization**
- **Urea thermolysis:**

$$CO(NH_2)_2 \rightarrow NH_3 + HNCO \ (4)$$

- **Urea hydrolysis:**

$$HNCO + H_2O \rightarrow NH_3 + CO_2 \ (5)$$

Once the molecules of ammonia formed inside the exhaust line, the reactions leading to the nitrous oxides reduction by the SCR take place on the catalyst, via the following main chemical reactions [9]:

- **Fast SCR:**

$$4.NH_3 + 2.NO + 2.NO_2 \rightarrow 4.N_2 + 6.H_2O \ (6)$$

- **Standard SCR:**

$$4.NH_3 + 4.NO + O_2 \rightarrow 4.N_2 + 6.H_2O \ (7)$$

- **$NO_2$ SCR :**

$$8.NH_3 + 6.NO_2 \rightarrow 7.N_2 + 12.H_2O \ (8)$$

### 2.1.3 Diesel Particulate Filter

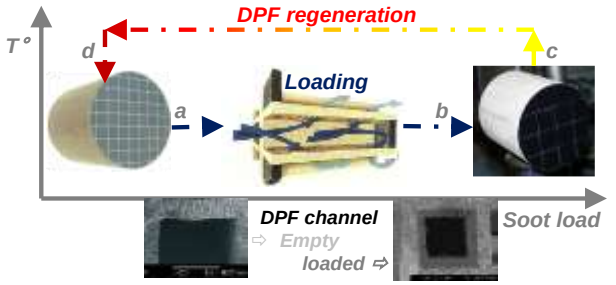


Figure 3. Schematic diagram of DPF loading and cleaning

The operating principle of a Diesel Particulate Filter (DPF) is introduced in figure 3. The DPF first of all goes from clean to soot loaded state (stages a ⇨ b), because of the gradually loading of trapped particles (Diesel soot and other particles like for example ash, salts, metals…). The DPF particle filtration efficiency simultaneously increases due to soot cake formation as the DPF loading goes along. When soot loading of the DPF is estimated appropriate by the engine control unit (ECU) to perform a successful regeneration of the filter (that is to say, not too low to avoid a fuel consumption penalty and nor too high to avoid a possible DPF failure; stage b), a DPF active regeneration is triggered (stage c). It mainly consists to increase the DPF temperature (target usually ≥ 600°C; stages c ⇨ d) via a Diesel fuel post-injection, to allow the combustion of the previously trapped particles. As a result of the gradually soot cake removal, particles filtration efficiency of the DPF simultaneously decreases. At the end of this process, a new DPF loading phase restarts (stages a ⇨ b), for a mileage that varied for this vehicle, between 670 and 1040 km.
In addition to the particulate emissions impact of the DPF regeneration process, the combustion of the soot particles previously trapped inside the DPF leads to the following main chemical reactions (reaction 9 and 10), while the not catalyzed DPF used here, does not allow (or in minor extent) to convert the CO formed in case of incomplete combustion of soot (reaction 11):

- **Incomplete soot combustion:**
$$C + ½.O_2 \rightarrow CO \quad (9)$$
- **Complete soot combustion:**
$$C + O_2 \rightarrow CO_2 \quad (10)$$
- **CO oxidation by catalyzed DPF:**
$$CO + ½.O_2 \rightarrow CO_2 \quad (11)$$

### 2.2 Exhaust emissions analysis

The IFPEN's chassis dynamometer used during the study is equipped with a full flow Constant Volume Sampling (CVS), three simultaneous raw gases analyzers

and a dedicated one for diluted gases; all of them include CO and $CO_2$ measurements by Non-Dispersive Infrared Sensor (NDIR), total hydrocarbons and $CH_4$ by Flame Ionization Device (FID), $NO/NO_x$ by Chemi-Luminescence Detector (CLD) and $O_2$ by Paramagnetic Detector (PMD). Particulate Matter (PM) measurement by conventional gravimetric procedure of normalized filters and Particle Number (PN) characterization via Particle Measurement Programme (PMP) protocol (dedicated to particles with ø > 23 m), are also available.
Besides these conventional equipments, a wide variety of less usual devices and analyzers are used. The diagram introduced by the Figure 4 shows the complete set of instruments and their related sampling configurations:

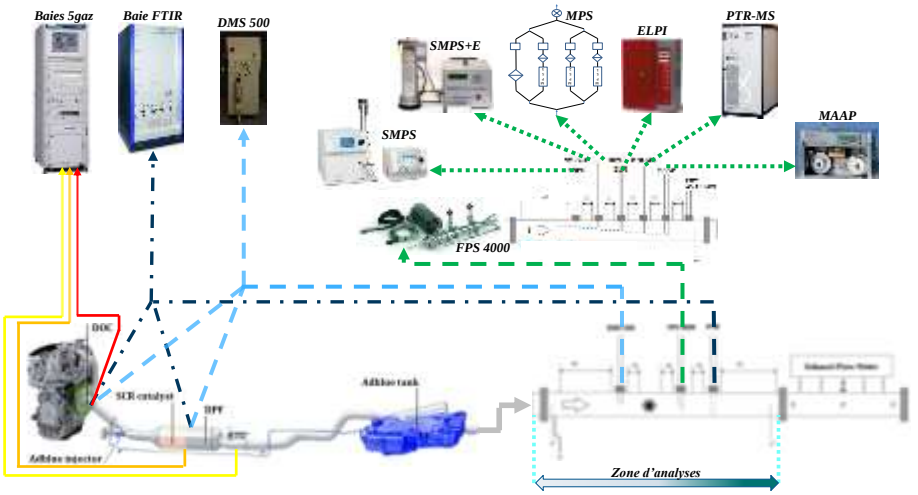


Figure 4. Diagram of the exhaust line and analyzers samplings

Analyzers whose results are presented in this paper are briefly introduced here. A fine particle sampler (Dekati FPS4000) operates the sampling and a fast double dilution of a part of the exhaust gases prior to their analyze by some of the following instruments. It is only used at the DPF's outlet, with a dilution ratio chosen during the whole tests described to be 11, the first dilution being hot and the second one cold.
A Fourier transform infrared spectroscopy (AVL FTIR) broadens the composition characterization of the raw gas phase along the exhaust line with additional compounds, among which $NH_3$, $N_2O$, $SO_2$, $CH_2O$, $C_2H_4O$, HCN and 9 hydrocarbons speciation, with a minimum detectable concentration (MDC) comprised between 0.25 and 5 ppm.
A differential mobility spectrometer (Cambustion DMS500) analyzes in real-time the number and size (electric mobility diameter) of particles in the range 5-1000 nm. This instrument has its own sampling and dilution device which is heated and set during the whole tests described (DPF downstream measures), between 4 and 5 with a hot first dilution only.

A scanning mobility particle sizer (TSI SMPS) analyzes the number and size (electric mobility diameter) of the particles in the range 14-674 of the previously diluted aerosols coming from the FPS4000. Due to its functioning, it is used as an SMPS during steady state tests to obtain both number and size information, but as a CPC during the transient tests to obtain continuous total particle concentration in the range 4 to 1000 nm.

### 2.3 Test plan

The vehicle emissions were first of all assessed under steady state conditions corresponding to New European Driving Cycle (NEDC) speed steps at 15, 32, 50, 70, 100 and 120 km/h.

Then, they were assessed during many days under transient conditions consisting of successive NEDC, WLTC (Worldwide harmonized Light vehicles Test Cycle) and CADC (Common Artemis Driving Cycles), with different engine starting conditions ranging from ambient temperature of the engine fluids, DOC, SCR and DPF (called "cold start" when the last test was done the day before) to hot temperatures starting (called "hot start", for few minutes since last cycle's end), additional conditions named "q-cold" (following a longer stop of the engine of approximately one hour) and cycles without engine start named " hot". In order to mix the testing conditions and avoid a potential systematic bias between the two vehicles due to their different emissions and control devices, different order of cycles were used, while the whole vehicle driving conditions were acquired and analyzed.

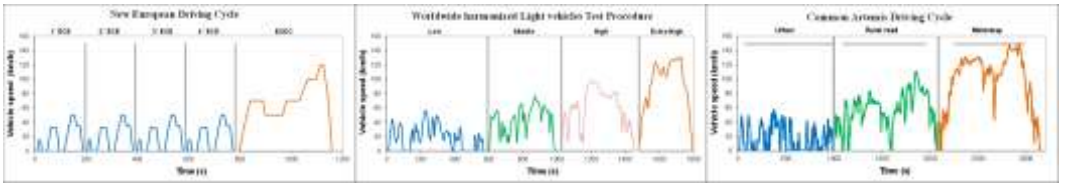

Figure 5. NEDC, WLTC and CADC cycles

## 3 Results

This article addresses the exhaust emissions of the Euro 6b vehicle equipped with close-coupled DOC and underfloor SCR + DPF. It focusses on the results obtained during the transient conditions tests under NEDC, WLTC and CADC cycles, depending on the different starting conditions introduced previously and the occurence or not of a DPF active regeneration. The results introduced synthesize for most of the following figures, up to 58 cycles with the following distribution:

- 30 NEDC (3 "cold start", 3 "q-cold start", 6 "hot start" and 18 "hot"),
- 18 WLTC (3 "cold start", 3 "q-cold start", 3 "hot start" and 9 "hot"),
- 10 CADC (2 "cold start", 3 "q-cold start" and 5 "hot start").

The particulate mass results (Figure 19) take into account a lower number of cycles (14, including 5 NEDC, 5 WLTC and 4 CADC, different of the previous ones), since only the cold and hot start conditions were tested. Finally, the particle size distributions (Figures 20 and 21) include only one mean value for each introduced conditions. It is important to bear in mind that these results are not obtained during normalized tests, under related conditions and with normalized instruments and protocols, but rather under several conditions and with a variety of instruments, with the aim of finely assess the emissions of the vehicle, nearer of realistic conditions. This, as well as the mileage and history of the vehicle, its estimated road law, the absence of vehicle preconditioning before each cycle can contribute to slightly different results compared to their theoretical certification values.

### 3.1 Gaseous emissions

#### 3.1.1 Unburnt hydrocarbons

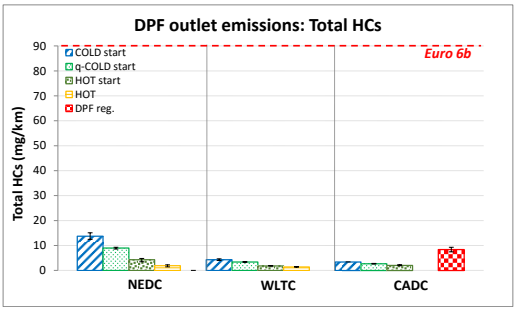


Figure 6. Total HCs

This study highlights the extremely low amount of HCs emitted (Figure 6) by the vehicle whatever the conditions, which remains well below the indirect tolerance fixed by the $HC+NO_x$ Euro 6b limit, since they never exceed 15 mg/km.

The warm-up phase of the engine mainly impacts the first minutes of the cycles, until the DOC's temperature becomes sufficient to oxidize HCs (reaction 1). As an example, the first ECE phase of the NEDC only represents 16% of the cycle duration but 58% of the whole cycle emissions, while the contribution of the first two ECEs reaches 75% of the emissions for only a third of the duration.

The effect of the occurrence of a DPF active regeneration is more important, since the HCs emissions during the CADC are increased by a factor 4.1 compared to the mean value of the hot CADC. This is due to the activation of the post-injection of Diesel fuel necessary to achieve the high temperatures ($\geq$ 600°C) needed to burn the particles trapped inside the filter.

A wide variety of species compose the HCs emitted during the cycles without DPF active regeneration, since 16 to 37 different compounds are detected and 15 to 24 quantified during the cold tests (HPLC analyses), most of them at extremely low concentrations. The mono and cyclo-olefins family is always the main

contributor (46-76%) to the total measured hydrocarbons, followed by aromatics, naphthene and paraffins (n+i). Regarding to individual compounds, the main contributors are methane ($CH_4$), ethene ($C_2H_4$), propene ($C_3H_6$), formaldehyde ($CH_2O$) and acetaldehyde ($C_2H_4O$). During the regenerations, HCs remain too low downstream the DOC to allow their partial speciation via the FTIR analyzer.

### 3.1.2 Carbon monoxide

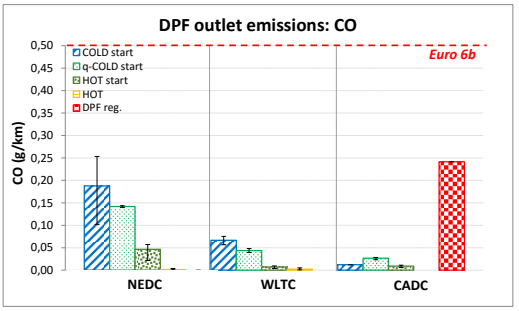


Figure 7. CO

Carbon monoxide emissions (Figure 7) remain in line with the Euro 6b standard whatever the conditions, since they never exceed half of the corresponding emission limit. The highest emissions are measured during the NEDC following a cold start that generates on average 0.188 g/km CO.

The warm-up phase increase the emissions compared to hot start, by a factor that ranges from 1.3 to 9.4 for CADC and WLTC respectively, and which is equal to 4 for NEDC. These various factors mainly depend on the sharpness of the temperature increase of the DOC and on the raw CO emissions of the engine. Like for HCs, these emissions are mainly observed during the first minutes of cycles, until the DOC reaches its oxidation light-off temperature (reaction 2).

The effect of a DPF cleaning is higher than the cold start impact, since the CO emissions during the CADC including an active regeneration are increased by a factor 27. This increase is mainly due to the combustion of the soot trapped inside the filter, which causes the release of $CO_2$ (reaction 10) if the combustion is complete and CO (reaction 9) otherwise. The DPF here being a Fuel Borne Catalyst DPF and not a catalyzed one, the CO emitted in case of incomplete combustion of the particles, cannot be converted to $CO_2$ (reaction 11).

### 3.1.3 Carbon dioxide

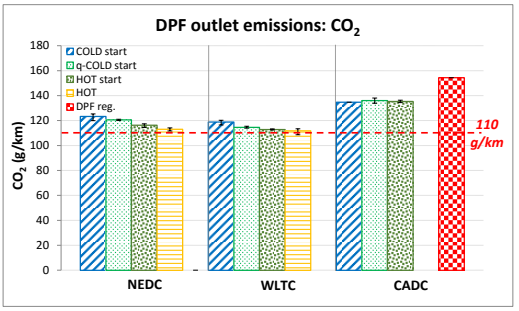


Figure 8. $CO_2$

Carbon dioxide emissions (Figure 8) exceed on the NEDC from 1.7% to 12.2% the reference value of 110 g/km claimed by the manufacturer. They are similar on WLTC while they achieve on CADC an average of 135 g/km.

The emissions observed during this study, even on NEDC cycles that differs from the exact certification conditions, agree with the recent results of the investigation commission of the French environment ministry, that reports for equivalent vehicles tested and slightly different NEDC conditions, a 13.7% difference [5]. The gap measured on the CADC during this study compared to the reference value of 110 g/km, is also consistent with those regularly assessed under real driving conditions, as reported by the EEA [12] with a 20% gap for a similar 2 liter Diesel engine (based on new passenger cars registration in Eu-27 between 2010 and 2013) or by the ICCT [13] that even reports a growing gap from 2001 to 2014 reaching of 37% for the latest passenger cars models.

Although it is non-existent on CADC, our study underlines the impact of the warm-up phase of the engine and the potential dedicated strategy to accelerate the temperature rise of the DOC, since $CO_2$ cold emissions are from 5.4 to 6.1% higher after cold start than after hot start (for WLTC and NEDC respectively).

The effect of a DPF active regeneration on $CO_2$ emissions is higher than the one observed for engine cold start and reaches 14 %, mainly because of the Diesel fuel post-injected to increase the DPF temperature.

### 3.1.4 Nitrous oxides

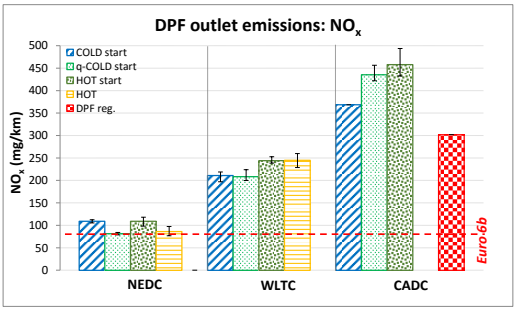


Figure 9. $NO_x$

Nitrous oxides emissions (Figure 9) vary considerably during our tests, depending on the starting conditions but even more on the driving cycle. The average emissions also exceed most of time the Euro 6b emission limit of 80 mg/km. For example, they exceed by 1.7 to 36.5% the NEDC limit, depending on the starting conditions. The gaps for WLTC and CADC are much higher with respective multiplicative factors 2.6 to 3.1 for WLTC and even 4.6 to 5.7 for CADC. The variations observed between the 3 cycles are mainly due to the raw $NO_x$ emissions of the engine which do not allow a constant efficiency of the SCR, particularly during the CADC. Indeed, the SCR catalyst efficiency remains equivalent whatever the cycle in case of cold start (51 to 55 % of efficiency), while it varies between 38 to 60% (CADC and NEDC respectively) after hot start and reaches up to 73% during NEDC hot cycles (on average).

These results are in good agreement with those reported by Kadijk & Al. [8] or the recent French, English and German investigation commissions [5] [6] [14], the 3 later confirming in particular the large variety of $NO_x$ emissions measured under real driving emissions tests (on tracks or on the road) or equivalent laboratory conditions.

The occurrence of a DPF active regeneration during a CADC lowers by 66% the $NO_x$ emissions compared to the average value observed during the cycles without regeneration with similar starting conditions (hot start). The higher amount of ammonia ($NH_3$) available in the exhaust line during this phase (as shown by figure 10) and to a lesser extent, the higher exhaust temperatures, probably contribute to this reduction.

### 3.1.5 Ammonia

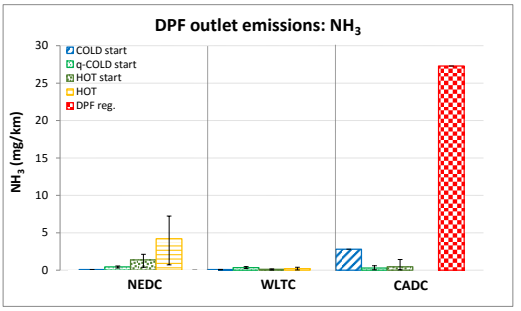


Figure 10. $NH_3$

This study highlights (Figures 10 and 11) a strong negative impact of the DPF active regenerations on ammonia emissions, which are 60* higher than those observed otherwise ; a similar effect (not presented in this article) was also noticed upstream the DPF during another active regeneration, while a third occurrence does not show any impact upstream of the SCR catalyst. From these results, it can be stated that both the engine raw emissions and the DOC are not related to $NH_3$ emissions increase, which could be explained by two different reasons: on the one hand, higher urea injection is needed at highest exhaust temperature to cool down the urea injector and avoid any damage (as seemed underlying the right graph of Figure 11), on the other hand, the decomposition of ammonium salts gradually accumulated inside the exhaust line during normal operation.

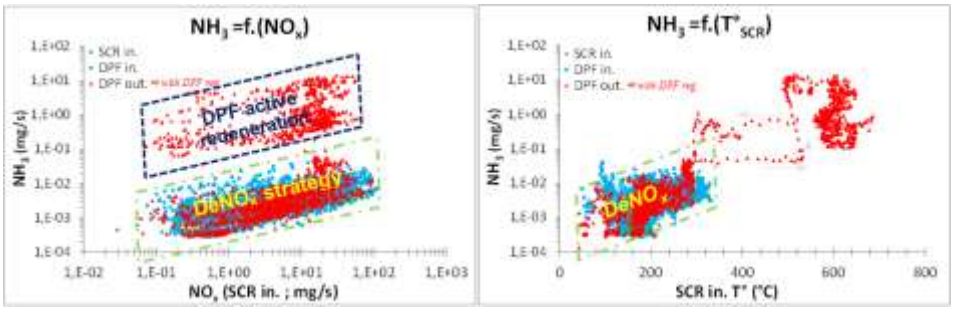


Figure 11. CADC hot w/wo DPF reg. - $NH_3$ slip (DPF out.)= f. ($NO_x$ abatement & T°SCR in.)

The $NH_3$ emissions during the cycles without DPF active regeneration always remain under 7.5 mg/km (similar to minimum detectable concentration (MDC) of the compound), although slight differences are observed during NEDC and CADC.

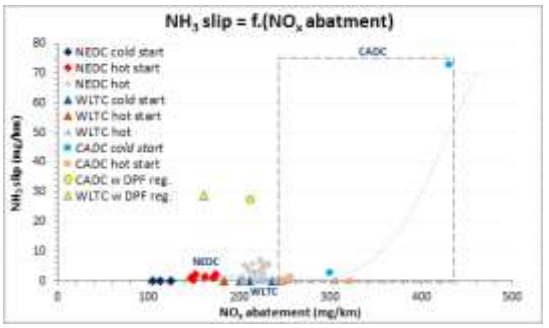


Figure 12. $NH_3$ slip (DPF out.)= f.($NO_x$ DPF out. – $NO_x$ SCR in.)

Figure 12 links the undesired $NH_3$ emissions to the calculated $NO_x$ abatement during the tests. $NH_3$ variations during NEDC are mainly associated to $NO_x$ reduction efficiencies which varies from 53 to 73 % (from cold start to hot cycles ; the higher the $DeNO_x$ efficiency, the higher the $NH_3$ slip). During CADC cold, the higher quantity of $NO_x$ to convert by the SCR catalyst compared to the 2 other cycles also leads to an increase in urea injection, but also to a lower SCR efficiency and higher $NH_3$ slip. The $NH_3$ slip during cycles including a DPF active regeneration, clearly appears to be higher than the equivalent cycles without, and not related to the $NO_x$ abatement by the SCR.
These observations emphasize the possible need of a new emission limit regulation for passenger cars towards $NH_3$, in accordance with continuous engines and after treatments evolutions and improvements, as already implemented for heavy-duty vehicles [4]. As suggested by this study, $NO_x$ emissions under more realistic driving conditions are higher than those measured under certification conditions and involve higher quantities of $NO_x$ to reduce. The necessary higher $NO_x$ abatement and the related need of a high efficiency, may involve higher $NH_3$ emissions. It may therefore make sense to include all realistic and normal operating conditions in the future certification procedures, as for example the DPF active regeneration [3], to allow an extensive and reliable limitation of the exhaust emissions.

### 3.1.6 Isocyanic acid

No significant isocyanic acid emissions were observed during this study, whatever the starting conditions and the occurrence of a DPF active regeneration, since calculated emissions always remain lower or equal to the MDC ($\leq$ 6 mg/km). It confirms the efficient hydrolysis decomposition of the HNCO (chemical reaction 5).

### 3.1.7 Nitrous oxide

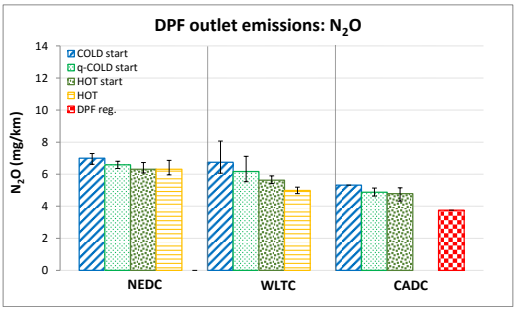


Figure 14 $N_2O$

This study highlights the presence of significant nitrous oxide emissions (compared to its MDC) whatsoever the cycle, the starting conditions or the presence or not of a DPF active regeneration, since the average emissions without DPF regeneration (Figure 14) vary from 4.8 to 7 mg/km.
These emissions are not constant, but regularly appear during the cycles, mainly during the vehicle accelerations for which the air to fuel ratio (AFR) of the exhaust gases is increased, while the catalysts temperatures sharply rise. Then, higher HCs content associated to the catalysts temperature variation can, depending on the catalyst characteristics, favor the occurrence of undesirable chemical reactions leading to the formation of $N_2O$. The temperature range for which this undesired reaction occurs is rather low, so cold start cycles tend to increase the time spent in the $N_2O$ emissions temperature window, leading to an increase of these emissions from 11 to 20 % depending on the cycle.
During the DPF active regenerations, the emissions are low (as observed for the dedicated CADC) because of the strong catalysts temperature increase, but two different behaviors are observed. $N_2O$ emissions first increase for few seconds following the post-injection activation, because of the exhaust AFR increase whereas the catalyst temperatures remain as usual; afterwards, the higher temperatures do not favor anymore the $N_2O$ formation and contribute to its global reduction at the time scale of the whole cycle. The emissions during the CADC including the DPF active regeneration is equal to 3.8 mg/km and represents a 21.5 % reduction compared to the equivalent CADC hot start without DPF cleaning.

### 3.1.8 Sulfur dioxide

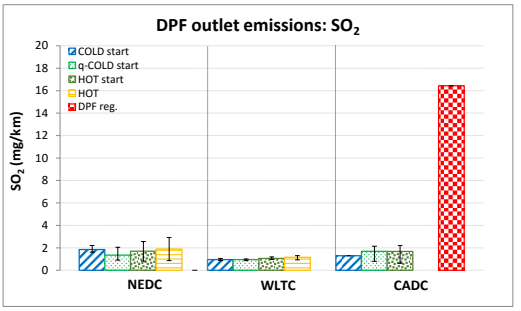


Figure 15. $SO_2$

The sulfur dioxide measurements (Figure 15) reveal the lack of significant emission and evolution during the cycles, except during the DPF active regeneration. In general, $SO_2$ emissions are low because of the gradual poisoning of the catalyst, due to the continuous storage of most of the emitted sulfur species coming from fuel and lubricant by the catalysts during normal operating conditions.
However, during DPF regeneration process, catalysts temperature rises and achieves values higher than 600°C due to the exothermic reaction (HCs oxidation by the DOC); such temperatures promote the desorption into the gas phase of sulfur species (as $SO_2$) previously trapped on the DOC and/or the SCR, as already observed during DPF active regenerations of Euro 5 Diesel vehicles [10]. Because of this considerable effect, $SO_2$ emissions during the CADC cycle with an active regeneration are multiplied by almost 10 and achieve 16.4 mg/km.

### 3.1.9 Aldehydes

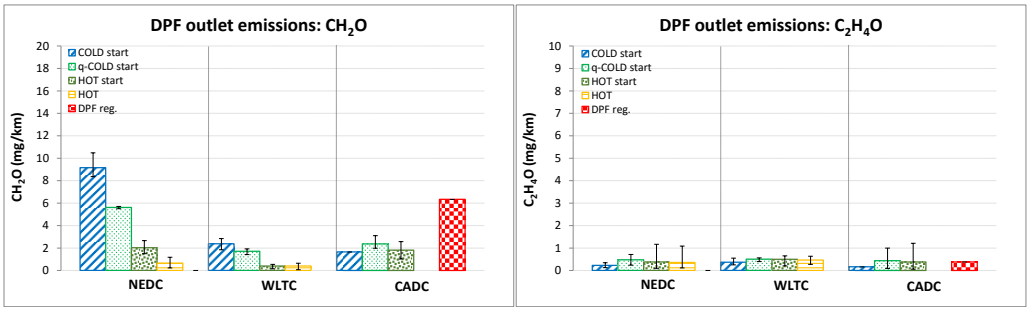


Figure 16. $CH_2O$ (left graph) & $C_2H_4O$ (right graph)

Formaldehyde demonstrates significant emissions and variability in accordance with the starting conditions or the occurrence of a DPF regeneration, while acetaldehyde concentration remains most of time lower than that of formaldehyde

and still near or lower its MDC.
In good agreement with the previously described hydrocarbons emissions, formaldehyde is largely emitted during the warm up phase of the engine following a cold start (until the DOC's temperature becomes sufficient to oxidize it (reaction 1)) and during DPF active regeneration as well. The $CH_2O$ average emissions during a cycle following a cold start are, for NEDC and WLTC respectively, 4.5 to 6.1 times higher than for equivalent cycle with hot start, while the DPF active regeneration multiplies by 3.5 the emissions in the case of the studied CADC cycle (compared to the equivalent cycle and starting conditions).
Considering the quality characteristics of AdBlue according to the ISO 22241-1 standard and its formaldehyde maximum content of 5 mg/kg, AdBlue maximum contribution to the measured $CH_2O$ exhaust emissions is estimated (Figure 17 right plot). This is done using the calculated AdBlue consumption during the whole cycles synthesized in this article.

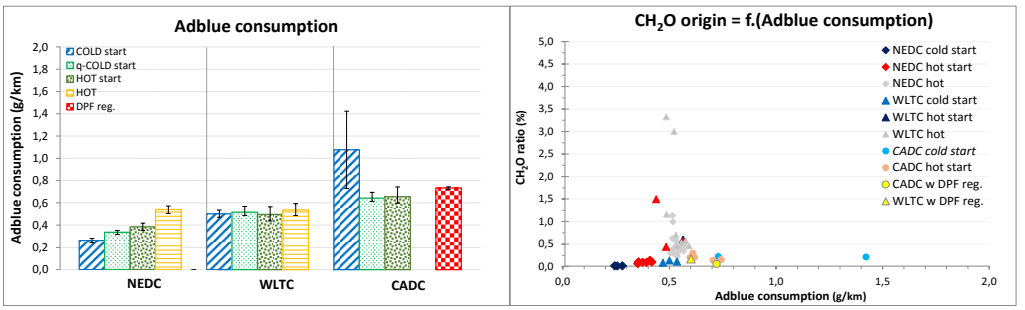


Figure 17. Estimated AdBlue consumption/cycle (left graph) & AdBlue's maximum potential contribution to $CH_2O$ (right graph)

To do this, the AdBlue consumption which is not measured, is estimated for each of the driving cycles from the amount of $NO_x$ treated by the SCR catalyst and also from the amount of undesired $NH_3$ emitted. These estimated average consumptions (summarized in the left graph of figure 17) vary from 0.26 to 0.54 g/km during NEDC cycles (following the $NO_x$ emissions and the efficiency of the SCR catalyst) and are stable during WLTC (0.50-0.54 g/km) for which SCR efficiency is more stable. They finally achieve during CADC, 0.64 and even 1.08 g/km for the cold start cycles, because of their higher $NO_x$ and $NH_3$ slip emissions. The ratio between $CH_2O$ resulting from the AdBlue consumption and $CH_2O$ measured at the outlet of the vehicle exhaust line via the FTIR, can then be calculated and plotted for each cycle (right graph of figure 17). These results highlight the limited potential contribution of AdBlue to the formaldehyde emissions. Indeed, its theoretical maximum potential contribution never exceeds 3.5 % (whatever the cycle and the starting conditions, or the presence of a DPF active regeneration) of the $CH_2O$ measured downstream the DPF and is most of time lower than 1.5 %.

### 3.1.10 Hydrogen cyanide

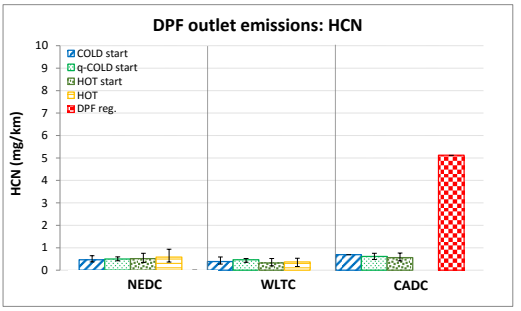


Figure 18. HCN

The hydrogen cyanide emissions (Figure 18) still remain quite stable and below its MDC during the cycles except for DPF regeneration and this, whatever the starting conditions. In contrast, HCN emissions during the CADC cycle including a DPF active regeneration, strongly increase and achieve 5.1 mg/km. Moreover, a similar effect (not presented in this article) is also noticed via the FTIR measurements upstream the DPF during another active regeneration on a WLTC cycle, while a third DPF regeneration during another CADC does not show any impact on HCN emissions upstream of the SCR catalyst.It can thus be affirmed from these results that DPF active regeneration of the evaluated Euro 6b Diesel vehicle equipped with SCR causes significant emissions of hydrogen cyanide. Elsewhere, the engine or the DOC, have nothing to do with this substantial HCN emissions increase, which only comes from the SCR catalyst and its related urea injection, under the DPF regeneration conditions that involve high temperatures, high $NH_3$ emissions and increased emissions of hydrocarbons due to the post-injection activation.

### 3.1.11 Nitric and formic acid

The nitric acid ($HNO_3$) and formic acid ($CH_2O_2$) emissions whose values still remain well below their respective MDC, do not highlight significant emissions or variations of this 2 compounds, whatever the cycle, the starting conditions or the presence or not of a DPF active regeneration.

### 3.2 Particulate emissions

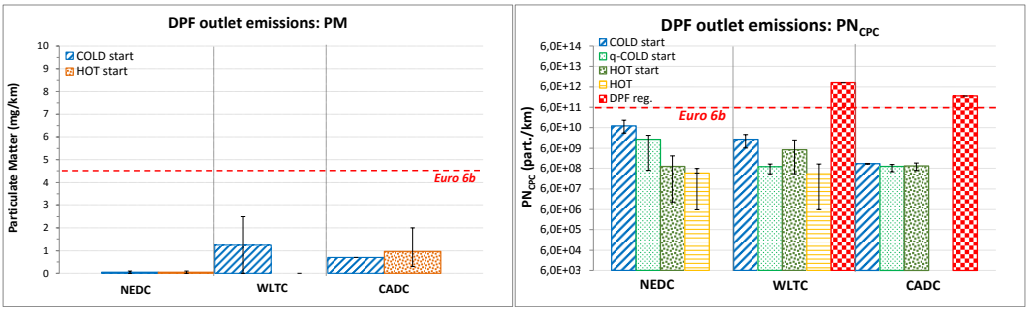


Figure 19. Particulate Matter (PM) and Particle Number (PN)

The particulate matter of the emitted aerosol, measured with the conventional gravimetric method, remains for the three cycles and for cold as well as hot conditions, largely under the Euro 6b emission limit of 4.5 mg/km, since the mean values never exceed 2.5 mg/km (left graph of Figure 19).

The particle number (right graph of Figure 19), measured thanks to the specific protocol defined for the project and described in figure 4, remains for the three cycles and for each starting conditions under the Euro 6b emission limit of $6.10^{11}$ particle/km, except for the two cycles including a DPF active regeneration, for which the number of emitted particles is sharply increased. Thus, the PN emissions vary whatever the cycle and the starting conditions considered, within $3{,}14.10^{8}$ part./km and $7{,}23.10^{10}$ part./km if no DPF active regeneration occurs, while it reaches $2{,}13.10^{12}$ part./km and $9{,}61.10^{12}$ part./km (respectively for CADC and WLTC) for cycles including an active regeneration.

Whatever the measurement protocol (PMP protocol with volatile particle remover [VPR] and $CPC_{PMP}$ with cut-off diameter [$d_{50}$] equal to 23 nm; or specific protocol with FPS4000 dilution, TSI $CPC_{R\&D}$ with $d_{50}$ = 4nm and without VPR), the impact of the warm-up phase is more easily observed with NEDC than with WLTC, while CADC cycle does not show any significant effect. Indeed, the PN are increased by factors varying between 98 and 162 (comparison between cold start and hot start, respectively with PMP and specific protocol) for NEDC, from 3.1 to 5.1 for WLTC; the trend is not so obvious for CADC for which the warm up phase involves a maximum 34% increase.

If the difference between PMP and CPC for NEDC results can seem excessive, it is necessary to keep in mind that these two analyzes, besides their significantly different protocols, are not simultaneous. Consequently, the raw emissions of the engine are first of all not exactly equal for both tests. Furthermore, particulate emissions downstream the DPF also vary accordingly to the DPF soot cake thickness which greatly depends on the vehicle mileage since the previous regeneration as emphasized by the right graph of the figure 20.

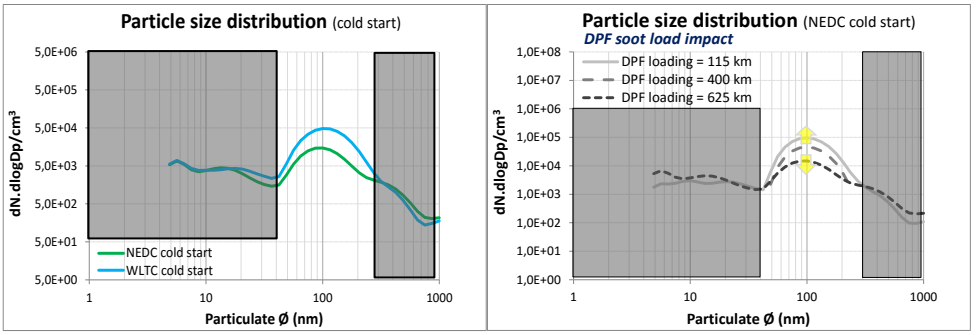


Figure 20. Mean particle size distribution during cold cycles without DPF regeneration

The graph on the right highlights the progressive reduction of the emitted particle number in the accumulation mode between 3 cold start NEDC cycles, for 3 different vehicle mileages (from 115 to 625 km) since the previous active regeneration. This evolution is linked to the DPF filtration efficiency increase, which results from the gradual growth of the DPF soot cake thickness. This accumulation mode is centered at 100 nm (count median diameter (CMD), calculated on the range 23-1000nm), which does not vary as a function of the DPF loading. These particles, also extensively assessed (results to be published) includes typical Diesel soot aggregates, mainly composed of a carbonaceous fraction on which are adsorbed a variety of volatile compounds, stem from engine fuel, lubricant as well as from AdBlue.

The impact of the DPF soot load having been previously underlined, the cycles can now be compared in terms of particle size distribution. Because of the absence of impact of cold start conditions on CADC cycles (as already shown in figure 19) and of the exclusively transient conditions reported in this article (DMS results, no SMPS measurements available), the particles size distribution related to CADC is not shown. Thus, left graph of figure 20 compares the average particles size distributions measured during NEDC and WLTC cycles following a cold start of the engine. It shows a slightly increased diameter (Count Median Diameter CMD, calculated on the range 23-1000nm) during the WLTC compared to the NEDC, with respective 105 and 99 nm.

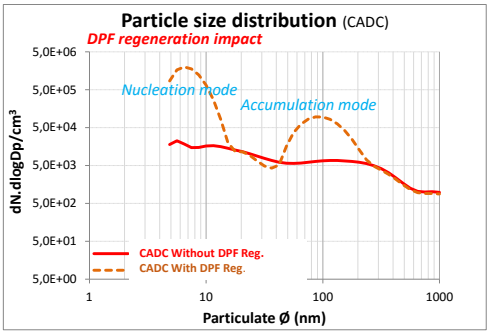


Figure 21. Particles size distribution (CADC, w/wo DPF regeneration)

DPF regeneration produces a dramatic increase of particle number (PN) emissions compared to the other studied conditions like cold start (Figure 19). Indeed, the two DPF active regenerations introduced in Figure 21 exceed the emissions limit of $6.10^{11}$ part/km defined by the Euro 6b standard (based on the PMP protocol), by a factor reaching respectively 3.6 and 16 during CADC and WLTC respectively. The analysis of the mean particle size distribution of the CADC including the DPF active regeneration (figure 21) highlights a bimodal distribution of the aerosol during the active regeneration of the DPF. This bimodal distribution is made up of a nucleation mode centered on 6.5 nm (nucleation mode CMD), containing extremely small particles and an accumulation mode centered on 94 nm (accumulation mode CMD), containing in particular the typical Diesel soot aggregates.

The nucleation mode encountered during the DPF active regeneration on the CADC cycle, essentially results from the high temperatures reached (≥ 600°C) that cause an intense desorption of the sulfur previously trapped on the catalysts, and the appearance of sulfur compounds (among which $SO_2$ which is measured by the FTIR) in the gaseous phase of the exhaust aerosol, that are major precursors of nucleation processes (as already observed during Euro 5 vehicles DPF active regeneration [10]). Inversely to the gradual DPF loading previously shown, the DPF active regeneration causes the progressive but faster combustion of the previously trapped particles and as a result, the progressive soot cake removal, the gradual decrease of the particles filtration efficiency of the DPF, leading to the accumulation mode appearance downstream the DPF [10].

## 4 Conclusion

The variety of driving and starting conditions covered in this work, composed of 3 cycles and 4 engine warm up conditions, as well as the large reproducibility offered by the 58 cycles performed, offer an extensive assessment of the vehicle emissions, further improved by the complementarity of the implemented analyses.

It highlights the negative impact of engine warm-up and DPF active regeneration

on some regulated and unregulated gaseous and particulate emissions of the Euro 6b Diesel vehicle studied, in particular:

- Engine cold start and warm up lead to HCs, CO, $CO_2$, $N_2O$ and $CH_2O$ emissions global increase (the two first however remaining compliant with their related emission limits), as well as higher particle number (also under Euro 6b limit),
- DPF active regenerations lead to more important HCs, CO, $CO_2$ and $CH_2O$ emissions, to dramatic $NH_3$, $SO_2$ and particle number (PN) increase; these procedures are also characterized by significant HCN emission and nucleation particles formation.

Taking into account the results achieved, the study finally tackles the need to further improve the related after-treatment's efficiencies, especially during the warming up and DPF active regeneration phases that remain major contributors to the pollutants emission of recent Diesel vehicles.

Furthermore, even if the latest European regulation evolutions (in particular the WLTC cycle introduction and the incoming of the new real driving emission (RDE) test procedure) pave the way to further reduce the automotive emissions, additional efforts may be proposed. Indeed, our results advocate for consideration of the specific running conditions consisting firstly in the DPF active regeneration in order to go beyond the latest commission regulation 2016/427 [15] dedicated to the new Euro 6 passenger cars RDE tests. Secondly, one could consider additional pollutant emissions limits for passenger cars, primarily regarding to the ammonia due to the SCR technology spread, but also for the particles smaller than 23nm which are numerously emitted during the DPF active regeneration process.

At last, the hydrogen cyanide emissions revealed by this study during the DPF active regeneration of this Euro 6b DOC+SCR+DPF Diesel equipped vehicle deserve to be more deeply studied.

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