Measurements of sub 23 nm particles emitted from late technology passenger cars, using a PMP compliant Volatile Particle Remover

A. Mamakos, C. Dardiotis, G. Martini, A. Perujo, A. Marotta, U. Manfredi
Sustainable Transport, Institute for Energy, Joint Research Centre
I-21027, Ispra (Va), Italy

Regulation (EC) No 692/2008 [1] introduced a particle number limit for the type approval of light duty diesel vehicles starting from 09/2011. The same regulation as well as the Official Journal of the European Union (2008/C 182/08) [2] foresee the introduction of a particle number limit for petrol passenger cars at a Euro 6 stage (09/2014).
The test procedure and the limit value (6×10^{11} #/km) applicable to diesel vehicles were developed in the framework of the Particulate Measurement Programme (PMP) [3] so as to necessitate the installation of the best wall flow Diesel Particulate Filters (DPF) available in the market. In the regulations it was recognized that this approach might not be suitable for petrol cars and accordingly further research was requested [1]. One particular concern pertains to the size of the emitted particles which is reported to be smaller than that of their diesel counterparts. Therefore a significant fraction of them might not be counted owing to the PMP requirement of 50% counting efficiency (d_{50}) at 23 nm.
In order to address this issue, some dedicated investigations were conducted at the Institute for Energy of the Joint Research Centre of the European Commission. The research work focused on the emission performance of late technology vehicles under both regulated and unregulated conditions. The vehicle sample consisted of a conventional Euro 5 compliant Port Fuel Injection (PFI) vehicle, a Euro 5 DPF-equipped diesel, a Euro 5 Flex-Fuel Ethanol Gasoline Direct Injection (G-DI) running on 5%, 75% and 85% ethanol/gasoline blends, a Euro 5 G-DI retrofitted with a wall flow particulate filter and a Euro 4 Bi-Fuel PFI vehicle running on gasoline or on either CNG or CNG/H_2 mixtures up to 70/30%. The vehicles were tested over the legislated New European Driving Cycle (NEDC) at ambient and sub-ambient test cell temperature as well as over the Common Artemis Driving Cycle (CADC).
In order to quantify the number emissions of sub-23 nm particles, three Condensation Particle Counters (CPCs) having nominal d_{50} values of 23 nm (TSI's 3790 or TSI's 3010D), 10 nm (TSI's 3010 which in some tests was also shifted to 6.5 nm by adjusting the operating temperatures) and 4.5 nm (Grimm's 5.403), were employed in parallel sampling downstream of a PMP compliant Volatile Particle Remover (VPR). One additional CPC, having a nominal d_{50} value of 3.5 nm was also employed monitoring the concentration of untreated particles in the Constant Volume Sampling (CVS) tunnel.
The two Euro 5 G-DI vehicles tested stood out as the highest particle emitters, with the emission levels under the legislated procedure exceeding the diesel limit by 4 to 6 times. The use of 85% ethanol in the fuel resulted in a 70% reduction of the number concentrations over the NEDC, where the emissions averaged at 8×10^{11} #/km. The data collected with the low d_{50} CPCs suggested that the fraction of undetected sub-23 nm particles was lower than 30% under most driving conditions. During the motorway part of the CADC test cycle however, larger differences were observed especially with the

CPC having a d_{50} at 4.5 ($CPC_{@4.5nm}$). The observed differences were found to decrease when increasing the dilution factor, suggesting that these higher counts were related to volatile material escaping vaporization or even re-nucleating downstream of the evaporating tube. The use of a wall flow particulate filter, optimized for G-DI applications, was found to effectively reduce the regulated particle number emissions bellow the diesel threshold of 6×10^{11} #/km but at the same time effectively remove sub-23 nm particles.

It needs to be stressed at this point that the d_{50} value at 23 nm does not correspond to a sharp cut-off. For example, convolution of lognormal distributions with the nominal detection efficiency curves of the CPCs employed, suggest that for a geometric mean diameter of 50 nm and a geometric standard deviation of 2.05 (typical for G-DI exhaust [4]) the $CPC_{@23nm}$ will count 25% less particles than the $CPC_{@4.5nm}$ with 70% of them being larger 23 nm.

The emissions from the PFI gasoline vehicles were found to be systematically below the diesel limit even when employing the $CPC_{@4.5nm}$. Most of the particles were emitted during short periods of sharp accelerations. Particle formation was enhanced under cold start operation with the emissions over the urban part of the cycle (ECE) being up to 20 times higher of those during the extra-urban part (EUDC). PFI vehicles emitted relatively higher concentrations of nanosized particles compared to their G-DI counterparts. The $CPC_{@4.5nm}$ counted 40% to 55% higher concentrations than the $CPC_{@23nm}$ over the NEDC. This fraction was lower over the ECE part (35%-50%) of the cycle, indicating that the increased emissions occurring under cold start operation are associated with the formation of relatively larger particles.

The use of CNG and CNG/H_2 mixtures on the Bi-Fuel vehicle resulted in an order of magnitude reduction in the particle number emissions, which averaged at 2.2×10^{10} #/km over the NEDC with the $CPC_{@23nm}$. In this case, almost all particles were emitted during a sharp spike occurring over the first 50 s of the ECE, following which they remained at near background levels. The low d_{50} CPCs suggested a high fraction of sub-23 nm particles which furthermore exhibited a negative correlation with the cycle average $CPC_{@23nm}$ concentrations. The differences were not affected by quadrupling the dilution factor. Interestingly, similar results were obtained with the $CPC_{@10nm}$ and $CPC_{@4.5nm}$, both suggesting that 50% to 80% of the emitted particles were not counted by the $CPC_{@23nm}$. This might point towards the presence of a distinct nucleation mode of non-volatile nature peaking at a size bellow 23 nm. It needs to be emphasized though, that the emission levels were very low, with the maximum number emission rate recorded with the $CPC_{@4.5nm}$ over the NEDC being 9×10^{10} #/km.

The Euro 5 technology DPF-equipped diesel vehicle tested was found to comply with the Euro 5 limit. The actual emission levels strongly depended on the fill status of the DPF, ranging from 2×10^{11} #/km for an empty DPF to as low as 5×10^{10} #/km when loaded, in good agreement with what was observed in the "golden" vehicle of the PMP inter-laboratory correlation exercise [3]. The contribution of nano-sized particles not counted with the $CPC_{@23nm}$ was found to depend on the operating conditions. Over hot start test cycles (EUDC and CADC), approximately 35% of the particles counted by the $CPC_{@4.5nm}$ were not detected with the $CPC_{@23nm}$. Over the cold start ECE, this fraction was as high as 63%. Tests at an ambient temperature of -7°C resulted in an approximately 60% lower particle number emissions for the same DPF fill status. This reduction was associated

with the operation of the engine at lower rates of Exhaust Gas Recirculation (EGR), to avoid condensation of water. While this reduction was generally observed in all size ranges under hot start engine operation, a twofold increase in the concentration of sub-23 nm was recorded over the cold start ECE. The observed differences were consistent at dilution factors spanning from 300 to 3000 and therefore the nano-particles counted are expected to be non-volatile in nature. In the particular tests, the concentrations of untreated particles measured with a $CPC_{@3.5nm}$ were found to be generally 10% to 30% higher than those of thermally treated samples measured with a $CPC_{@4.5nm}$. Therefore, this increased emission of nano-sized particles can not be attributed to a potential formation of solid particles through pyrolysis of volatile material inside the evaporation tube of the VPR [5]. These are rather non-volatile particles emitted from the vehicle.
Overally, the results suggested the presence of nano-sized particles in the exhaust of all vehicles tested, that can not be counted by a PMP compliant CPC due to the relatively large 50% cut-off size and the relatively flat counting efficiency curve. The fraction of particles escaping detection was around 30% in the case of the two G-DI vehicles, and around 50% for gasoline PFI vehicles and the late technology DPF equipped diesel. At the even lower emission levels of the bi-fuel PFI vehicle running on CNG or CNG/H_2 mixtures and the DPF vehicle tested at sub-zero ambient temperatures the fraction of particles escaping detection with the $CPC_{@23nm}$ could reach up to 80%. However, in this case the absolute emissions were well below the diesel limit of 6×10^{11} #/km. The data also provided evidence of volatile material interference in the responses of sub-23 nm CPCs. This suggests that a potential shift to lower cut-off sizes will require further development of the VPR (e.g. incorporation of catalytic strippers [5]). Conclusively, the data collected indicate that the PMP methodology should be applied unedited for the certification of gasoline vehicles at a Euro 6 stage. Further research is required in order to better understand the nature of these nano-particles and investigate more robust approaches to measure them.

References:

[1] Commission Regulation (EC) No 692/2008 of 18 July 2008
[2] Official Journal of the European Union 2008/C 182/08,
[3] Andersson J., Giechaskiel B., Munoz Bueno R., Sandbach E. and Dilara P. 2007. EUR 22775 EN
[4] Harris S. and Maricq M., 2001, Journal of Aerosol Science, 32:749-764.
[5] Swanson J, Kittelson D. 2010. Journal of Aerosol Science, 41:1113-1122.

Joint Research Centre

www.jrc.ec.europa.eu

Measurements of sub 23 nm particles emitted from late technology passenger cars, using a PMP compliant Volatile Particle Remover

A. Mamakos, C. Dardiotis, G. Martini, A. Perujo, A. Marotta, U. Manfredi

Introduction

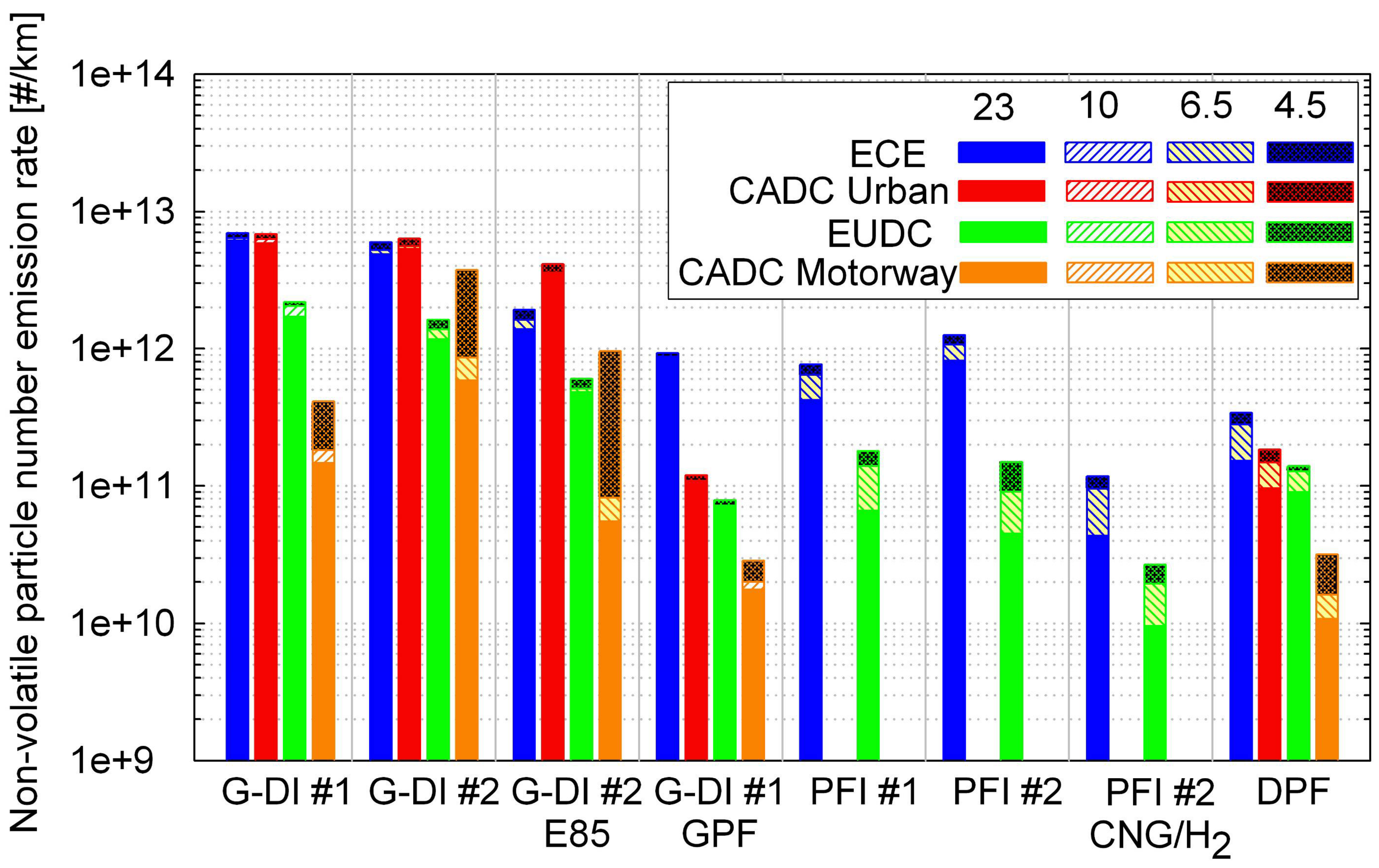
Regulation (EC) No 692/2008 foresees the introduction of a particle number limit for the certification of petrol passenger cars at a Euro 6 stage (09/2014). One issue of concern is the suitability of the 50% counting efficiency at 23 nm, that is currently applicable to diesels, given the reported smaller size of gasoline exhaust particles.

Experimental

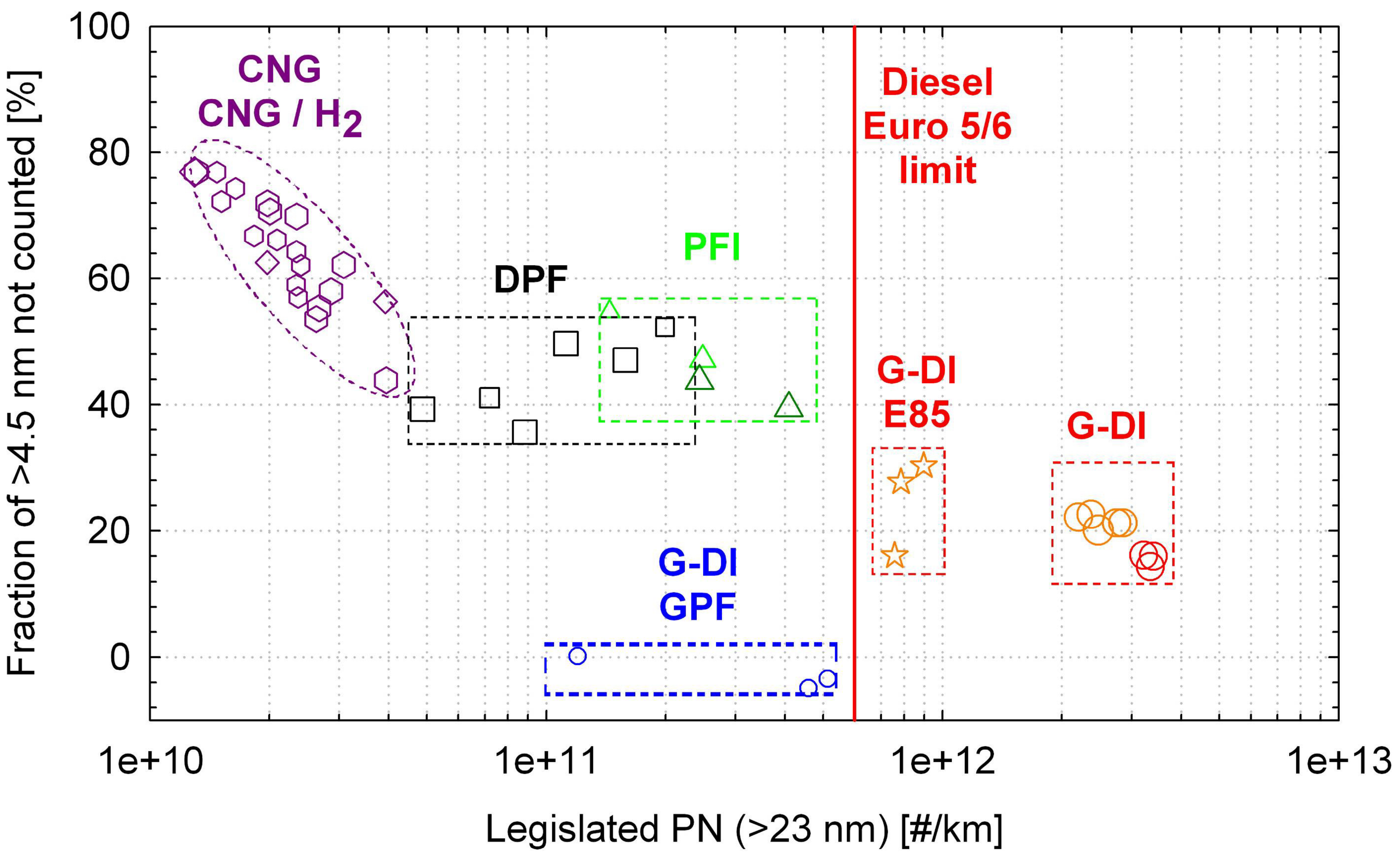
In this study, the particle number emissions of five late technology passenger cars were characterized using a PMP compliant Volatile Particle Remover (VPR). Three Condensation Particle Counters (CPC) having nominal 50% detection efficiencies at 23 nm, 10 nm (shifted to 6.5 nm in some tests by means of adjusting the operating temperatures) and 4.5 nm were employed sampling in parallel downstream of the VPR. A fourth CPC with a cut-off size at 3.5 nm was sampling directly from the Constant Volume Sampling (CVS) tunnel.

The vehicle sample consisted of a conventional Euro 5 Port Fuel Injection (PFI), a Euro 5 diesel equipped with a Diesel Particulate Filter (DPF), a Euro 5 Flex-Fuel Gasoline Direct Injection (G-DI) running on 5%, 75% and 85% ethanol/gasoline blends, a Euro 5 G-DI retrofitted with a wall flow particulate filter (GPF) and a Euro 4 Bi-Fuel PFI running on gasoline, CNG and CNG/H_2 mixtures up to 70/30%. The vehicles were tested over the legislated New European Driving Cycle (NEDC) at ambient and sub-ambient temperature as well as over the Common Artemis Driving Cycles (CADC).

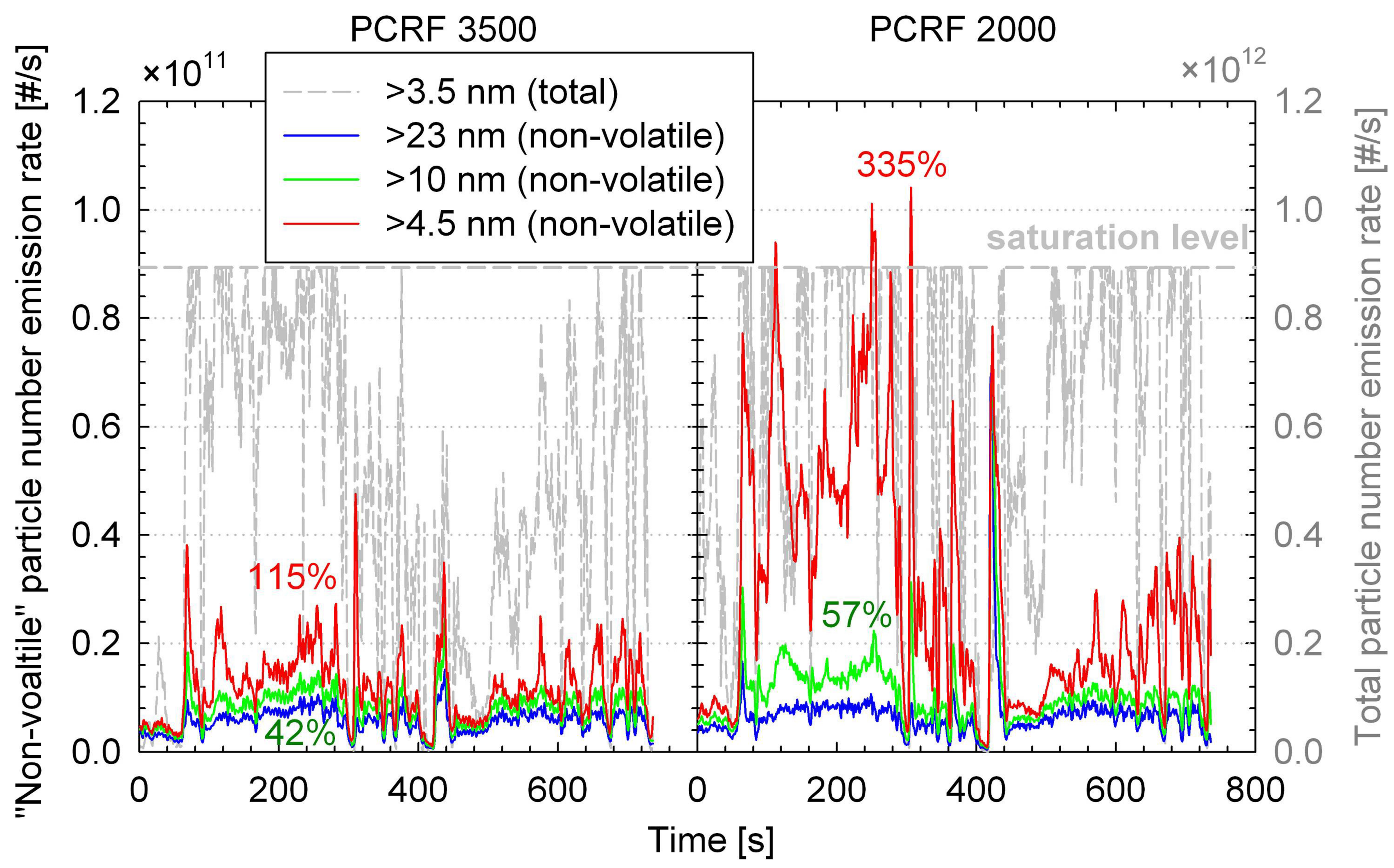
Results



Cycle average "non-volatile" particle number emissions recorded with the different CPCs for the different vehicle technologies tested.



Fraction of sub-23 nm non-volatile particles not counted by the PMP compliant CPC over the NEDC.



Indications of volatile material interference in the responses of the sub-23nm CPCs over the motorway part of the CADC for a G-DI.

Conclusions

- The fraction of "non-volatile" sub-23 nm particles emitted by the four gasoline vehicles tested were found to be at the same levels or even lower than that of the late technology DPF-equipped diesel.
- The use of a GPF optimized for G-DI applications was effective in achieving the diesel Euro 5 limit of 6×10^{11} #/km and at the same time controlling the emission of sub-23 nm particles.
- A potential shift towards lower CPC cut-off sizes introduces the risk of volatile material interference under certain operating conditions.

Contact

Giorgio Martini
European Commission • Joint Research Centre
Institute for Energy
Tel. +39 0332 789293
E-mail: giorgio.martini@jrc.ec.europa.eu

JRC
EUROPEAN COMMISSION