**On the feasibility of measuring the number of sub-23 nm non-volatile particles following the PMP procedure**

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Starting from September 2011, a Particle Number (PN) limit was introduced in the European legislation for the certification of Euro 5 technology diesel passenger cars [1]. A similar limit will enter into force at a Euro 6/VI stage for petrol vehicles [1] and diesel heavy duty engines [2].

The regulated procedure is largely based on the findings of the Particulate Measurement Programme (PMP), and only tackles the non-volatile fraction of the emitted particulates [3]. This is achieved by means of hot dilution (above 150°C) and thermal treatment (at 300-400°C) in the so called Volatile Particle Remover (VPR). In order to further safeguard against volatile particle interference (e.g. formed by re-nucleation of evaporated species downstream of the VPR), a Condensation Particle Counter (CPC) having a relatively large cut-off size ($d_{50}$ at 23 nm – CPC@23) is employed for the measurement of the number concentrations. This however, comes at the expense of not detecting non-volatile particles lying below the detection limit of CPC@23. This limitation raised concerns with regards to the suitability of this measurement procedure to petrol vehicles [1], which have been reported to emit smaller particles compared to their diesel counterparts [4, 5].

In order to assess the suitability of the regulated PN methodology for petrol vehicle exhaust, some dedicated investigations were conducted at the Institute for Energy and Transport 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 (PFI1) vehicle, a Euro 4 Bi-Fuel PFI tested on gasoline (PFI2) and CNG/$H_2$ mixtures (PFI2 CNG), two Euro 5 diesel vehicles equipped with DPF (DPF1, DPF2), a Euro 5 Flex-Fuel Gasoline Direct Injection (G-DI) running on 5% (G-DI2 E5) and 85% ethanol/gasoline blends (G-DI2 E5), a Euro 4 gasoline utilizing two injectors per cylinder allowing both direct injection and port-fuel injection (G-DI PFI) and a Euro 5 G-DI (G-DI1) which was retrofitted with a wall flow particulate filter in selected tests (G-DI1 GPF). The vehicles were tested over the legislated New European Driving Cycle (NEDC) and the Common Artemis Driving Cycle (CADC) [6]. Tests were conducted at ambient temperatures of 22°C and -7°C.

In order to quantify the number emissions of nonvolatile particles escaping detection with the CPC@23, two additional CPCs were employed in parallel sampling downstream of the VPR, having nominal $d_{50}$ of 10 nm (CPC@10) and 4.5 nm (CPC@4.5). One additional CPC, having a nominal $d_{50}$ at 3.5 nm (CPC@3.5) was also employed to monitor the concentration of particles upstream of the VPR.

Figure 1 summarizes the non-volatile particle number emissions determined with the CPC@4.5 and the CPC@23 over the NEDC at 22°C for all vehicles tested. G-DIs were the highest emitters, exceeding the diesel PN limit by up to one order of magnitude. All other vehicle technologies emitted below this threshold even if the CPC@4.5 was used for the quantification of the number concentrations.

The fraction of non-volatile particles that were not counted by the CPC@23 ranged between 5-25% for G-DIs, 25-50% for DPFs and PFIs and approximately 65% for PFI2 vehicle tested on CNG/$H_2$ mixtures. The wall flow particulate filter introduced in G-DI1 was found to be very efficient in collecting these nano-sized particles, reducing the fraction of undetected particles to 0%.

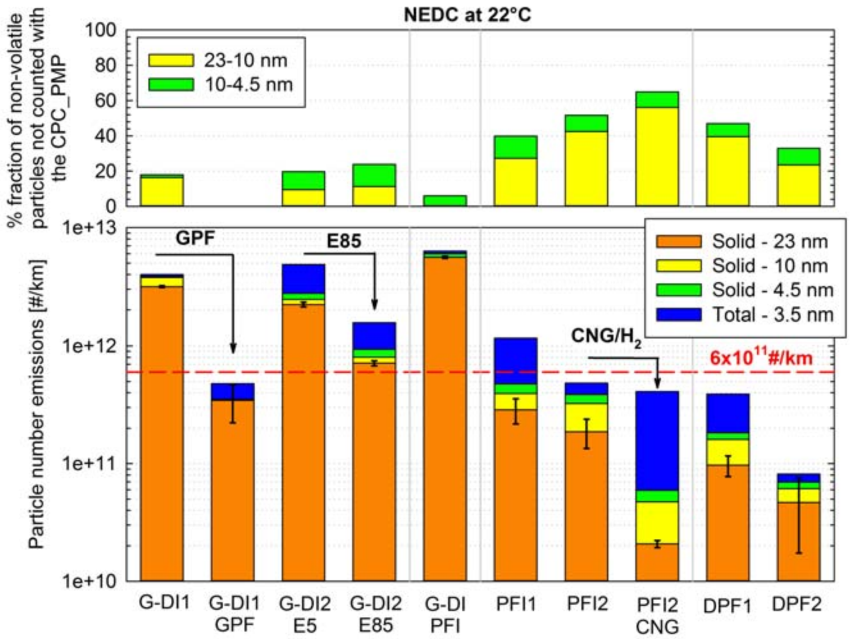


Figure 1: Lower panel: Overview of the particle number emissions over the NEDC, determined with the different CPCs. Upper panel: fraction of non-volatile particles not detected by the CPC@23.

The relatively high excess counts of CPC@4.5 in the tests of the two diesel vehicles, most probably reflect excessive engine-out emissions of nanoparticles. The relevance of engine-out particle emissions was verified in the NEDC tests of one of the diesels at -7°C. At these operating conditions, the engine operated at reduced EGR rates to avoid the formation of condensates in the EGR line. This resulted in a four-fold increase of the nitrogen oxide (NOx) emissions which was accompanied by an approximately three-fold reduction of the regulated particle numbers emissions (CPC@23), in line with the well known NOx-PM trade-off. Under these operating conditions, the CPC@23 detected only 85% of the emitted non-volatile particles, indicating the presence of a distinct non-volatile nucleation mode particle. This observation was in good agreement with the results of de Filippo and Maricq (2008) [7], who also observed a solid nucleation mode in the exhaust of two diesel vehicles which was suppressed when the EGR was turned on.

A limited formation of volatile particles was observed over the NEDC (figure 1). However, under conditions favouring volatile particle formation in the CVS tunnel (in particularly under motorway driving), some indications of volatile artefact were observed in the responses of the low cut-off size CPCs (CPC@10 and CPC@4.5). A characteristic case is illustrated in figure 2, which summarizes the emissions of G-DI2 over CADC Motorway at 22°C. The fraction of excess particle counts detected by the low cut-off size CPCs, was found to increase as the dilution ratios were decreased or as the concentration of solid particles decreased (through the use of 85% ethanol) for similar concentration of volatile particles. This behaviour is indicative of volatile particles forming by homogeneous nucleation downstream of the VPR.

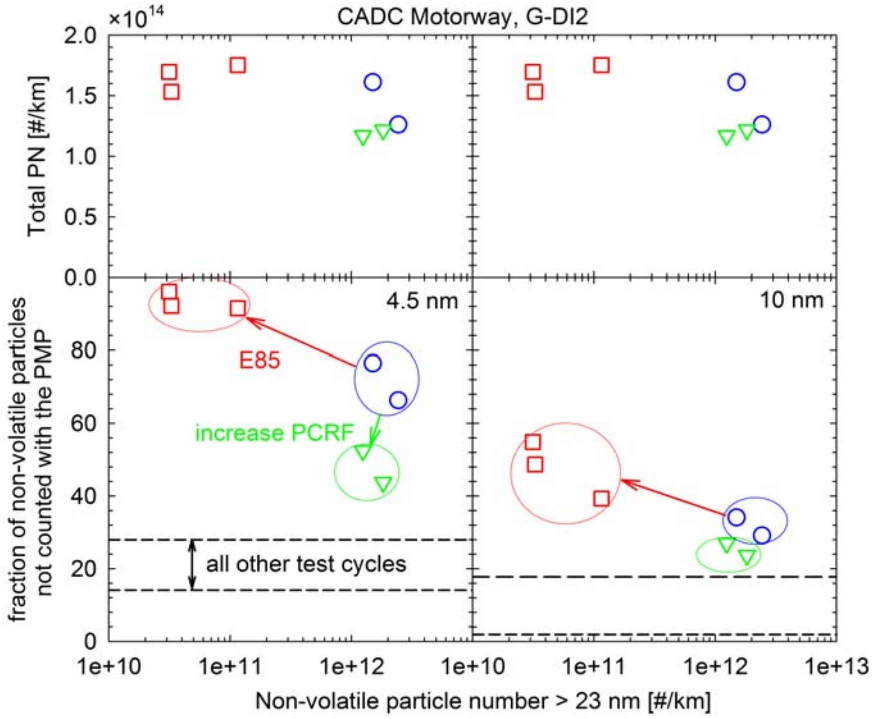


Figure 2: Dependence of the fraction of excess particles detected by CPC@4.5 (left-hand panel) and CPC@10 (right-hand panel), on the dilution ratio (3500:1 for green symbols, 2000:1 for blue and red symbols) for a flexi-fuel G-DI tested on 5% ethanol (blue-green symbols) and 85% ethanol (red symbols).

Overall, the experimental data indicated the presence of large fractions of non-volatile particles that can escape detection in PMP systems due to their small size. Interestingly, the situation was more pronounced in the tests of DPF-equipped diesels, particularly under conditions where the EGR rate was lowered (i.e. urban driving at -7°C). However, the experimental data under conditions favouring volatile particle formation in the CVS tunnel, provided evidence of volatile particle interference when low cut-off size CPCs are employed downstream of VPR systems. This suggests that a potential shift pf the regulation to lower cut-off sizes will require further development of the VPR (e.g. incorporation of catalytic strippers [8]).

**References**

[1] Regulation (EC) No 692/2008 of 18 July 2008
[2] Regulation (EC) No 715/2007 of 20 June 2007
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[5] Mohr, M. et al. (2006). Environmental Science and Technology 40: 2375-2383.
[6] André, M. (2004). Science of the Total Environment, 334-335:73-84.
[7] De Filippo, A and Maricq, M. (2008). Environmental Science and Technology, 42:7957-7962.
[8] Swanson J, Kittelson D. 2010. Journal of Aerosol Science, 41:1113-1122.

# On the feasibility of measuring the number of sub-23 nm non-volatile particles following the PMP procedure

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- Robustness of the PMP methodology against volatile nanosized particles
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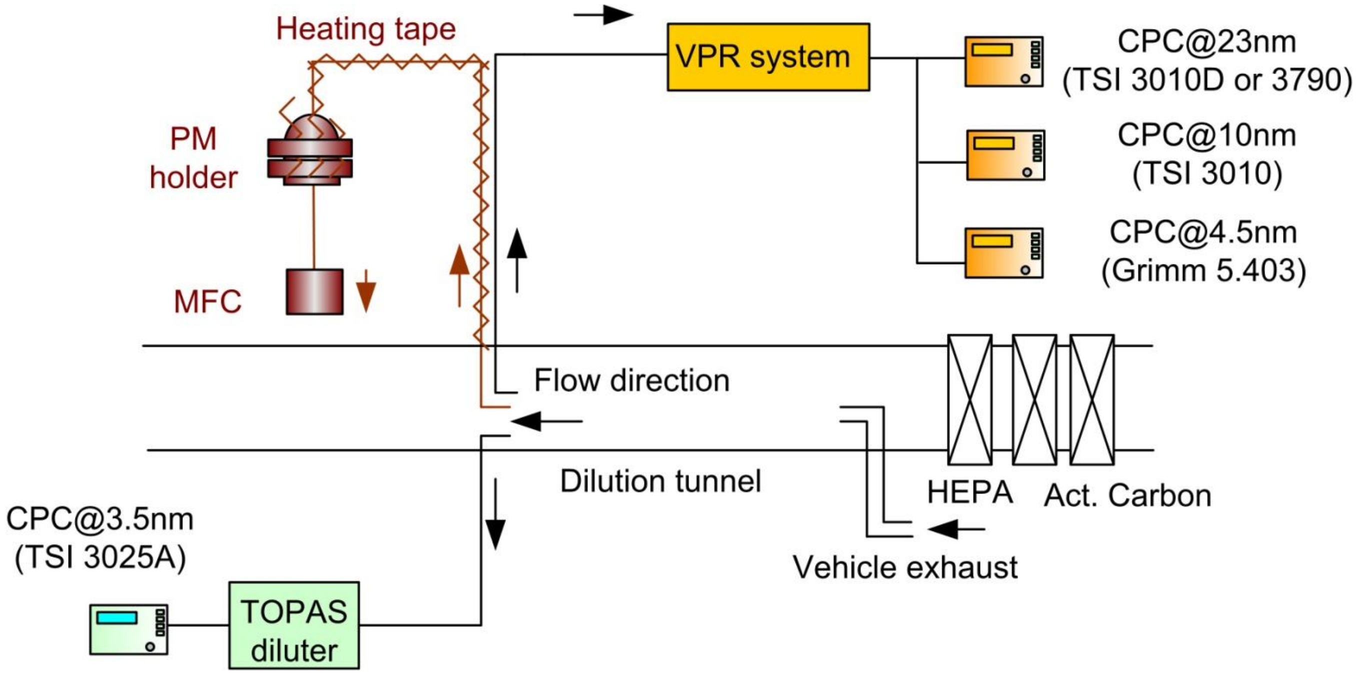
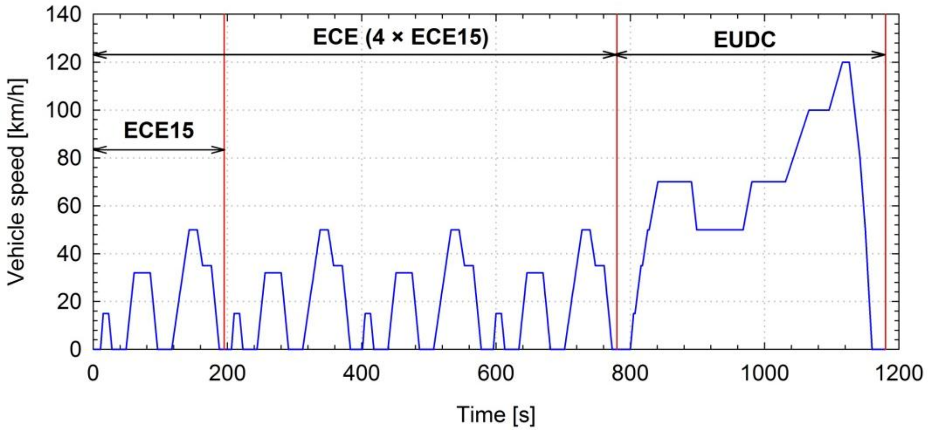
# Experimental

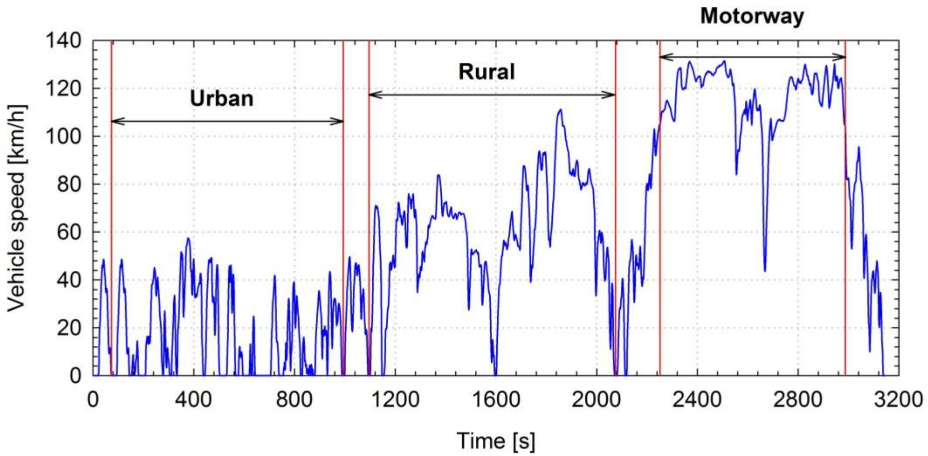



- ⇨ Two low cut-off size CPCs ($d_{50}$ at 10 and 4.5 nm) downstream of the VPR
- ⇨ A low cut-off size CPC ($d_{50}$ at 3.5 nm) upstream of the VPR

# Test matrix

Test cycles:




Vehicle sample:

⇨ Port Fuel Injection (PFI) Gasoline:
- 1 × Euro 5
- 1 × Euro 4 Bi-Fuel tested on gasoline and CNG/$H_2$ mixtures

⇨ Direct Injection Gasoline (G-DI):
- 1 × Euro 5 Flexi-Fuel
- 1 × Euro 5 retrofitted with a Gasoline Particulate Filter (GPF)
- 1 × Euro 4 G-DI/PFI

⇨ Diesel with Particulate Filter (DPF):
- 2 × Euro 5

Test cell temperatures:

⇨ -7 & 22° C

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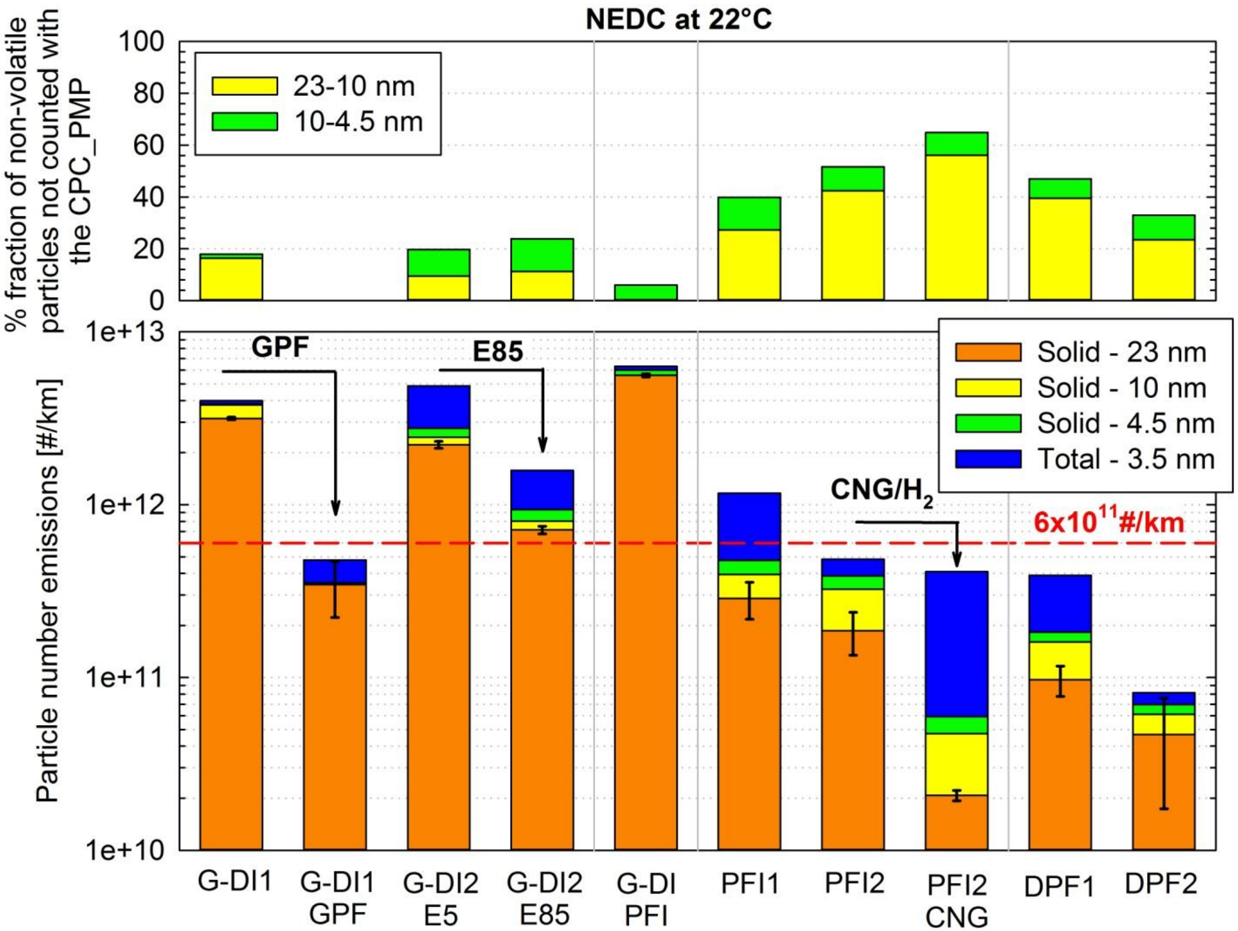
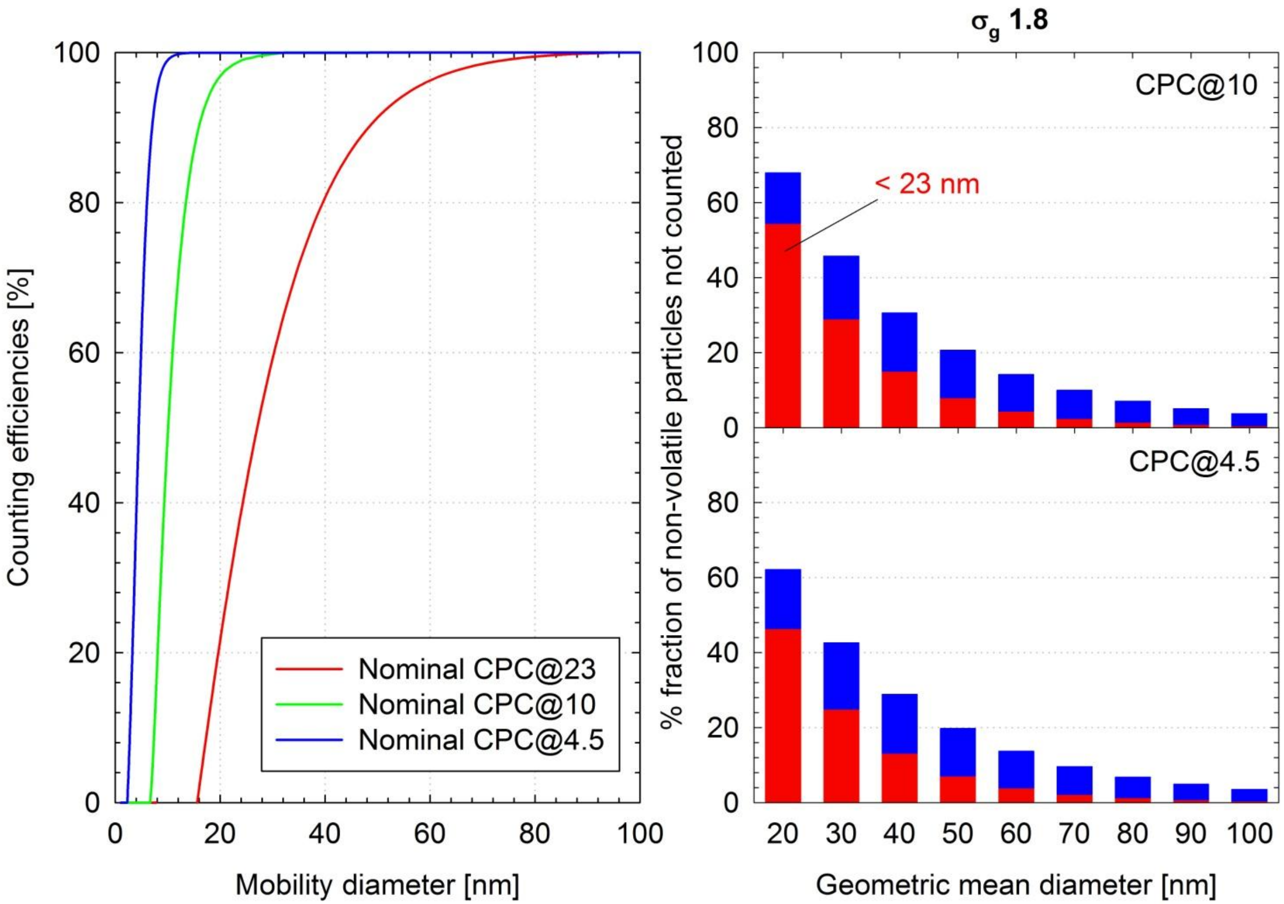
# PN emission performance of LDVs



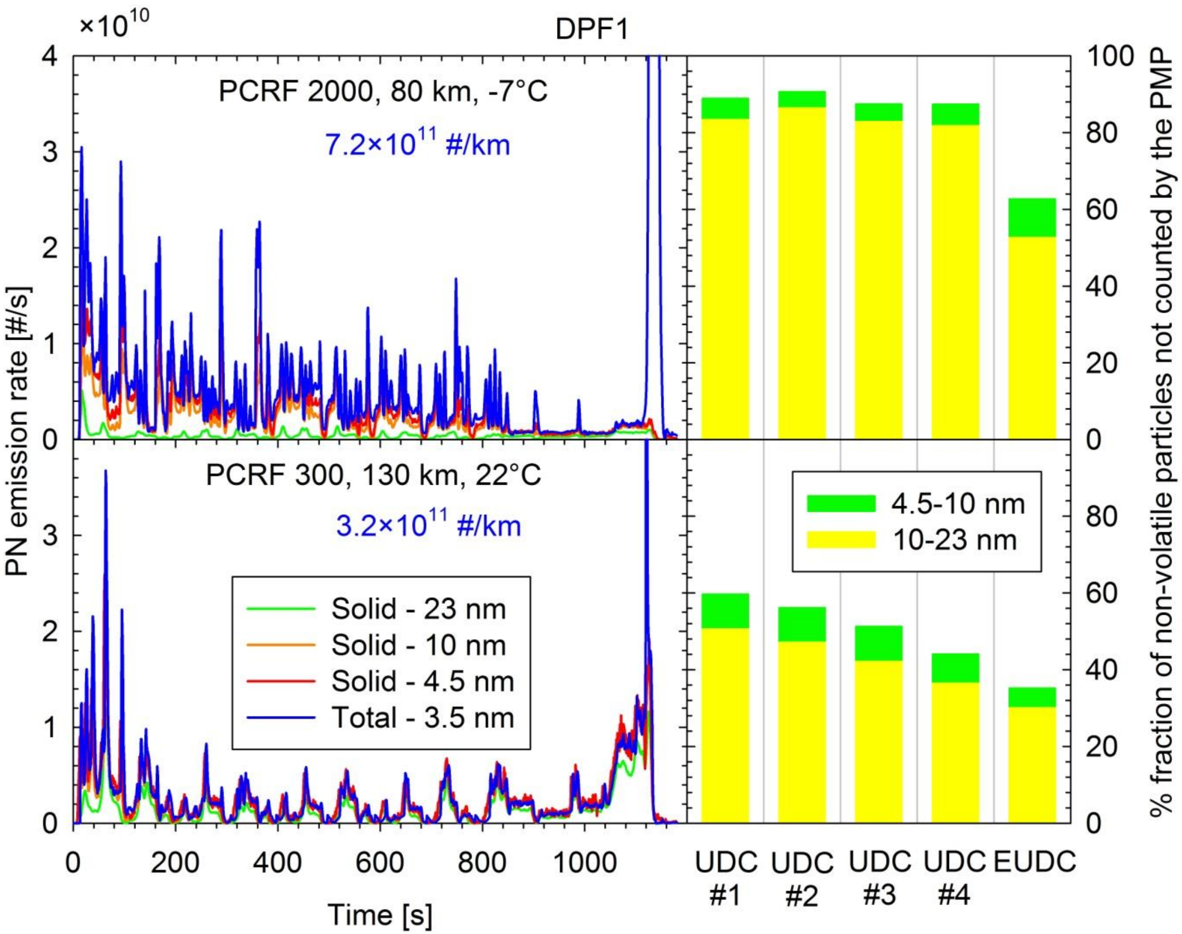

- ⇨ Undetected fraction:
  - G-DIs: 5-25%
  - PFIs: 25-65%
  - DPFs: 25-50%
- ⇨ 10 nm CPC measured most of the undetected fraction

# Simulated fraction of undetected particles



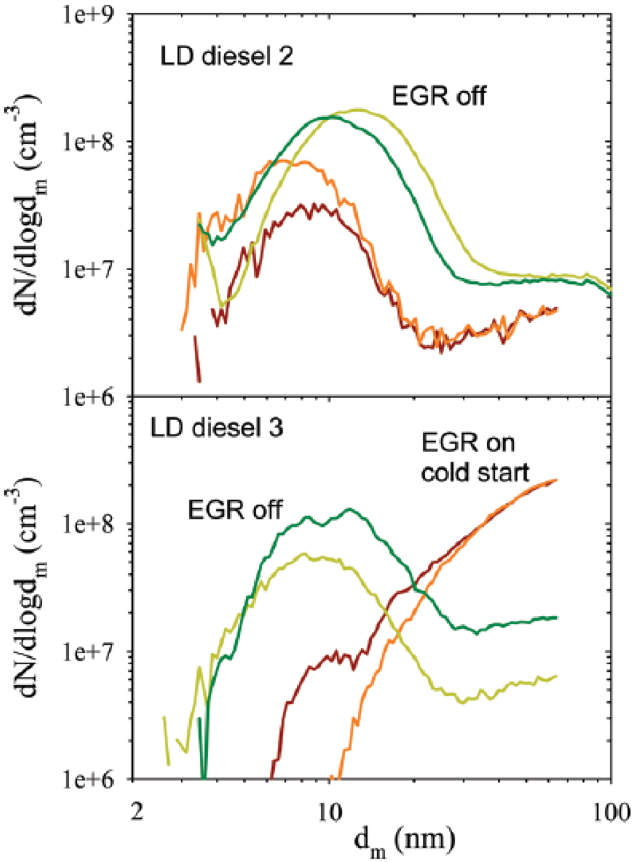

- ⇨ Convolution of the CPC counting efficiencies with lognormal distributions:
  - G-DIs: 45-90 nm
  - PFIs: 20-45 nm
  - DPFs: 30-45 nm
- ⇨ Exact quantification of the mean particle size requires information on VPR losses

# Non-volatile nanoparticles in DPFs




- ⇨ Reduced EGR rates at sub-zero operation resulted in:
  - Lower engine-out PN
  - Disproportionally higher excess particle counts especially over the urban part

# Published data on the effect of EGR




De Filippo, A. & Maricq, M. (2008). Env. Sc. & Tech. 42, 7957–7962:

*"We present evidence here of a "solid" particle nucleation mode that accompanies normal soot emissions in the case of two modern light-duty diesel vehicles run with ultralow sulfur fuel. This mode is most prominent at idle, but also appears at speeds below ~30 mph, and is highly sensitive to the level of exhaust gas recirculation (EGR)."*

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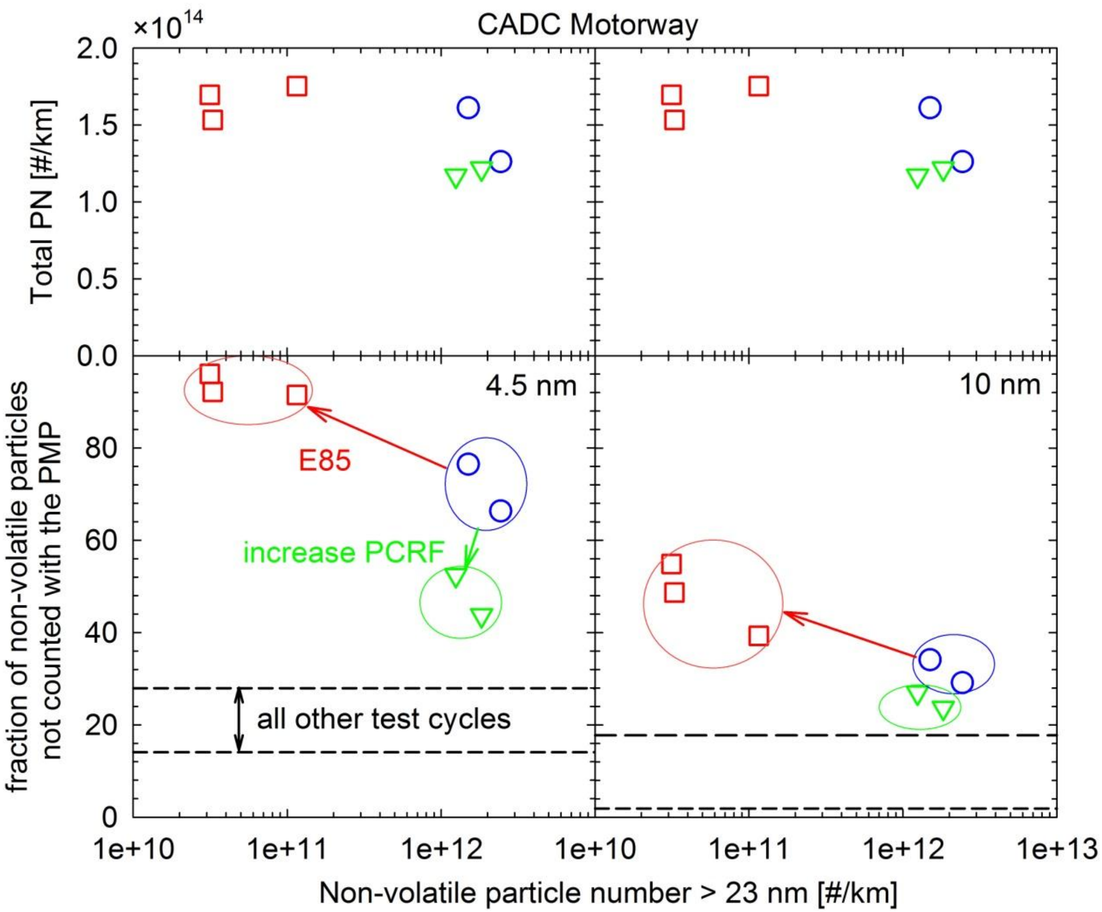
# Volatile artefact – Motorway tests of a G-DI




- ⇨ Excessive particle counts downstream of the VPR under conditions favouring nucleation mode formation in the CVS tunnel
- ⇨ The excess fraction was higher at:
  - – Lower dilution ratios
  - – Lower solid concentrations
- ⇨ Volatile interference

# Contents

# Conclusions

- The PMP system was found to detect more than 75% of the non-volatile particles emitted by Euro 4 and Euro 5 technology G-DIs over the NEDC.
- PFI and DPF vehicles emitted smaller particles, with up to 65% of them not being detected by the PMP compliant CPC. In absolute terms though, the emissions of all DPF and PFI vehicles tested remained below the diesel threshold of $6 \times 10^{11}$ #/km.
- Under conditions favouring volatile particle formation in the CVS tunnel, a volatile artefact was observed in the responses of low cut-off size CPCs.

# *Thank you for your attention*

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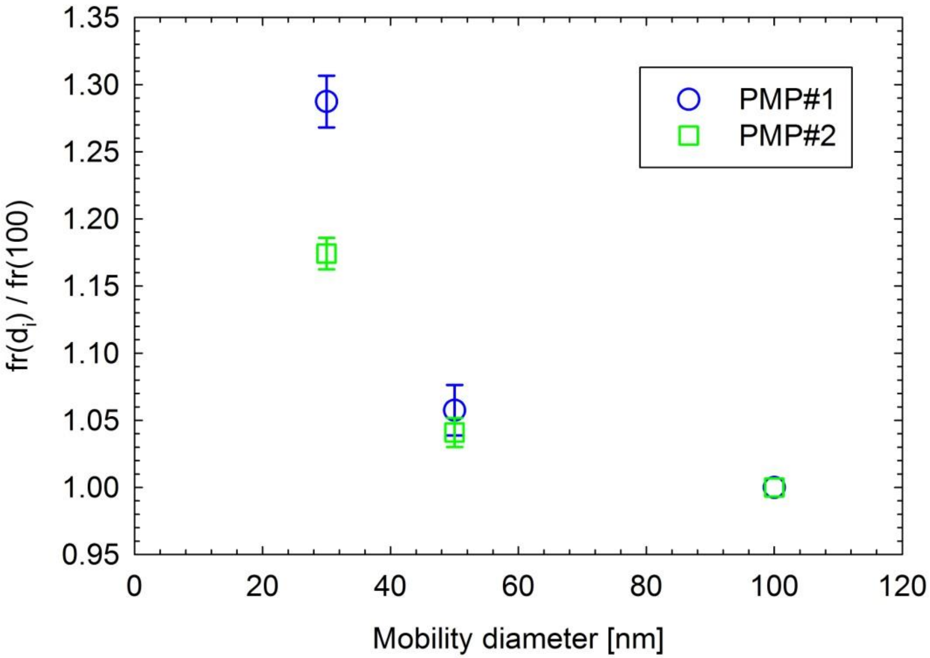

PMP#1
PMP#2
fr(d_i) / fr(100)
Mobility diameter [nm]
1.35
1.30
1.25
1.20
1.15
1.10
1.05
1.00
0.95
0
20
40
60
80
100
120