PMP: SUB 23 NM

REVIEW

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Outlook

- *Introduction*
- *Primary particles*
- *Solid <23 nm (review)*
- *Experimental investigation at JRC*
- *Feasibility of sub 23 nm measurement for PNCs*
- *Feasibility of sub 23 nm measurement for VPRs*
- *Summary*

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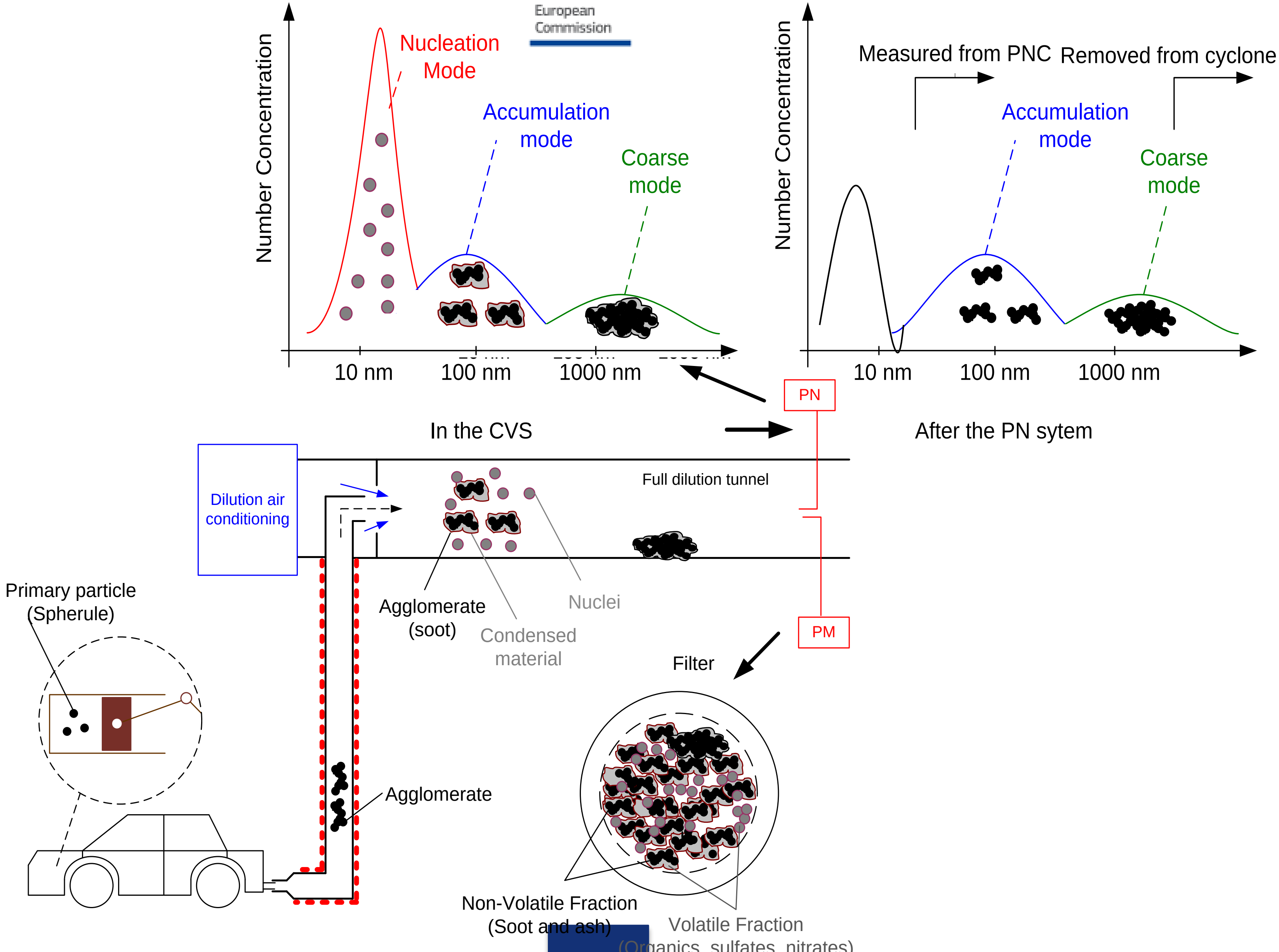
PMP method

- *Introduction in the Light-Duty vehicles emissions legislation (R83)*
  - From Euro 5b (2011) for Diesel
  - From Euro 6 (2014) for Gasoline Direct Injection
- *Introduction in the Heavy-Duty engines emissions legislation (R49) from Euro VI (2014)*



Number Concentration
Nucleation Mode
Accumulation mode
Coarse mode
10 nm
100 nm
1000 nm
Measured from PNC
Removed from cyclone
Number Concentration
Accumulation mode
Coarse mode
10 nm
100 nm
1000 nm
PN
In the CVS
After the PN sytem
Dilution air conditioning
Full dilution tunnel
Primary particle (Spherule)
Agglomerate (soot)
Condensed material
Nuclei
PM
Filter
Agglomerate
Non-Volatile Fraction (Soot and ash)
Volatile Fraction (Organics, sulfates, nitrates)

PCRF

$PCRF_{30} \leq 1.3\ PCRF_{100}$

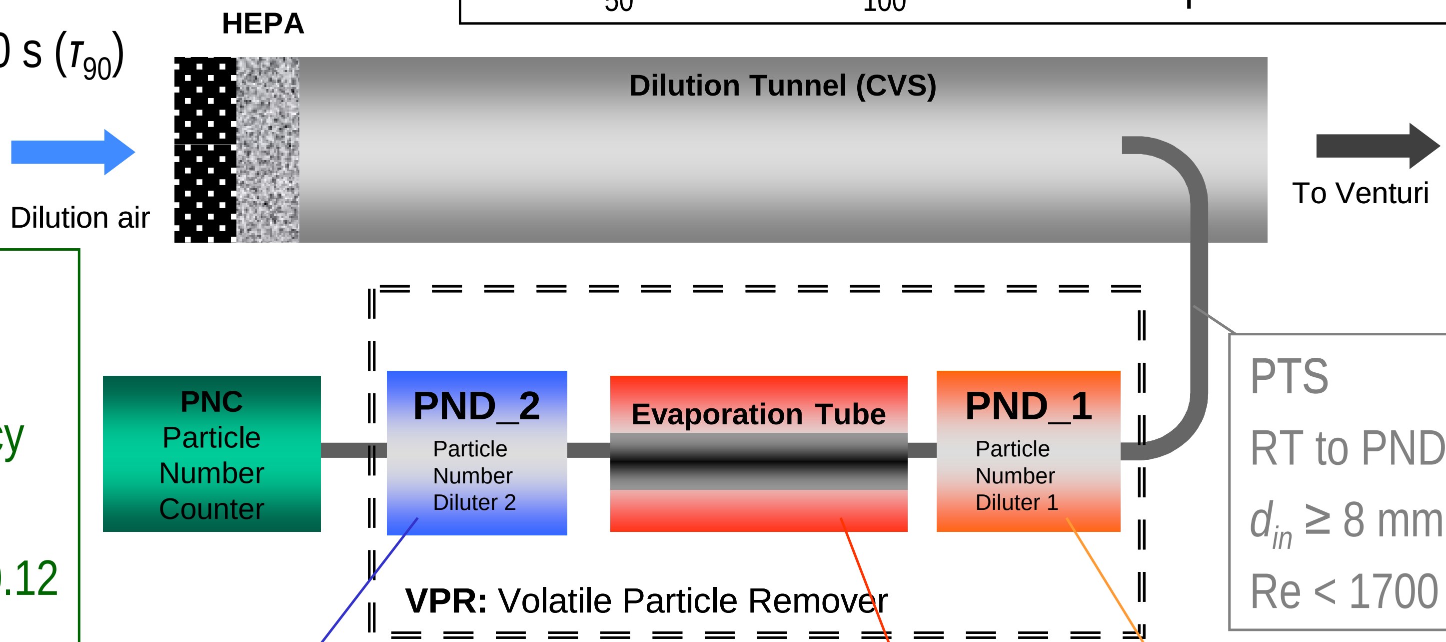
$PCRF_{50} \leq 1.2\ PCRF_{100}$

Volatile Removal Efficiency

>99% of ≥30 nm tetracontane

with 10^4 p/cm^3

Total RT ≤ 20 s (τ_{90})



PNC

Full flow

±10% accuracy

$\tau_{90} < 5$ s

$CE_{23} = 0.50 \pm 0.12$

$CE_{41} = \geq 0.9$

PTS

RT to PND_1 ≤ 3 s

$d_{in} \geq 8$ mm

Re < 1700

PND_2 (Not required)

t to PNC <35°C

RT to PNC ≤ 0.8 s ($d_{in} \geq 4$ mm)

Evaporation Tube

300-400°C wall temperature

no RT restriction

PND_1

DF >10

PND_1 t_{sample}>150°C

UNECE Reg. 83

Objectives

- *Existence of <23 nm solid particles*
- *Feasibility of <23nm measurements*
  - PNCs
  - Volatile Removal Efficiency of the VPR
  - Formation of particles in the VPR

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Primary particles

- *Primary particles are around 25 nm.*
- *Similarly for GDI particles. However for GDIs:*
  - The distribution of primary particles is wider, so larger percentage of particles will exist <23 nm.
  - The structure of primary particles is sometimes different (more amorphous) probably due to unburned hydrocarbons or volatile organics due to fuel impingement at early fuel injection time.
  - Differences in thermal pre-treatment might be important

Size distributions

	Technology	PN	CMD	σ	PM	Ash	Soot	Organic	Sulfate
		[p/km] or [p/kWh]	[nm]	[-]	[mg/km] or [mg/kWh]	[%]	[%]	[%]	[%]
HD	Diesel	$5x10^{13}-2x10^{14}$	50-100	1.7-2.1	20-80	5-10	40-75	20-50	0-15
HD	DPF	$5x10^{10}-2x10^{12}$	60-75	1.6-2.0	1-4	0-5	5-20	20-50	5-60
LD	Diesel	$2x10^{13}-2x10^{14}$	40-80	1.7-1.9	10-40	0-5	55-90	10-40	5-15
LD	DPF	$5x10^{10}-6x10^{11}$	45-75	1.7-2.1	0-2	0-5	0-15	40-75	5-35
LD	G-DI lean	$2x10^{12}-2x10^{13}$	50-85	1.7-2.1	1-20	0-5	55-80	20-40	0-5
LD	G-DI stoich.	$1x10^{12}-8x10^{12}$	40-75	1.7-2.0	1-10	0-5	75-90	10-25	0-5
LD	G-PFI	$2x10^{10}-6x10^{11}$	45-75	1.6-2.2	0-2	0-5	10-25	45-80	10-40

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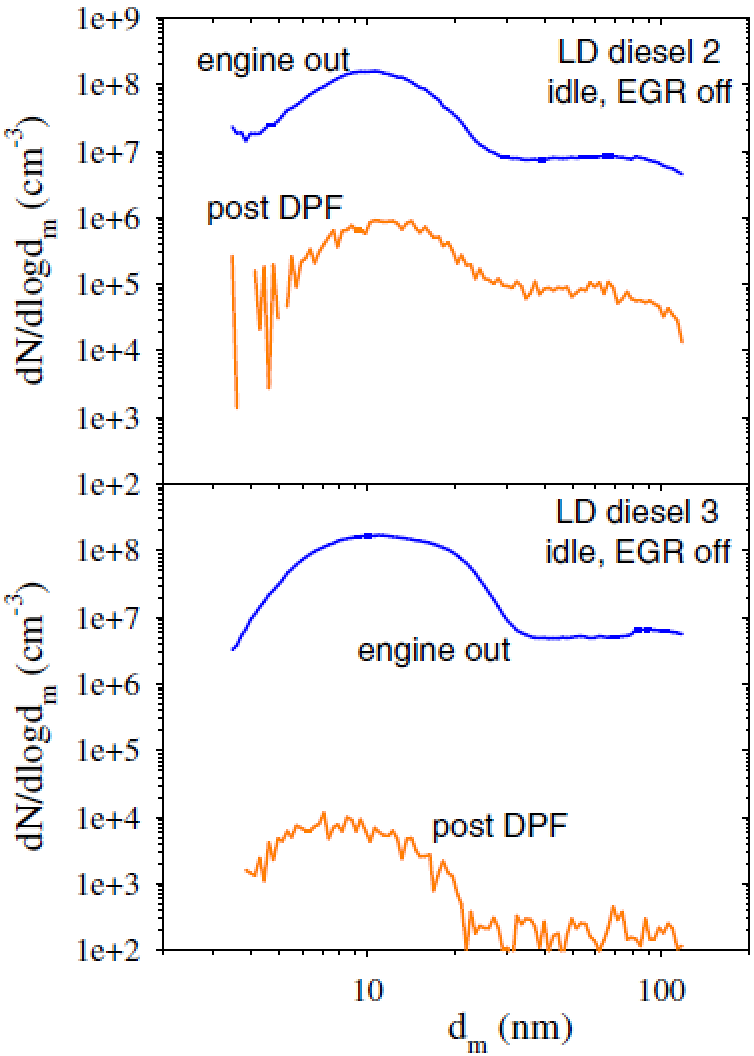
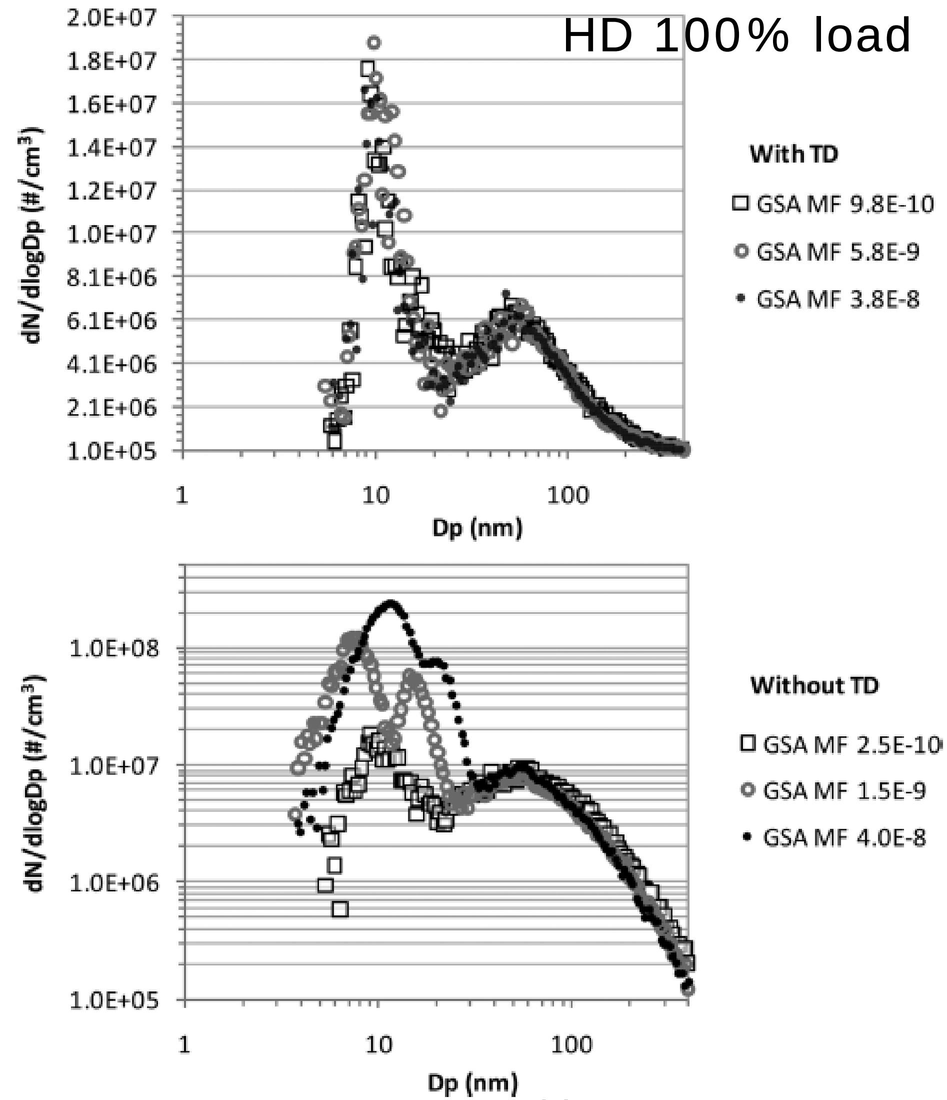
Solid <23 nm particles review

- *Diesel (40 engines and vehicles):*
  - Sub23 nm particles can be found at older and modern without exhaust after-treatment or with low particle collection efficiency filters and/or DOCs. They appear mostly at low loads (but even at high).
  - Probably formed in the combustion chamber. Fuel aliphatic hydrocarbons or lubricating oil metals or fuel additives can also contribute.
  - Regeneration can also result in increased emissions of sub-23 nm solid particles



DeFilippo & Maricq 2008

HD 100% load



Rönkkö et al. 2013

Solid <23 nm particles review

- *GDIs (10 engines and vehicles):*
  - A shoulder at 20 nm appears. A separate solid nucleation mode is not typical, but the size distribution can peak at small sizes (20 nm or lower) in some operation modes.
- *Gasoline (8 vehicles):*
  - Often observed→ from the metals of the lube oil or from fuel additives.
- *Moped (12 mopeds):*
  - Very often, probably from the lube oil. In some cases it can be a sampling artifact.

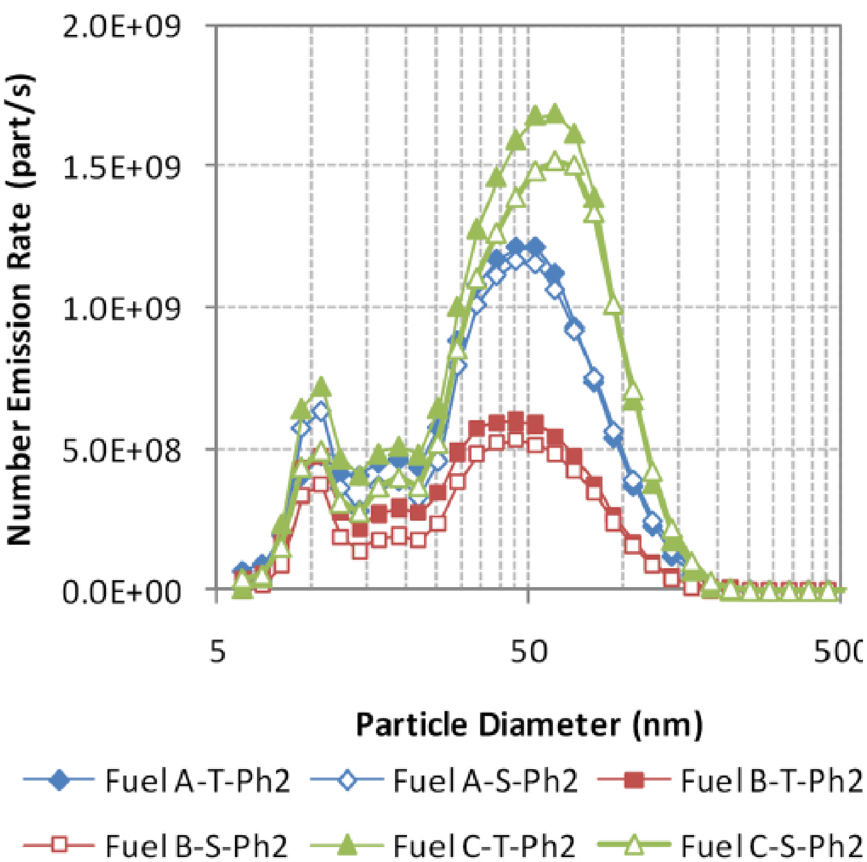
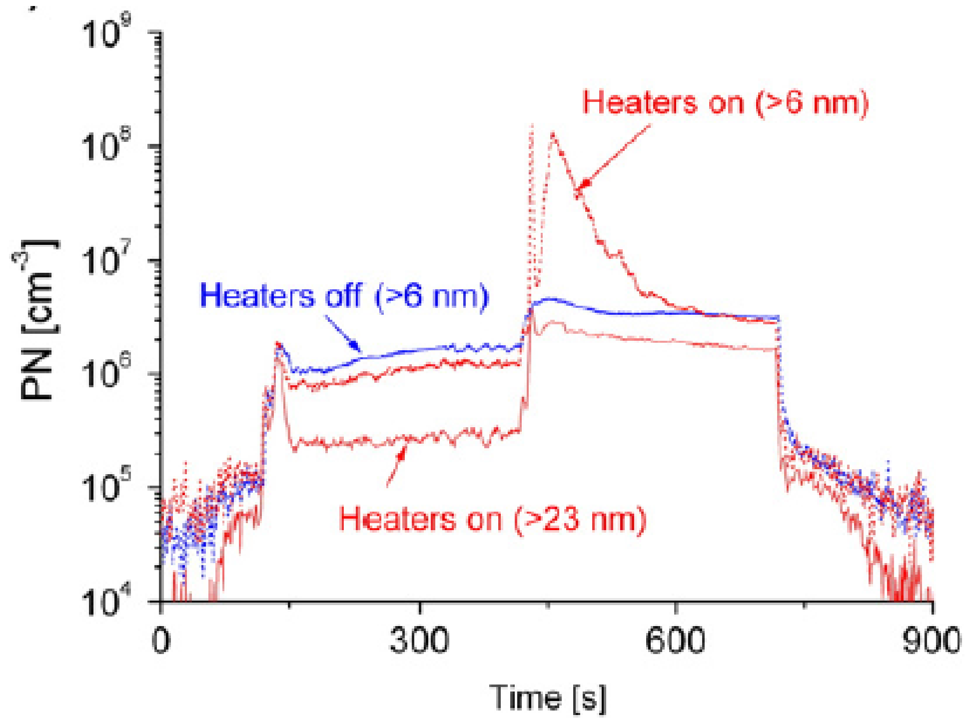


Figure 13. Phase 2 Total and Solid Particle Number-Weighted Size Distribution for Fuels A, B, and C



GDI, vehicle Khalek et al. 2010

Moped Giechaskiel et al. 2010

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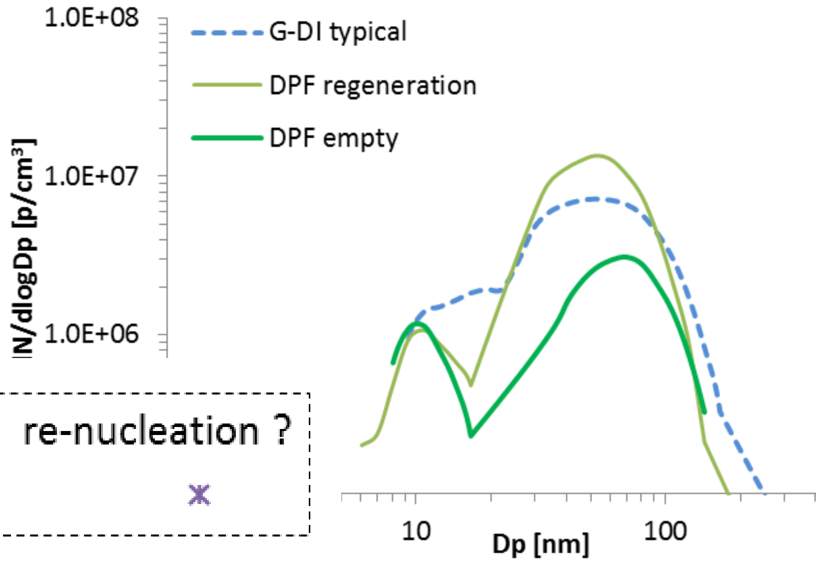
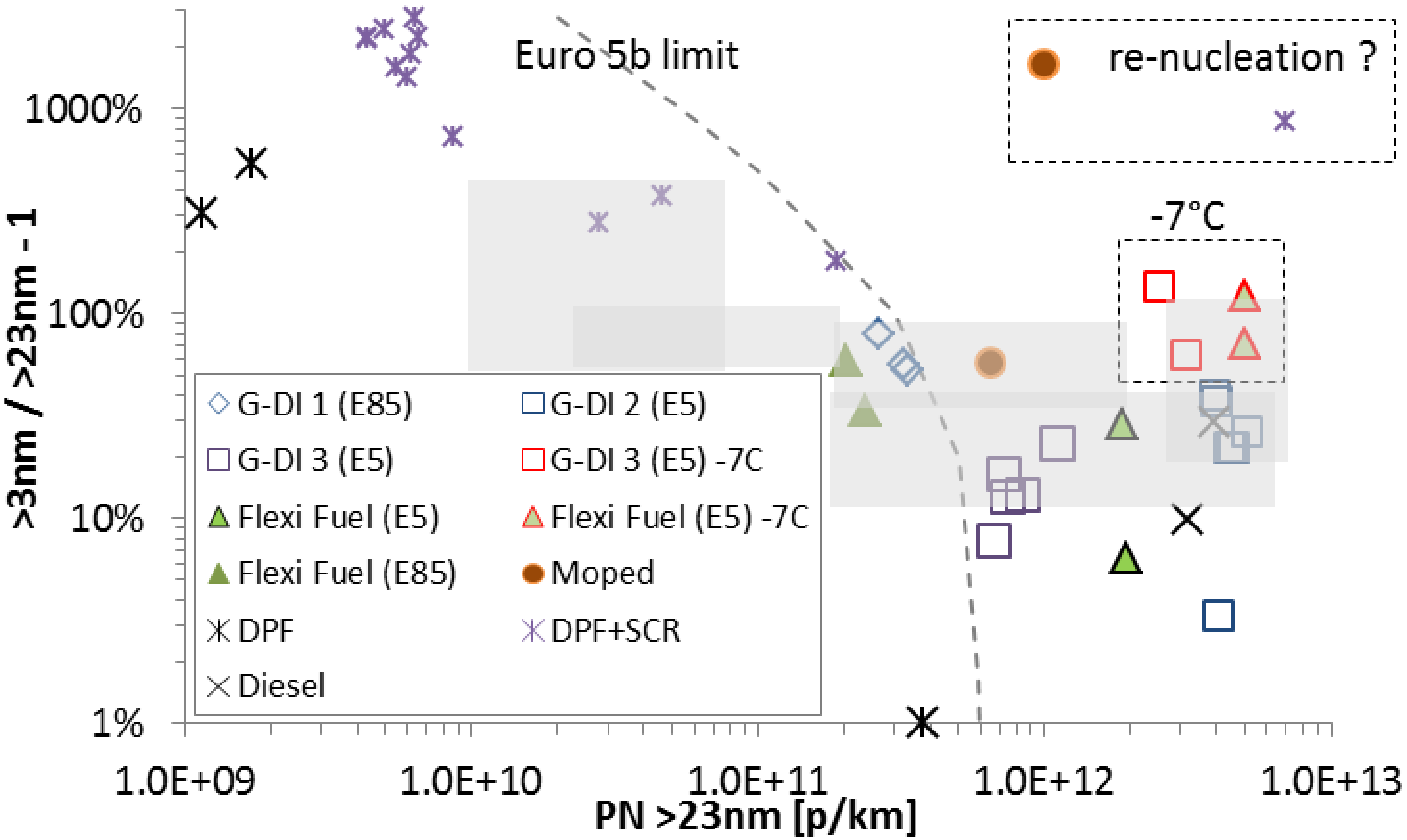
JRC investigation





JRC investigation

- *GDIs have slightly higher percentage of solid sub23 nm particles compared to diesel vehicles*
- *The percentages are typically <60%*
- *Size distributions showed nucleation mode peaking at 10 nm.*
- *No extreme percentages at the 10^{12} p/km range*
- *The percentage seems to increase with lower emission levels. However, this could be due to the lower concentrations measured with the 3025A (which uses internal averaging)*

JRC investigation

- *Low temperatures (-7°C) increase these percentage*
- *Regeneration showed similar percentages*
- *Size distributions during regeneration showed no distinct solid nucleation mode particles.*
- *One case with high percentage was due to re-nucleation in the VPR*

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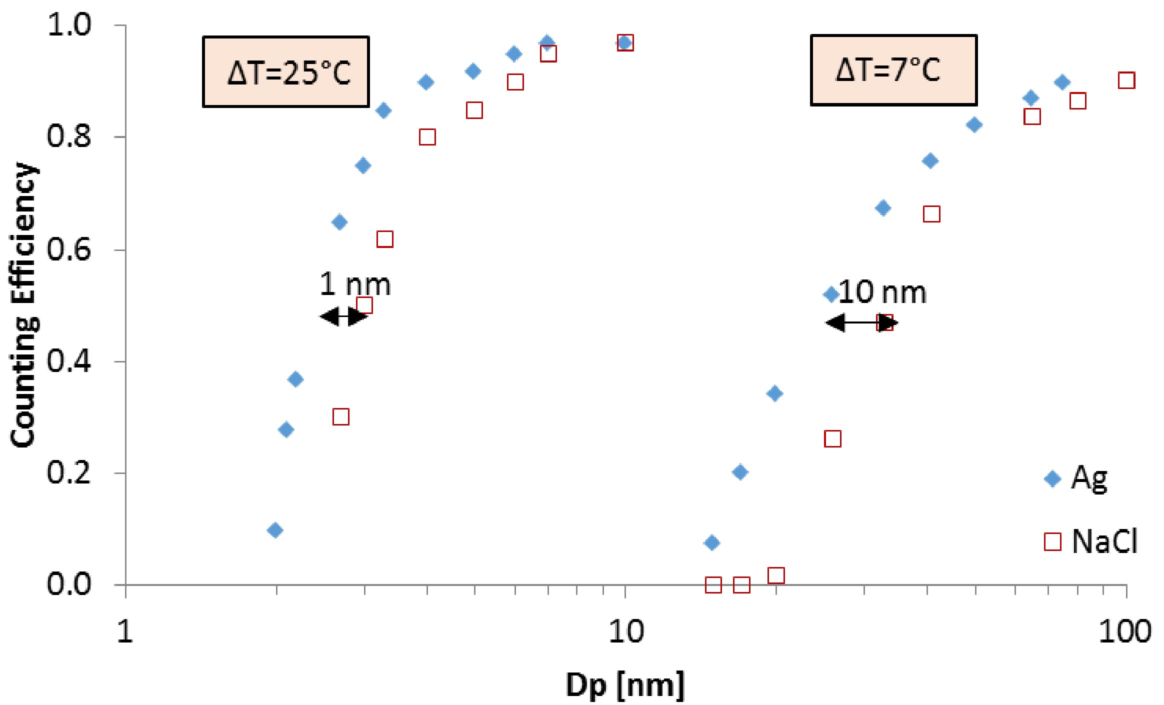
Feasibility of sub23: PNCs

- *Lowering the cut-off of PNCs is advantageous: smaller material dependence*



Feasibility of sub23: PNCs

- *Down to 10 nm possible with existing PNCs (no extra investment costs)*
- *Below 10 nm the calibration material has to be re-investigated, because it's not so easy to produce small particles at high enough concentrations.*
- *Below 10 nm, electrometers might be necessary since full flow reference PNCs with even lower cut-off size might not exist.*

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Outlook

- *Feasibility of sub 23 nm measurement for VPRs*
  - Penetration
  - Formation of solids
  - Volatile Removal efficiency

    -Evaporation tube (ET)

    Evaporation in the VPR

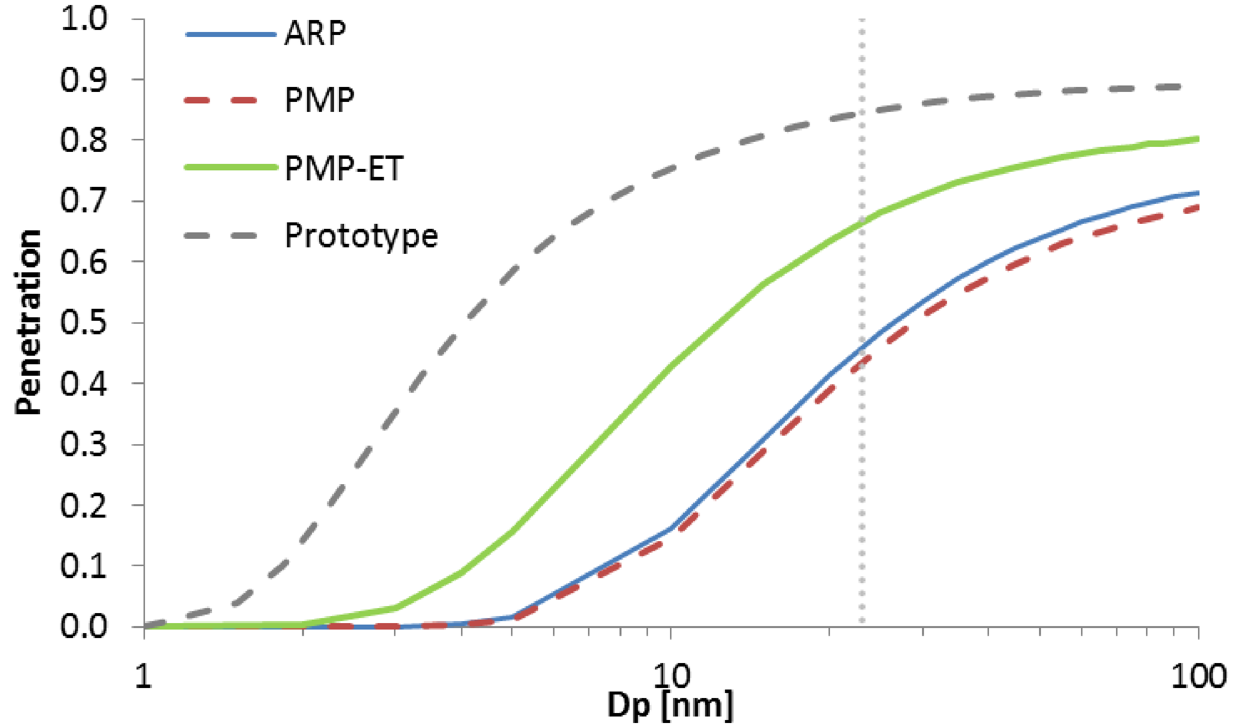
    Re-nucleation after the VPR

    -Thermodenuder

    -Catalytic stripper (CS)

VPR Penetrations

- *Losses increase significantly <23 nm*
- *10-40% penetration at 10 nm*

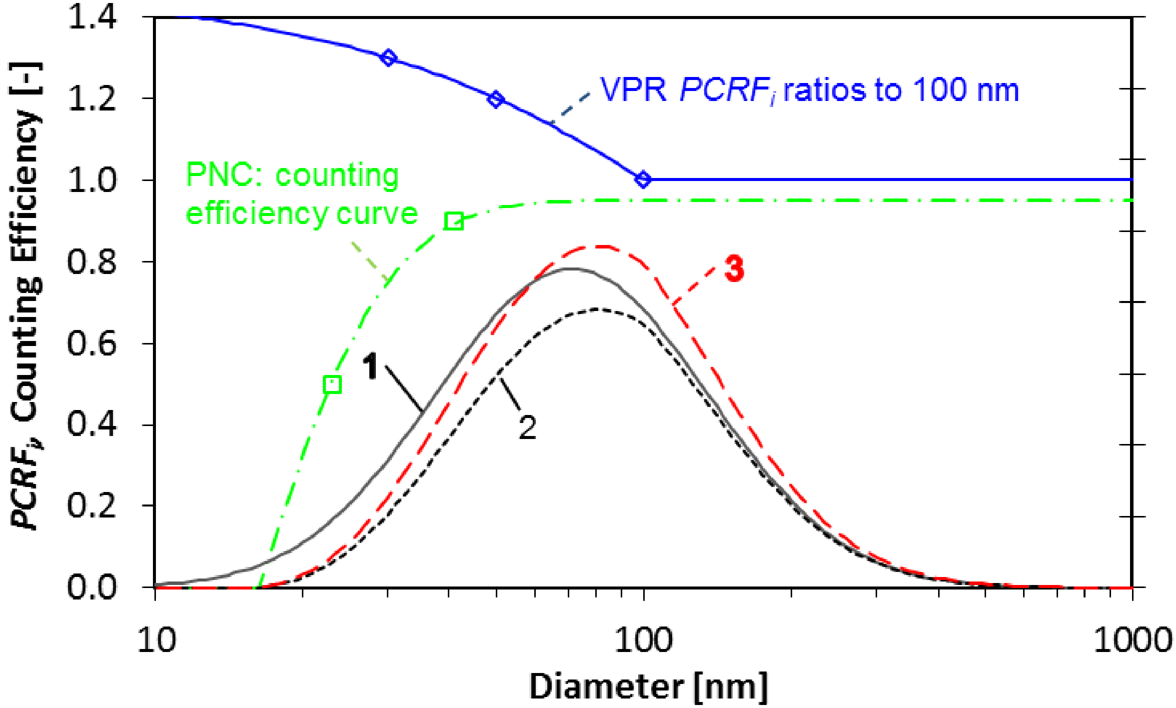


VPR penetration

- *Losses of VPRs: They increase significantly and down to approximately 10 nm is feasible only as indication of existence of particles (the accurate quantification is extremely difficult).*
- *Even in that case the PCRF determination should remain based on monodisperse particles of 30, 50 and 100 nm.*
- *Generation of <30 nm solid particles for the VPR calibration: It is much more difficult but not impossible even with one generator.*

Effect of VPR on PN (example)

- *(1) Inlet size distribution*
- *(3) Final measured, corrected for PCRF and slope*



PCRF average determination

	Case	PMP	ARP	PMP-4
PNC	$CE_{50\%}$	23 nm	10 nm	0.38
	$CE_{90\%1}$	41 nm	15 nm	0.90
	slope	1.00	1.00	1.10
VPR	$PCRF_{15}$	-	-	2.21
	$PCRF_{30}$	1.30	1.30	1.30
	$PCRF_{50}$	1.12	1.12	1.12
CMD	σ	Final PN concentration compared to inlet concentration		
10 nm	1.3	0%	18%	30%
20 nm	1.4	29%	64%	105%
30 nm	1.6	61%	83%	135%
40 nm	1.7	78%	92%	151%
50 nm	1.8	88%	98%	160%
70 nm	1.9	100%	105%	172%
90 nm	2.0	105%	109%	178%
10 nm (50%) + 50 nm (50%)	1.3 + 1.8	44%	58%	95%

Formation of particles in the VPR

- *Indications when sulfur exists*
- *Formed solid particles were <10 nm*
- *Difficult to justify*
- *Example is reaction of sucrose with strong sulfuric acid*
- *More research is needed*

Volatile Removal efficiency (ET)

- *Evaporation of compounds in the ET*
  - Theoretical calculations show that the evaporation is a fast process (ms) and >200°C most volatiles will evaporate.
  - A few experimental studies confirmed this
  - Tetracontane tests with big sizes (>70 nm) show reduced removal efficiency

Volatile Removal efficiency (ET)

- *Re-nucleation after the ET*
  - Hydrocarbons
  - Tetracontane will re-nucleate at >10^7 p/cm^3 or 3 mg/m^3
  - Diesels without DOCs can emit up to 70 mg/m^3, typically 5 mg/m^3. With oxidation catalysts the values significantly decrease
  - Considering the dilution in the CVS and the primary diluter, re-nucleation is unlikely for modern technol.
  - Mopeds can reach 700 mg/m^3. Re-nucleation is possible

Volatile Removal efficiency (ET)

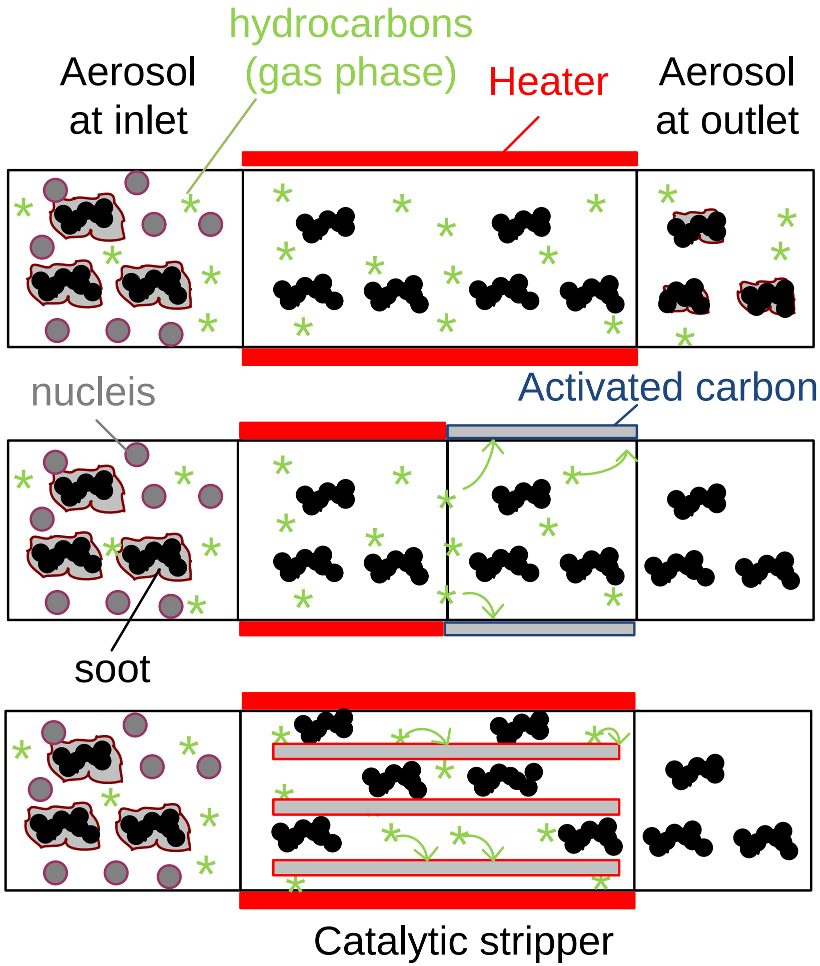
- *Re-nucleation after the ET*
  - Sulfuric acid
  - (Theoretically) will re-nucleate at 0.7-3.5 μg/m^3
  - Diesels without DOCs can emit up to 200 μg/m^3, with DOC up to 10 mg/m^3.
  - Fuel <10 ppm and lube <10000 ppm and 100% SO_2 to SO_3 conversion translates to <300 μg/m^3.
  - Even when considering the dilution in the CVS and the primary diluter, re-nucleation is likely.
  - Experimentally it has been shown that in some cases sub23nm were re-nucleated particles

Volatile Removal efficiency (ET)

- *Growth after the ET*
  - The re-nucleated nucleis are 1-2 nm
  - Organics are necessary for the nucleis to grow
  - Theoretical calculations and experimental results show that they can grow to 6 nm (10^{11} p/cm^3 organics) or 20 nm (10^{14} p/cm^3 hexadecane, <5 ppm C3)
  - HC emissions at the outlet of the VPR can be as high as 100 ppm (vehicles) or 3000 (mopeds) at cold starts, thus particles can grow

Volatile Removal Efficiency (TD)

- ***<u>Thermodenuder</u>***
- *Heater and adsorber*
- *Adsorption efficiency decreases with time*
- *Unknown dependency on compounds*
- *High losses*



Volatile Removal Efficiency (CS)

- ***Catalytic Stripper (CS)***
- *Removes volatiles by oxidation*
  - Even >35 times highest HC concentration (eg moped)
  - Better removal efficiency of tetracontane
- *Traps sulfur*
  - Up to 10 mg/m^3
- *Might oxidize SO_2 to SO_3*
- *Particles might be formed if saturated*
- *Higher particle losses*

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Summary

- *Primary particles*
  - Typically 25 nm, but smaller can exist
- *Solid <23 nm (review)*
  - A lot of studies have measure solid sub23nm particles
- *Experimental investigation at JRC*
  - Existence of sub23nm particles was confirmed in percentages of <60% of >23nm (GDIs at the high range)

Summary

- *Feasibility of sub 23 nm measurement for PNCs*
  - It is advantageous to decrease the cut-off size
  - Down to ~10 nm no major modifications for existing equipment
- *Feasibility of sub 23 nm measurement for VPRs*
  - Penetrations decrease at small sizes. Acceptable down to 10 nm
  - Evaporation of volatiles typically not an issue
  - Pyrolysis might be an issue with sulfur (<10nm)
  - Re-nucleation and growth is probable

Summary

- *With existing equipment reducing the cut-off size is not recommended*
- *Decreasing the size to ~10 nm is possible but the addition of a CS is recommended. However some issues need to be resolved:*
  - Saturation with sulfur
  - Formation of particles
  - SO_2 to SO_3 conversion
- *Below 10 nm is extremely difficult to measure for legislation purposes.*

Next steps

- *Is it necessary to measure lower sizes?*
  - Investigation will go on
- *Open issues to be investigated*
  - Regeneration
  - Pyrolysis
  - CS performance
  - Calibration procedures (VPR and PNC) to be updated

Next steps

- *Measurements in parallel with PMP systems with ET and CS devices with both 23nm and ~10 nm PNCs.*
- *Tests without CS should be conducted with as high PCRF as possible (at least 100x10)*
- *When high sub23nm concentrations are measured the tests should be repeated with 10x higher PCRF*

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Thank you for your attention!