Issues associated with solid particle measurement

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ARB Chairman's air pollution seminar series
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Outline

- Challenges quantifying diesel emissions
- Issues with particle number measurement
- Background
- Test results
- Conclusion

Challenges quantifying ultra low diesel emissions

- PM (particle mass) of <50% of 2007 standard drives the total uncertainty >30% in the gravimetric method:
  - Swanson et al. SAE 2009-01-1516.
  - Burtscher et al. JAS, 2005, 36, 896.
  - And several papers by other researchers.
- Nuclei mode particles are difficult to have a repeatable conditions.
  - Solid particle number (PN) method (a.k.a. PMP=Particle Measurement Programme)
  - Integrated particle size distribution (IPSD)
  - Chemically reconstructed mass method
  - Measurement of precursors of nuclei mode particles (organic acids, sulfuric acid)

Outline

- Challenges quantifying diesel emissions
- Issues with particle number (PN) measurement
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Issues with number measurement

- Current PMP method regulates “solid” particles larger than 23 nm
  - For engines equipped with particle filters regulating to 23 nm effectively regulates all sizes.
  - For engines without filters (advanced fuels, combustion modes, gasoline) there may be large concentrations of solid particles below 23 nm that are not counted by current method.
  - The next generation of high efficiency direct injection gasoline engines are challenged by the current standard even with the 23 nm limit.

Issues with number measurement

- Extending solid PN (particle number) measurements to 10 nm.
  - Significant semi-volatile particles downstream of PMP VPR (Volatile Particle Remover) often observed.
  - No significant semi-volatile formation downstream of catalytic stripper (CS) in this size range.
- Extending solid PN (particle number) measurements to below 10 nm – problematic
  - Particles as small as sub 3 nm formed in large concentrations downstream of PMP VPR (Volatile Particle Remover).
  - Some evidence of solid particle formation by VPR.
  - Sub 10 nm particle formation observed downstream of catalytic stripper (CS) under some conditions.
  - Removal of sulfate or other low vapor pressure species is critical.

Recent papers raised issues about solid particle measurements, especially when applied to particles smaller than 23nm.

- Work done at University of California, Riverside, CE-CERT
  - Johnson et al. (2009). Evaluation of the European PMP Methodologies during On-Road and Chassis Dynamometer Testing for DPF Equipped Heavy Duty Diesel Vehicles, *Aerosol Science and Technology*, 43, 962–969, 2009.
  - Zheng et al. (2011). Investigation of solid particle number measurement: existence and nature of sub 23 nm particles under PMP methodology, *Journal of Aerosol Science*, 2011, 42, 883-897
  - Zheng et al. (2011). Nature of sub 23 nm particles in the solid particle number measurement: a real time data perspective, *Aerosol Science and Technology*, 2012, in review
- Work done at the University of Minnesota, CDR
  - Swanson and Kittelson (2010). Evaluation of thermal denuder and catalytic stripper methods for solid particle measurements, *Journal of Aerosol Science*, 41, 12, 1113-1122.
- Work done at California Air Resources Board
  - Herner et al. (2007). Investigation of ultrafine particle number measurements from a clean diesel truck using the European PMP protocol, SAE 2007-01-1114

Outline

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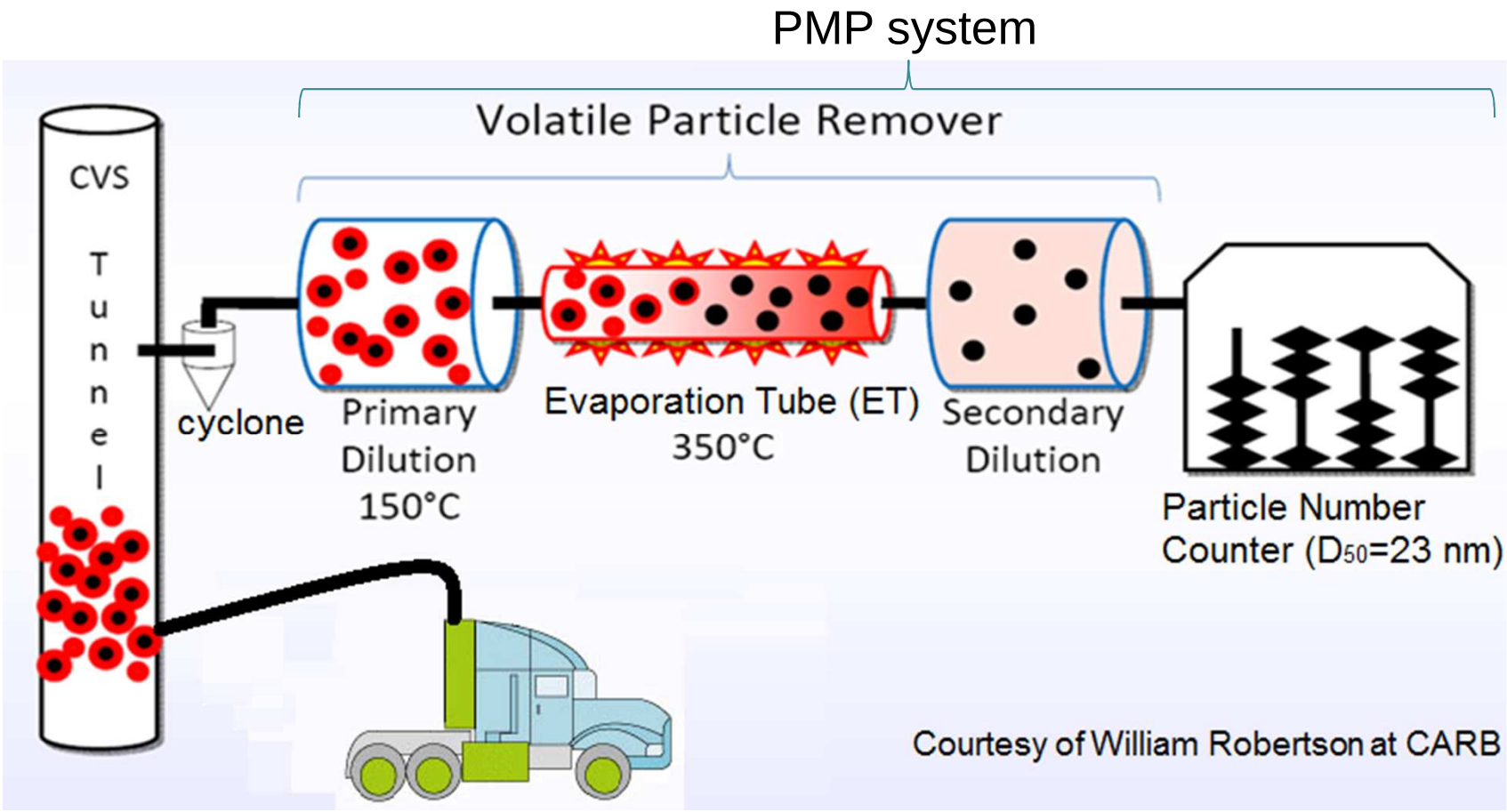
- Issues with particle number measurement
- Background of Particle Measurement Programme (PMP)
- Test results
- Conclusion

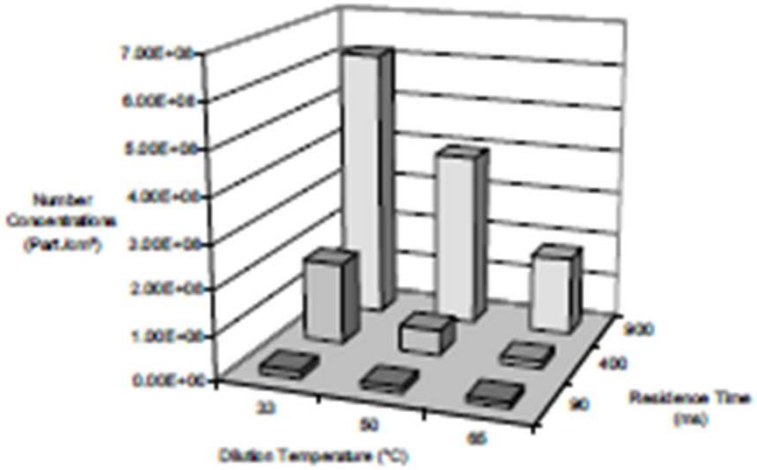
Particle measurement programme

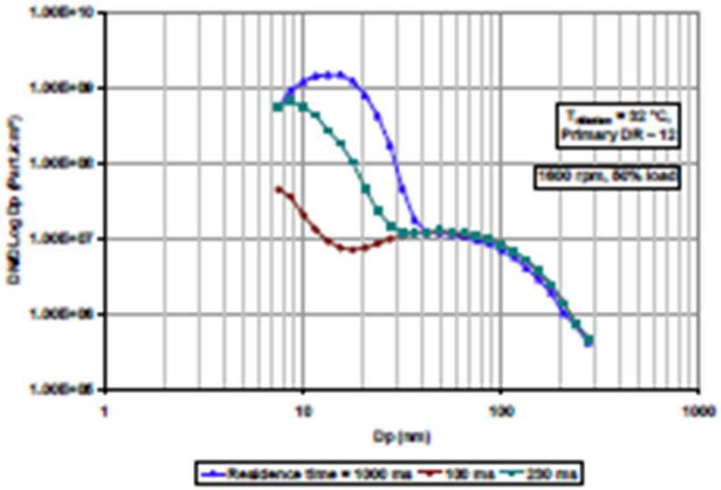


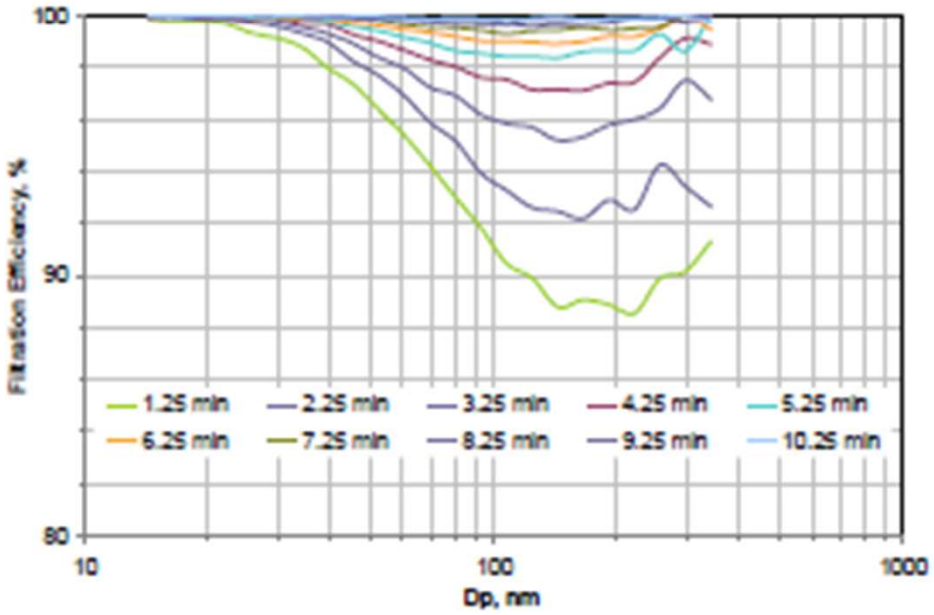
Red: Semivolatile particles

Black: Solid (mostly soot) particles

Why solid, why only larger than 23nm?







- The concentration of volatile nucleation mode particles is very dependent on sampling conditions
- Most of these particles are smaller than 23 nm
- If the engine is fitted with a particle filter particles below 50 nm or so are very effectively removed
- Thus regulating solid particles above 23 nm is really regulating soot particles is effectively regulating all particles for a trap equipped
- Without a trap the story is different

Courtesy of Dr. Kittelson

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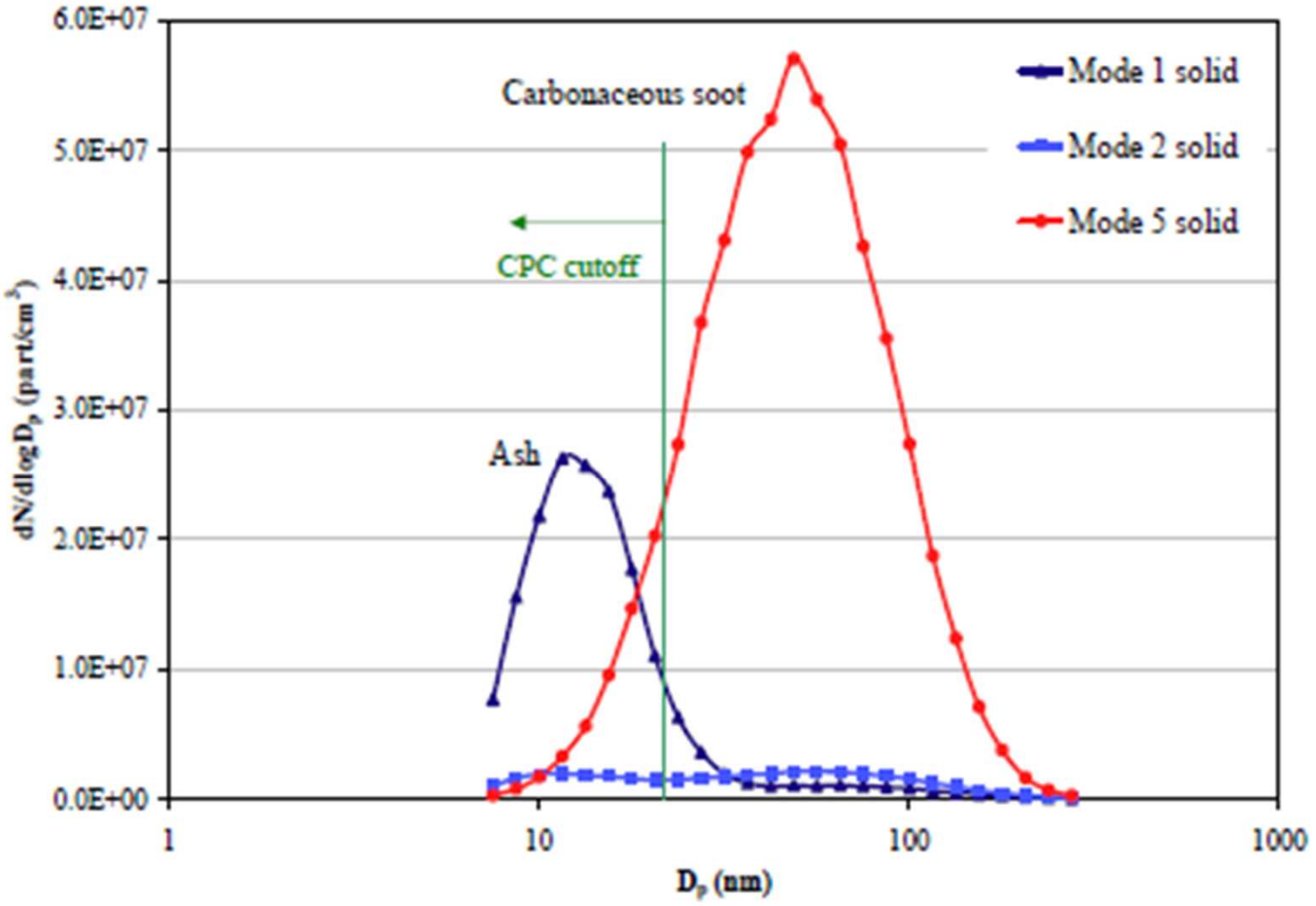
Engine out, light-load, low soot conditions: Most of the number emissions are solid with D_p<23nm



Cummins 2004 ISM engine, BP 50 fuel, AVL modes

Courtesy of Dr. Kittelson

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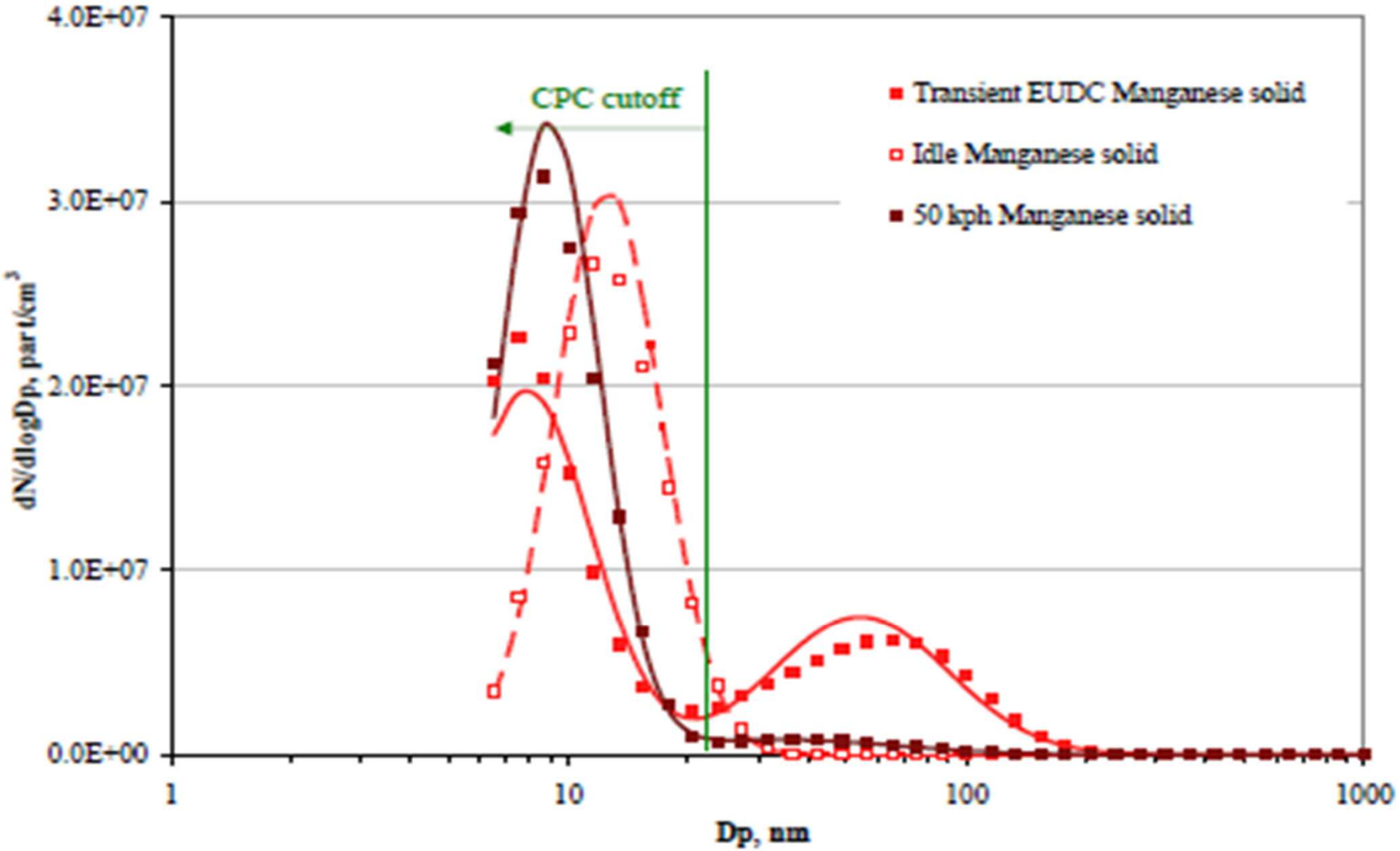
Spark ignition engines with metal additives show solid particles below 23nm.



Gidney, Jeremy T., Martyn V. Twigg, and David B. Kittelson, 2010. Effect of Organometallic Fuel Additives on Nanoparticle Emissions from a Gasoline Passenger Car, Environmental Science and Technology, v 44, n 7, p 2562-2569.

A modern gasoline direct injection engine shows solid particles below 23nm

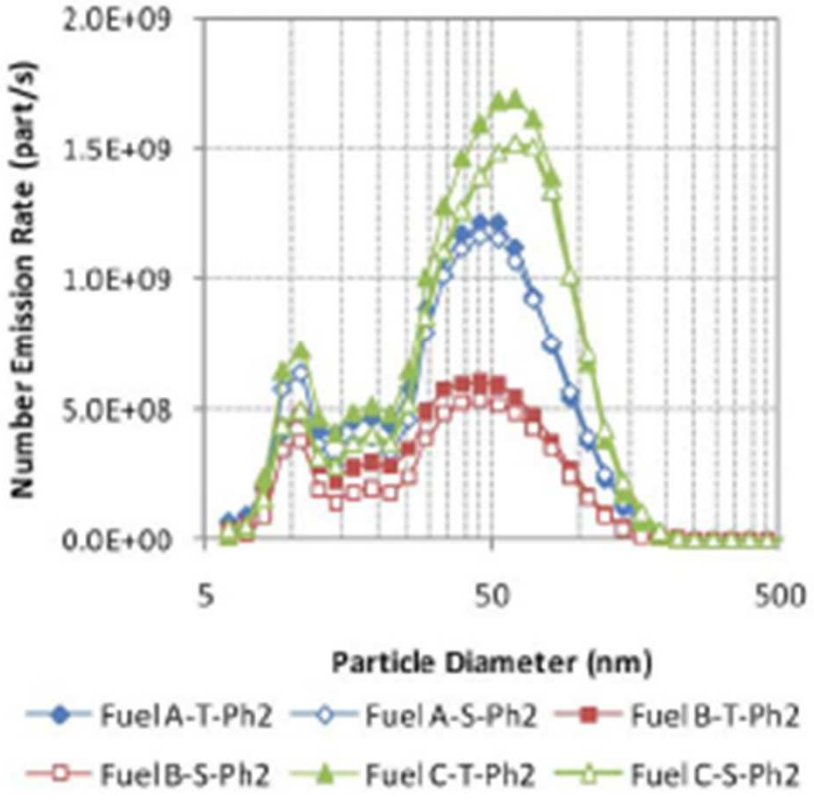


Figure 13. Phase 2 Total and Solid Particle Number-Weighted Size Distribution for Fuels A, B, and C

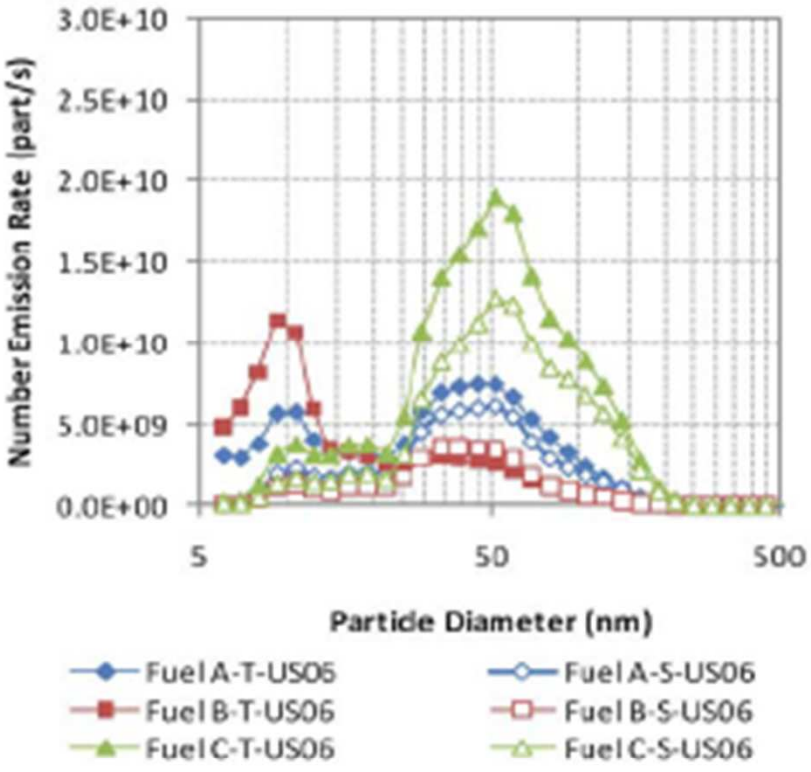
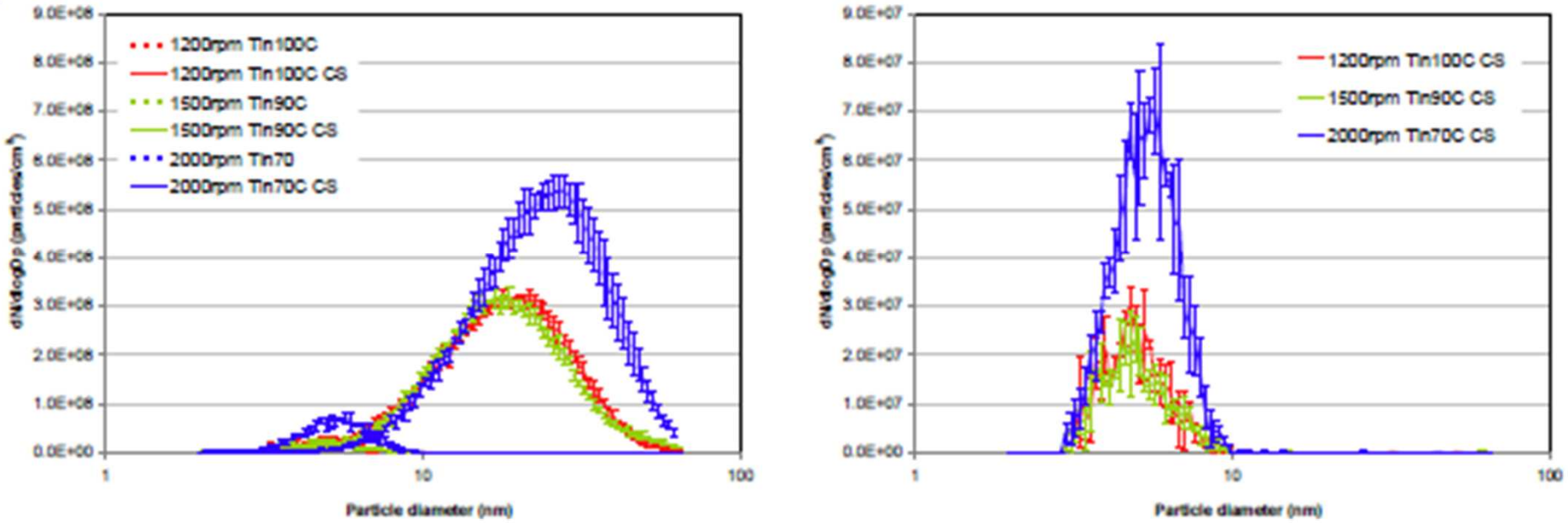


Figure 15. US06 Total and Solid Particle Number-Weighted Size Distribution for Fuels A, B, and C

From: Khalek, Imad A., Thomas Bougher, and Jeff J. Jetter, 2011. Particle Emissions from a 2009 Gasoline Direct Injection Engine Using Different Commercially Available Fuels, SAE paper number 2010-01-2117.

Gasoline engine in pure HCCI mode shows no solid particles above 10nm.



- Emissions depend upon speed, load, temperature – in-cylinder thermal processing
- Solid PN measured with catalytic stripper (CS) total PN without
- Right plot shows solid fraction on 10x expanded scale
- Most of the particles emitted are volatile but the solid ones are very small

No solid particles above 10nm

From: David Kittelson, 2011 Particles Emissions from a Soot Free Engine, 15th ETH-Conference on Combustion Generated Nanoparticles

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Outline

- Challenges
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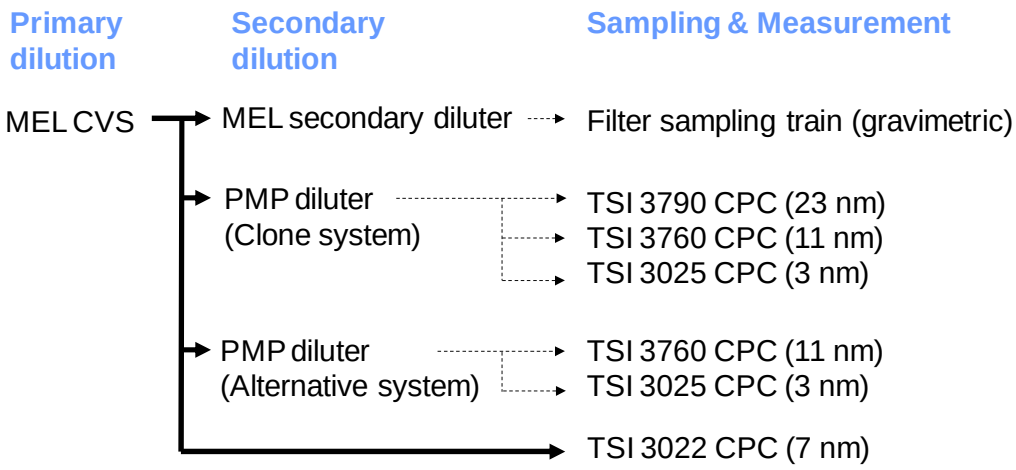
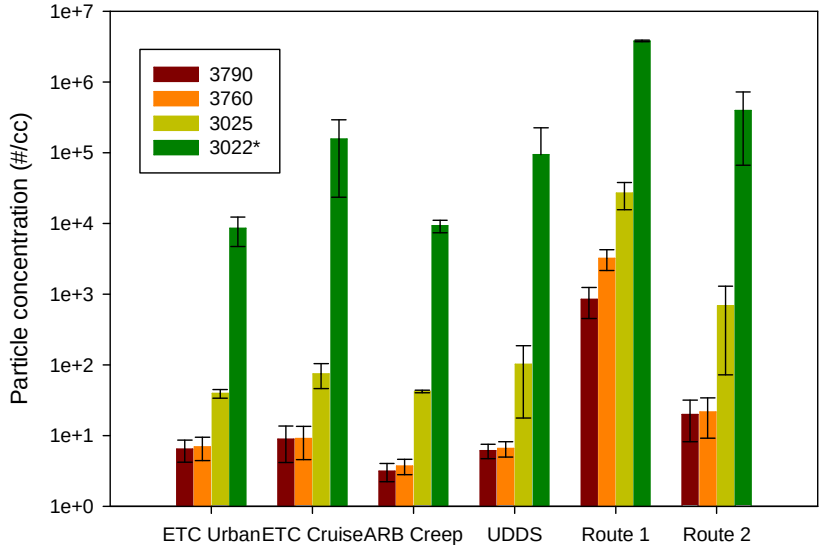
  - Using exhaust particles
  - Using lab-generated model particles
- Conclusion

Unexpectedly large “solid” particle concentrations during UCR’s previous PMP study

- A heavy-duty truck equipped with a CRT (continuously regenerating trap) was tested over different driving cycles on road.
  - It showed large concentration of “solid” particles below 23 nm at high load conditions.
  - These conditions favor sulfate particle formation.
  - Filtration efficiency for particles below 23nm should be very high.





Johnson et al. 2009, ASnT, 43, 962

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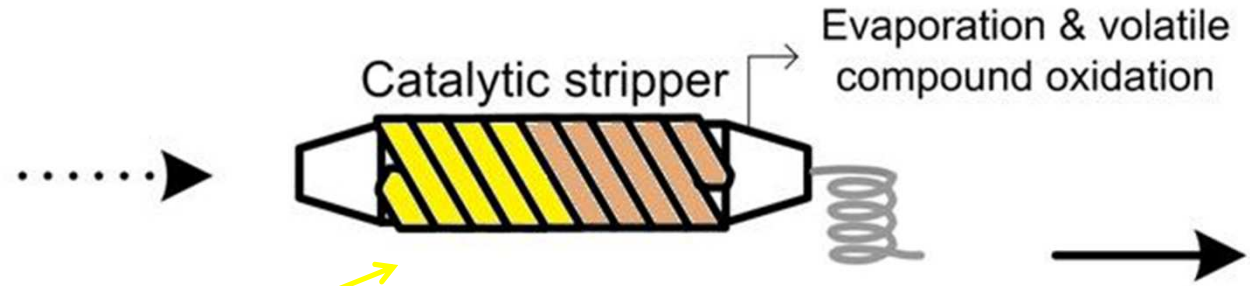
Objectives

- Investigation of the nature of sub 23nm particles downstream the PMP system.
- Evaluation and comparison of the PMP and CS systems.

Catalytic stripper (CS)



- Oxidation catalyst:
  - Wall temperature: 300℃
  - Length: 11 cm
  - Diameter: 3.2 cm
  - 75 g/ft^3 of Pt
    - Particle penetration
      - 5% at 3 nm
      - 75% at 100 nm
- Sulfur-trap (S-Trap):
  - Wall temperature: 300℃
  - Length: 11 cm
  - Diameter: 3.2 cm
  - $BaO + SO_3 \rightarrow BaSO_4$

Kittelson D.B.; Stenitzer, M. *A New Catalytic Stripper for Removal of Volatile Particles*. 7th ETH Conference on Combustion Generated Particles, Zurich, 18–20th August, 2003

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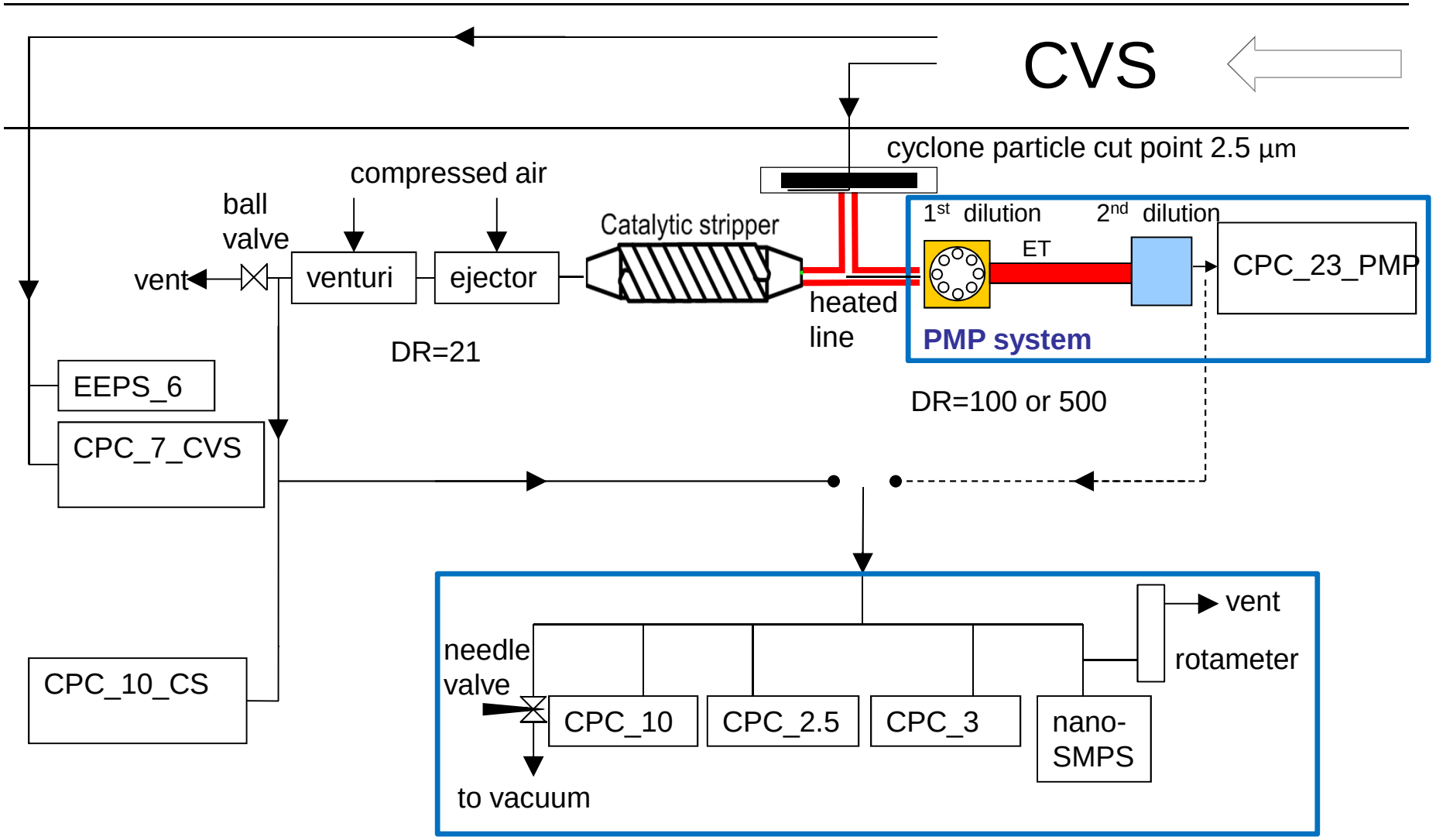
Test conditions

- Comparisons of fully compliant PMP system and catalytic stripper system
  - Use a variety of counting instruments with different lower size cutoffs
    - TSI 3022 – 7 nm
    - TSI EEPS – 6 nm
    - TSI 3790 – 23 nm
    - TSI 3772 – 10 nm
    - TSI 3025A – 3 nm
    - TSI 3776 – 2.5 nm

    Notation CPC_cutoff diameter_location
    CPC_7 or CPC_7_PMP
  - Tests with exhaust aerosols from heavy-duty vehicle operating on chassis dynamometer
    - Freightliner class 8 truck with 14.6 liter, 2000 Caterpillar C-15 engine, equipped with Johnson Matthey Continuously Regenerating Trap (CRT™)
    - Two steady state cruise conditions, constant speed 56 mph at 26% and 74% of full load
  - Tests with laboratory challenge aerosols

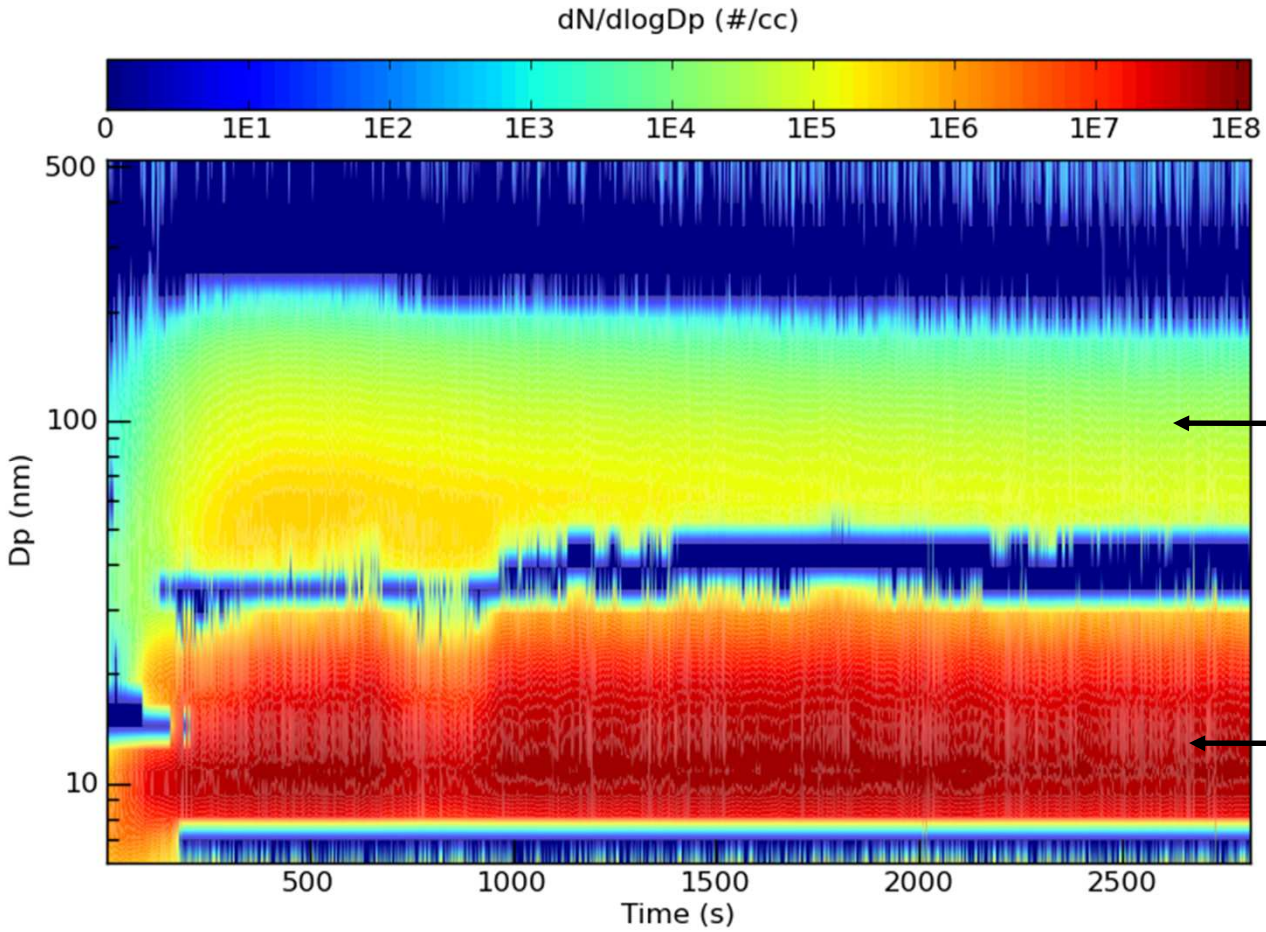
Experimental set up for chassis test



Alternate between the PMP and CS systems

Steady state 74% load strongly bimodal

Measurement by Engine Exhaust Particle Sizer (EEPS) at the CVS.



Accumulation mode

Nucleation mode

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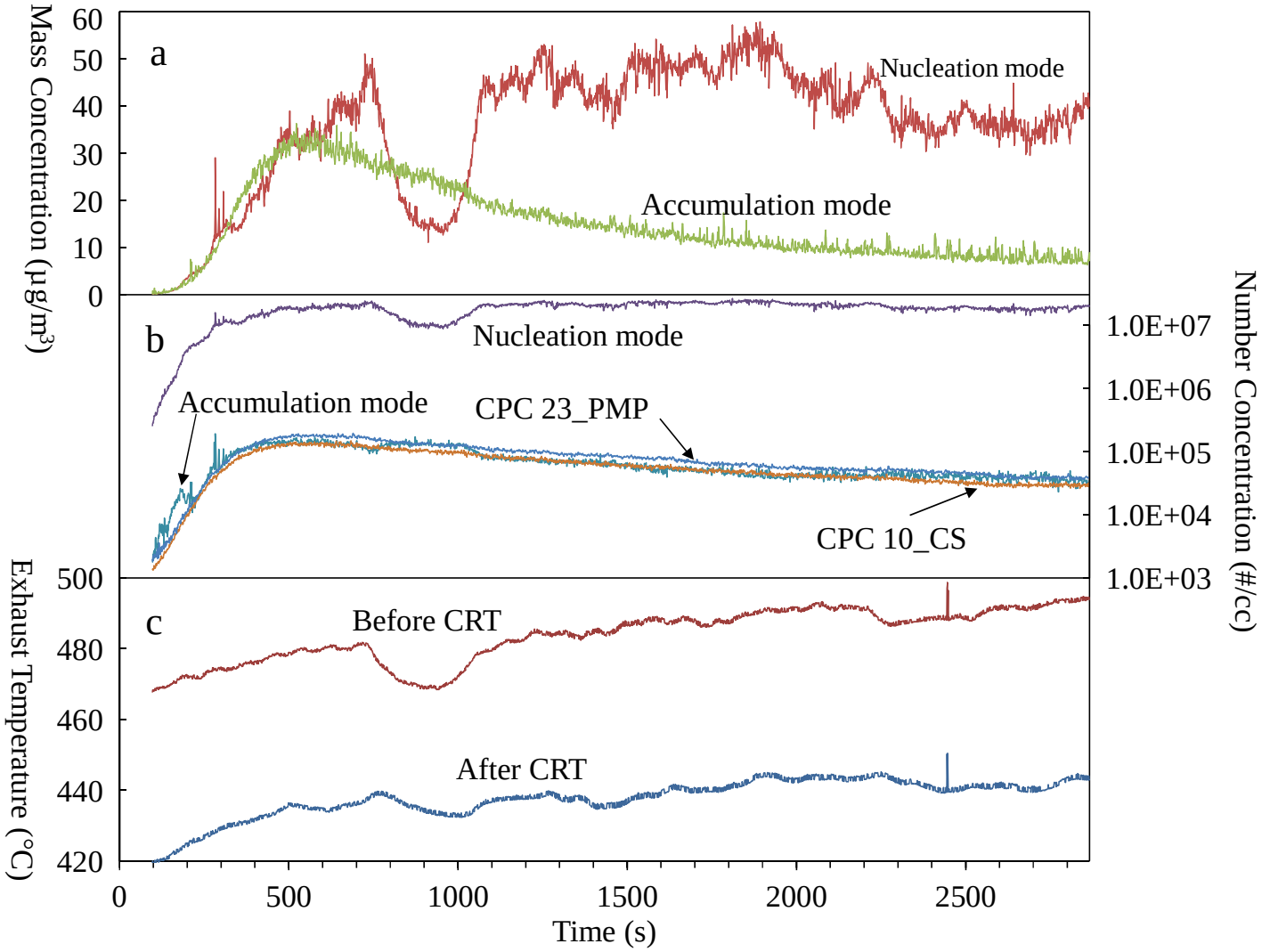
At 74% load PMP compliant system closely tracks the accumulation mode



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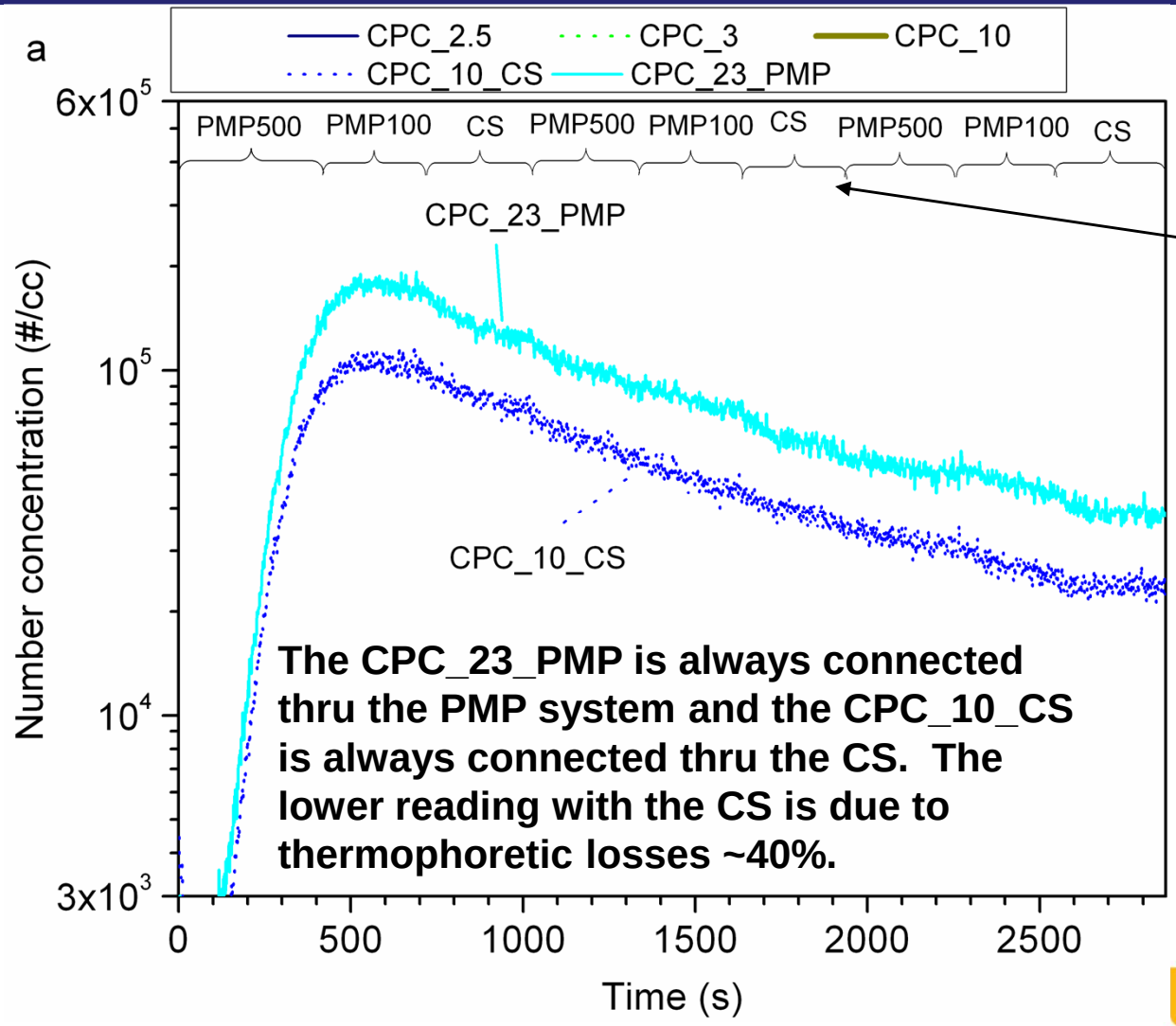
74% load, CPC_23_PMP and CPC_10_CS

Changing PMP dilution ratio does not change results - it should not.



PMP500-PMP system, 500 dilution ratio

PMP100-PMP system, 100 dilution ratio

CS-Catalytic Stripper

CVS-sampling directly from main dilution tunnel, no removal of volatile particles

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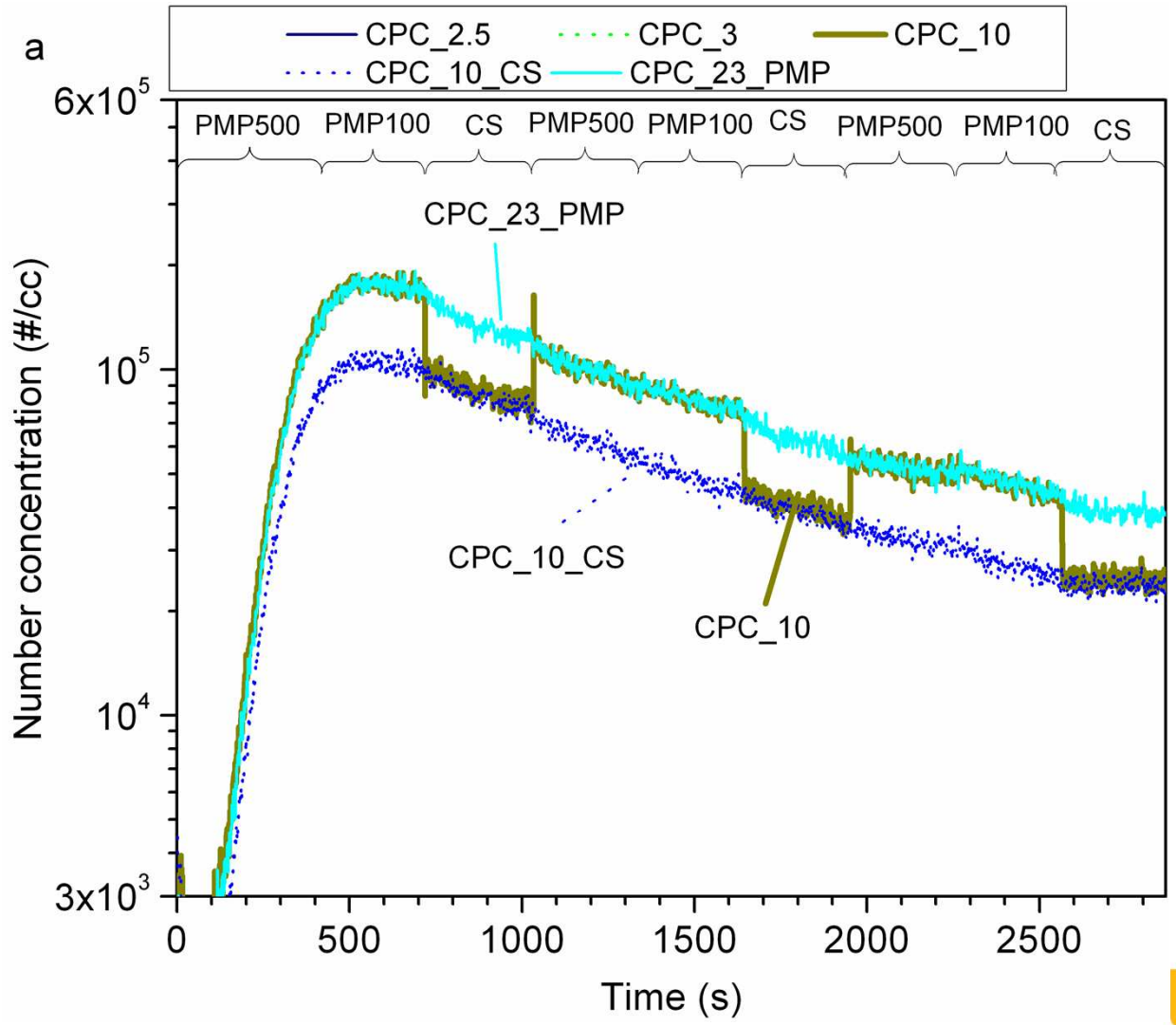
74% load
CPC_10 switched between PMP and CS system



No particles between 10 and 23nm under APC

Switching from 100 to 500 overall dilution ratio has no impact on the PMP results-the desired result

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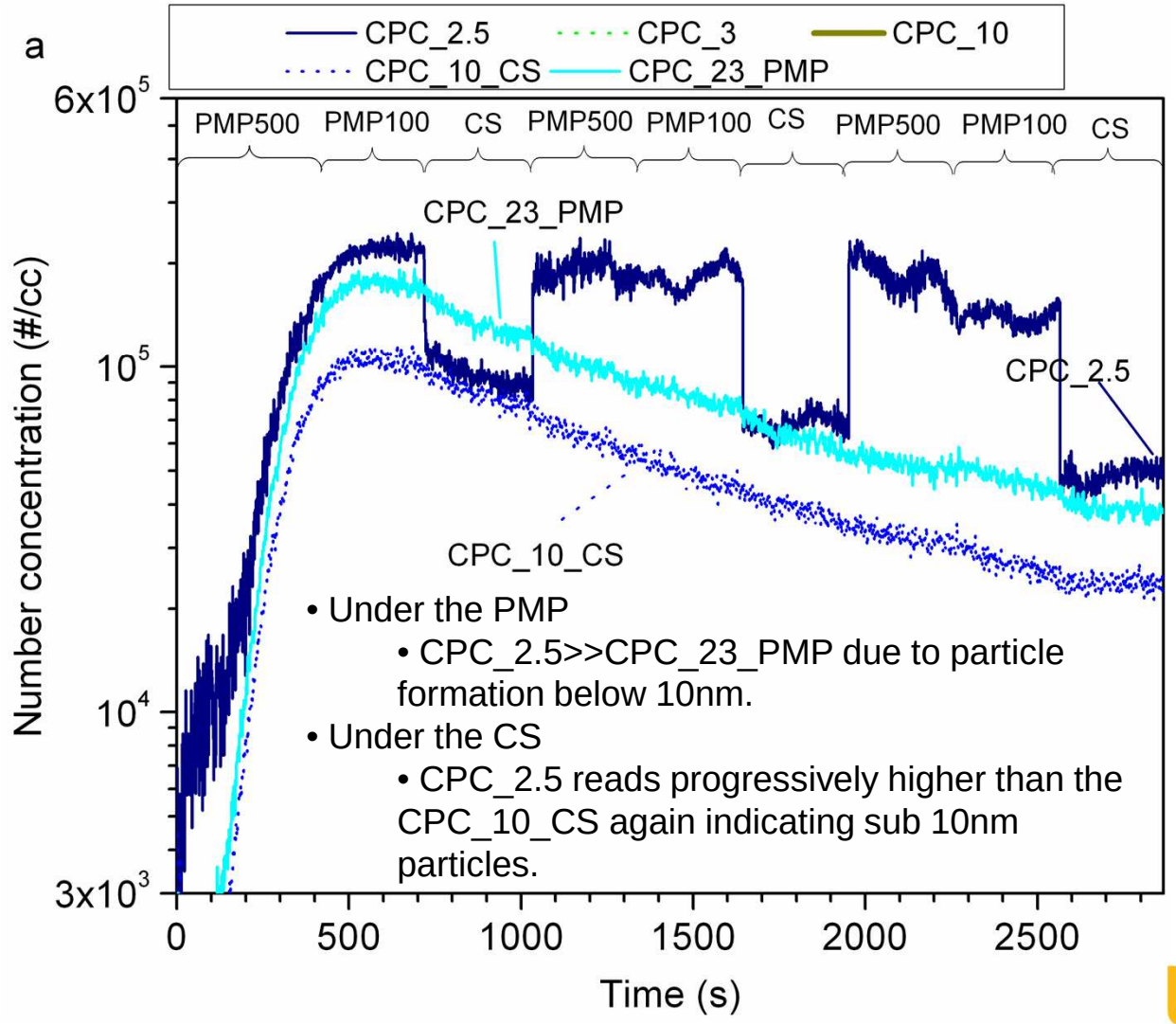
74% load
CPC_2.5 switched between PMP and CS system



- Under the PMP
  - CPC_2.5>>CPC_23_PMP due to particle formation below 10nm.
- Under the CS
  - CPC_2.5 reads progressively higher than the CPC_10_CS again indicating sub 10nm particles.

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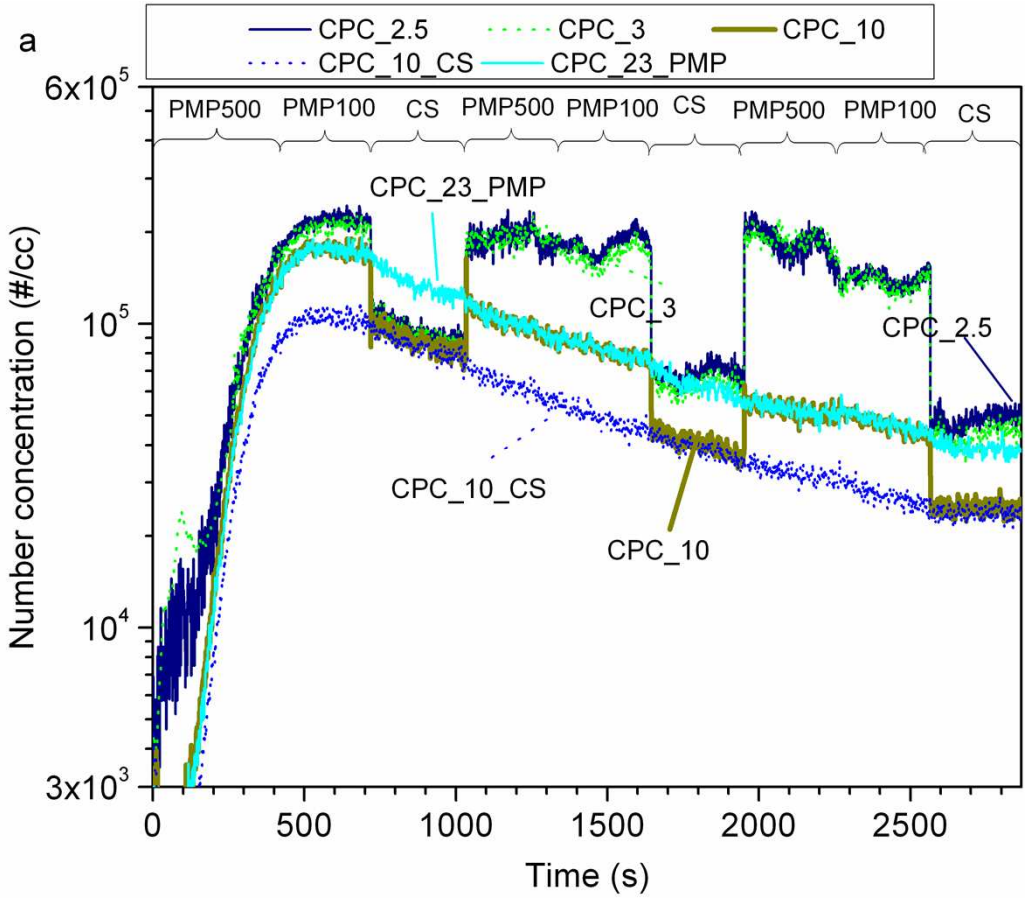
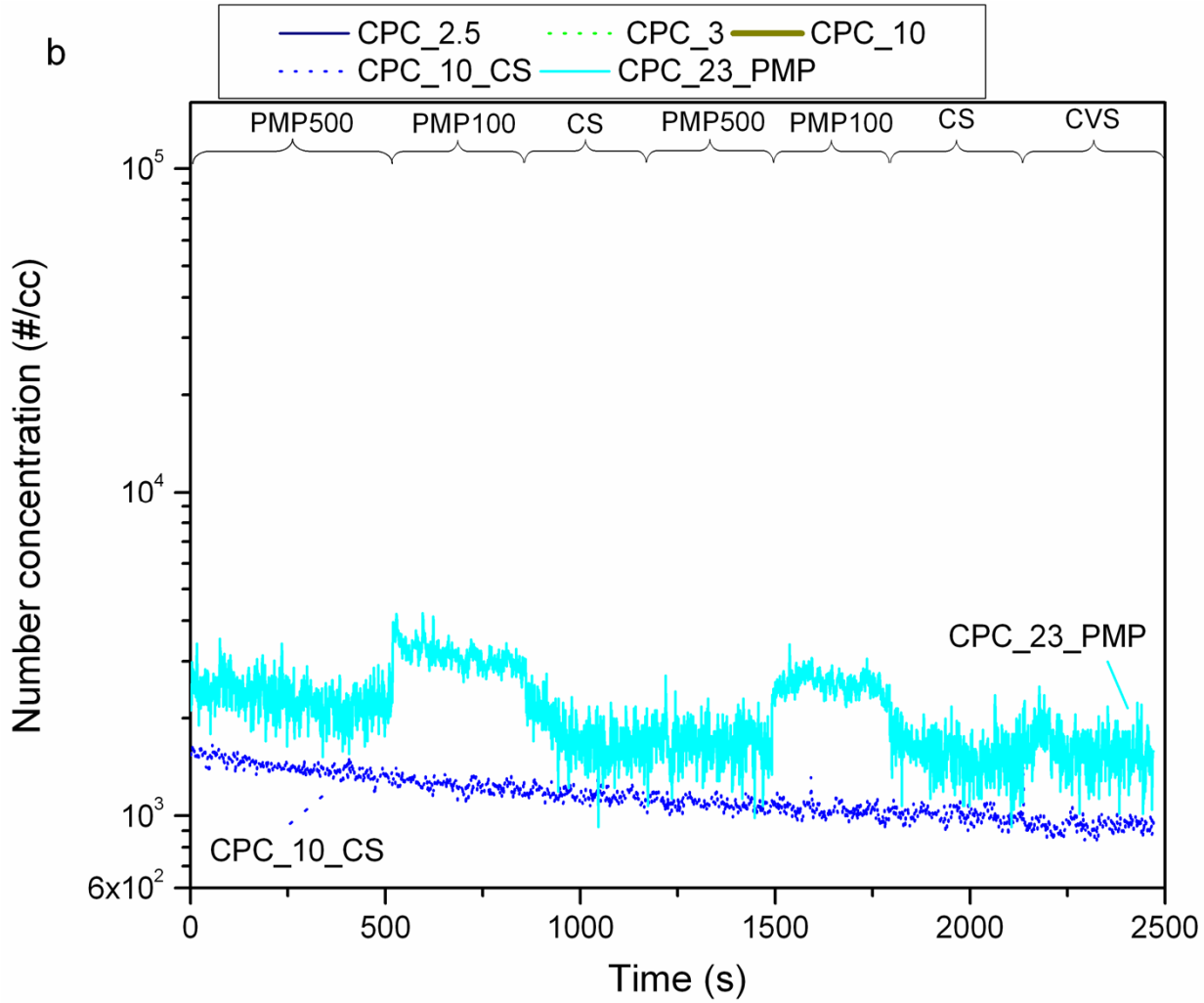
Summary of the results at 74% load cruise



- Downstream of PMP system
  - − CPC_23_PMP and CPC_ 10 agree-no particles between 10 and 23nm
  - − CPC_3 and CPC_2.5 agree and read progressively higher than CPC_10 and CPC_23_PMP as time goes on - particles forming between 3 and 10nm
  - − Same trend at 100 and 500 dilution ratio
- Downstream of CS
  - −In first time window all instruments agree-no particle below 23nm
  - −In second and third time windows CPC_2.5 and CPC_3 read higher than CPC_10_CS-particle formation between 3 and 10nm

26% load, CPC_23_PMP

Changing PMP dilution ratio changes results - it should not.



PMP500-PMP system, 500 dilution ratio

PMP100-PMP system, 100 dilution ratio

CS-Catalytic Stripper

CVS-sampling directly from main dilution tunnel, no removal of volatile particles

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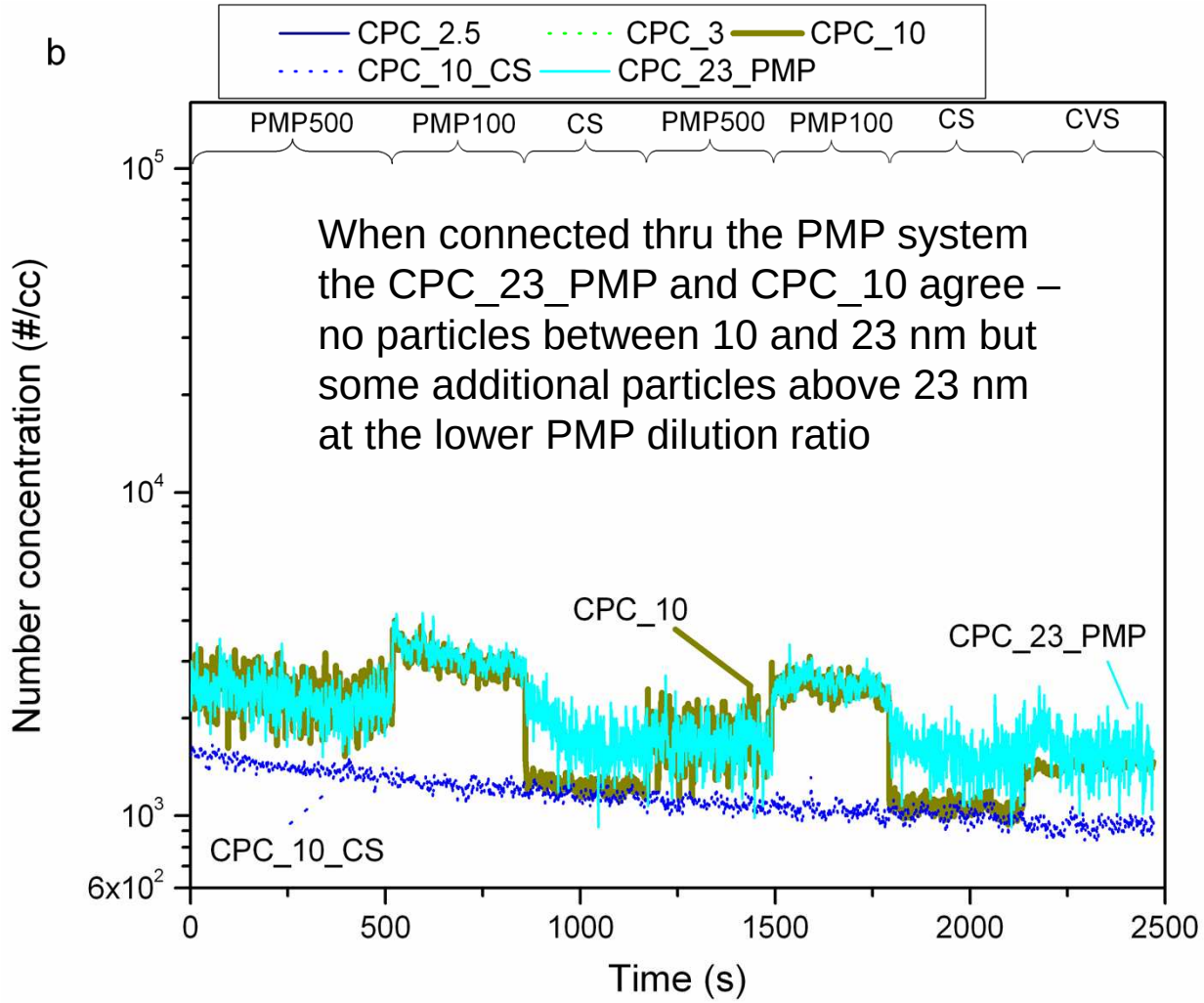
26% load
CPC_10 switched between PMP and CS



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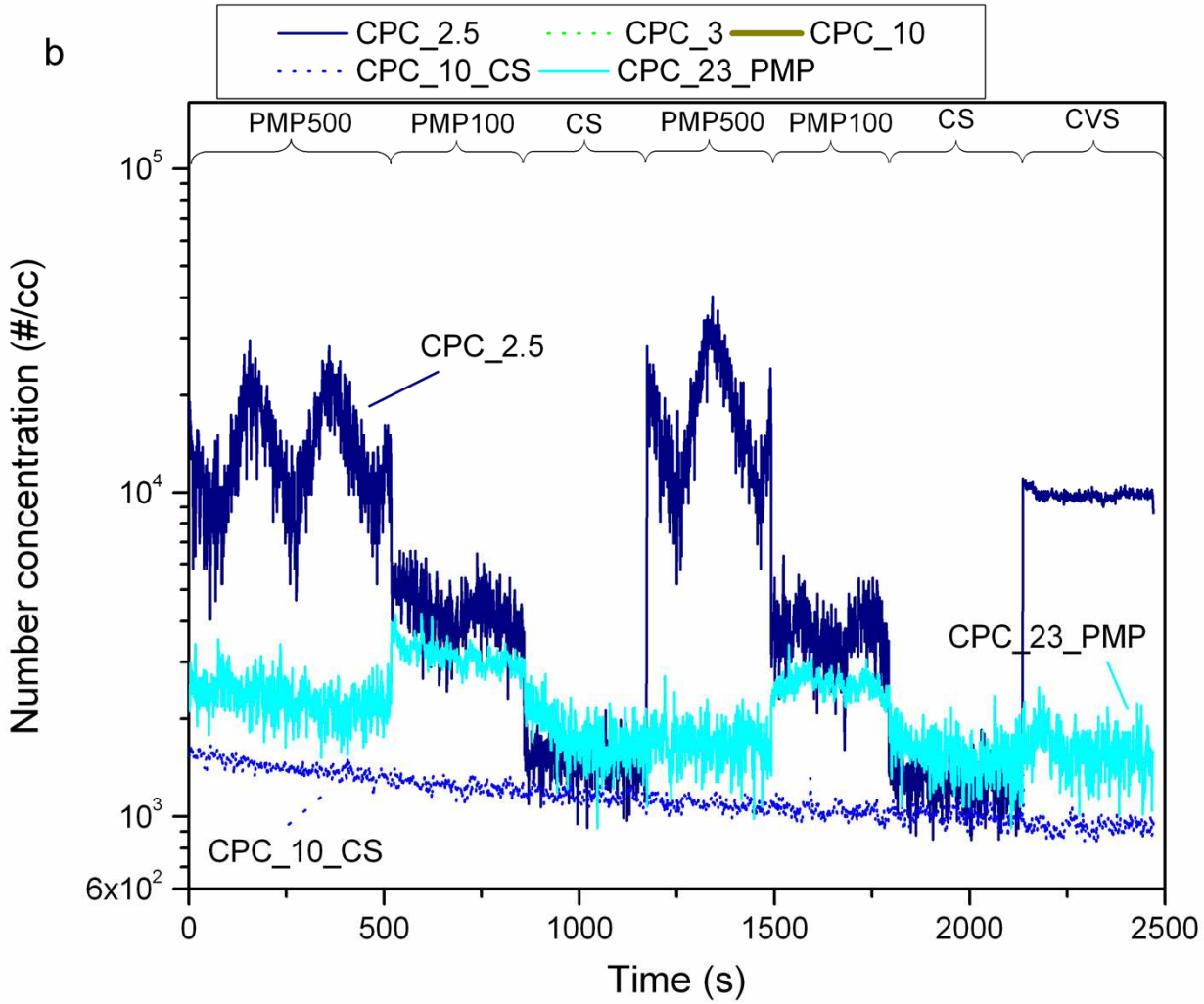
26% load
CPC_2.5 switched between PMP and CS



When connected thru the PMP system the CPC_2.5 shows higher concentration than the CPC_23_PMP indicating particles below 10nm, especially at higher dilution ratio, little evidence of this with CS.

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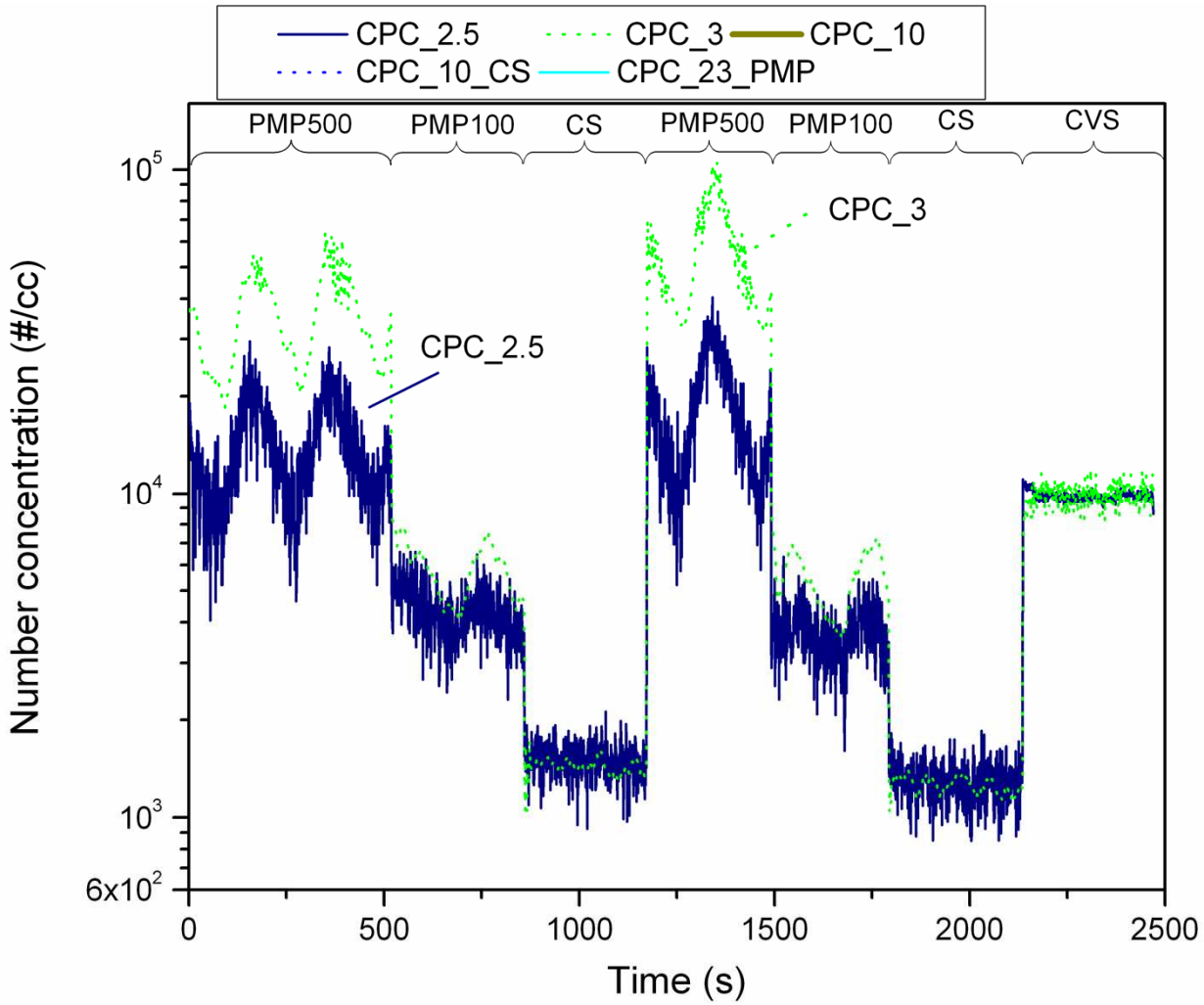
26% load
CPC_2.5 and CPC_3



The CPC_2.5 and CPC_3 disagree at the higher dilution ratio downstream of the PMP system but agree for 50 nm calibration aerosols suggesting that the particles are near the lower detection sizes of the instruments, < 3 nm.

When connected directly to CVS, no removal of volatiles, CPCs agree and show lower concentration than when volatiles are removed at 500 DR

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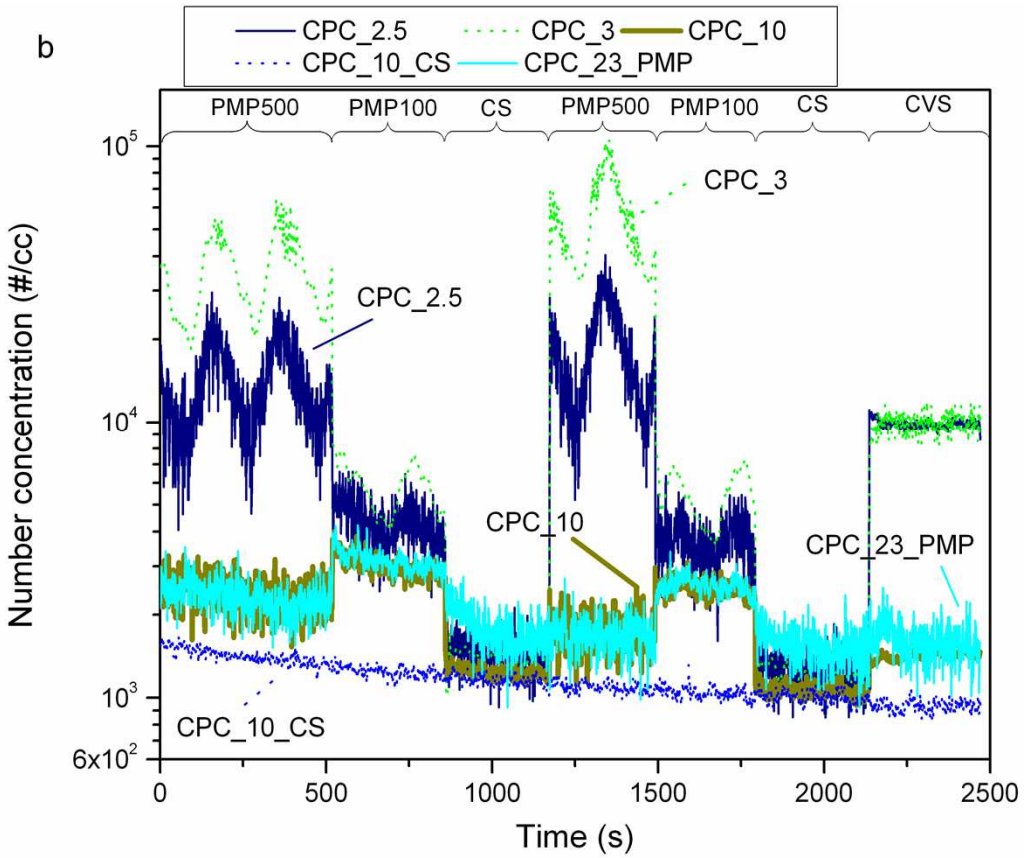
Summary of results at 26% load cruise



- Much lower concentrations than at 74%
  - Downstream of PMP system
    - In first time window, DR = 500
      - CPC_23_PMP and CPC_10 agree – no particles between 10 and 23 nm
      - CPC_2.5 and CPC_3 read much higher and disagree – many particles below lower cutoff size of these instruments, 2.5 to 3 nm
    - In second time window, DR = 100
      - CPC_23_PMP and CPC_10 read higher but agree – no particles between 10 and 23 nm but formation above 23 nm
      - CPC_2.5 and CPC_3 agree but read only slightly higher than CPC_23_PMP and CPC_10 – nearly all particles have grown to above 23 nm
  - Downstream of CS
    - Consistently lower reading and agreement between instruments

- In last time window instruments bypass volatile particle removal systems and are directly connect to CVS – measure total solid and volatile particles – fewer particles than DR = 500 PMP, clear evidence of particle formation by PMP system.

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  - Using lab-generated model particles
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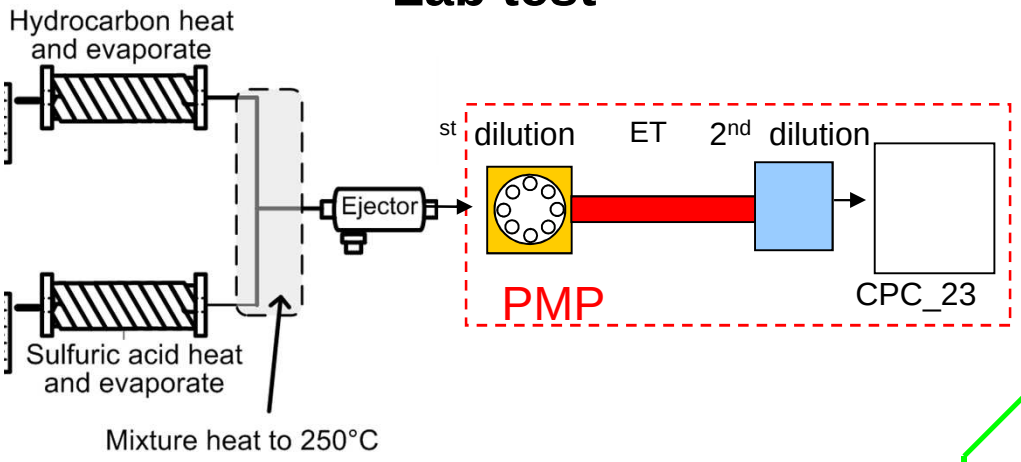
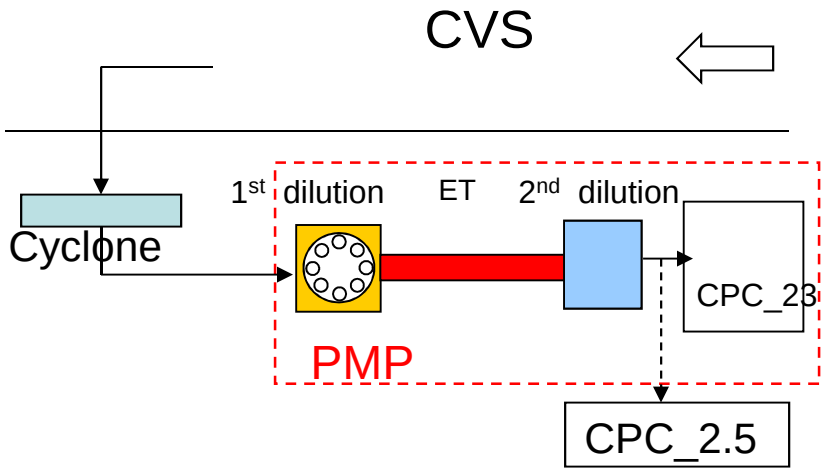
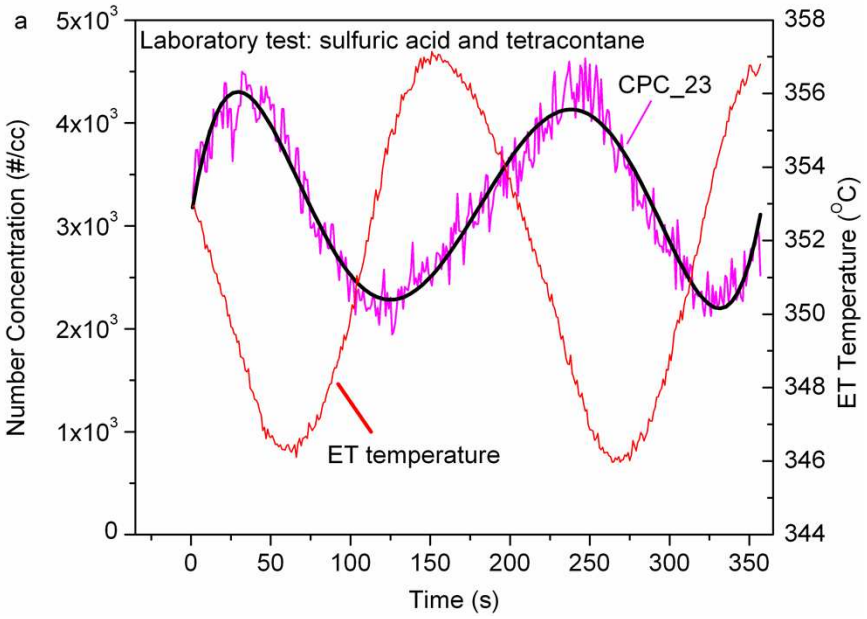
Lab and engine tests both show concentration swings tracking evaporation tube (ET) temperature

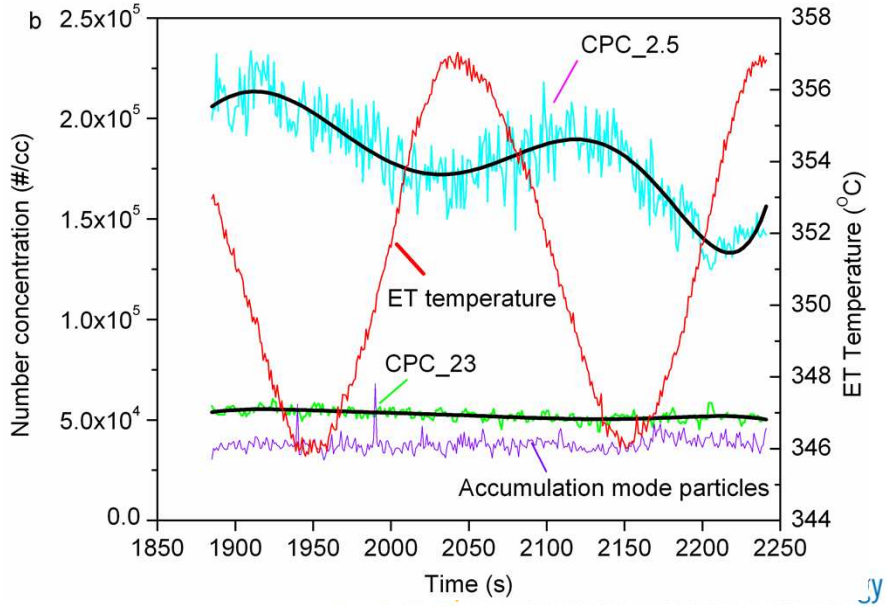
Lab test



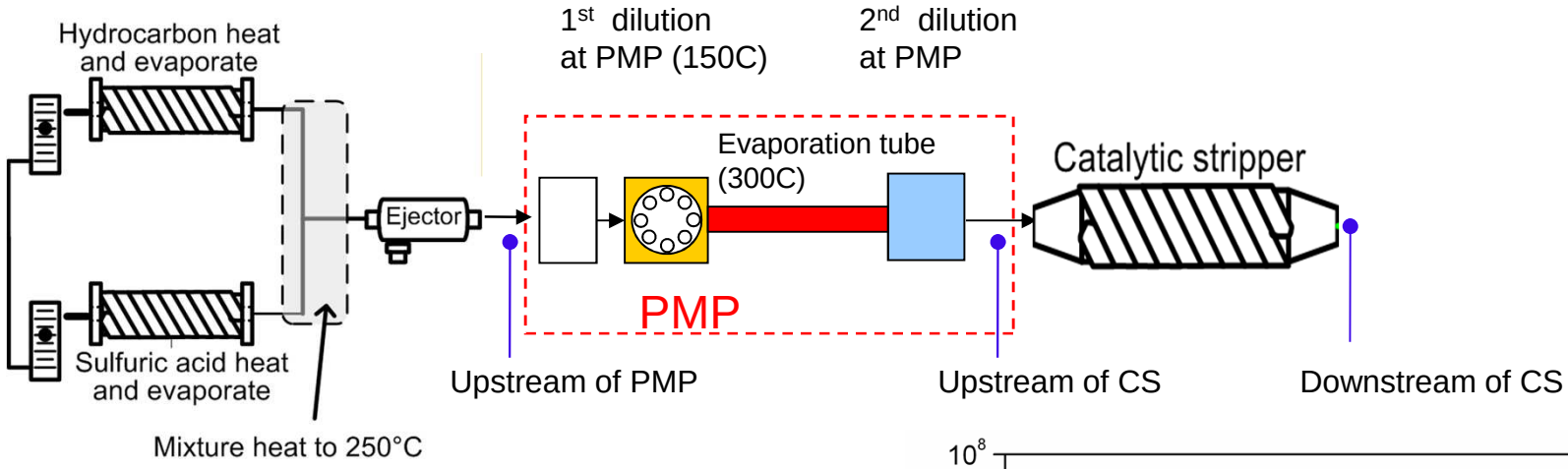
Chassis test (74% load)







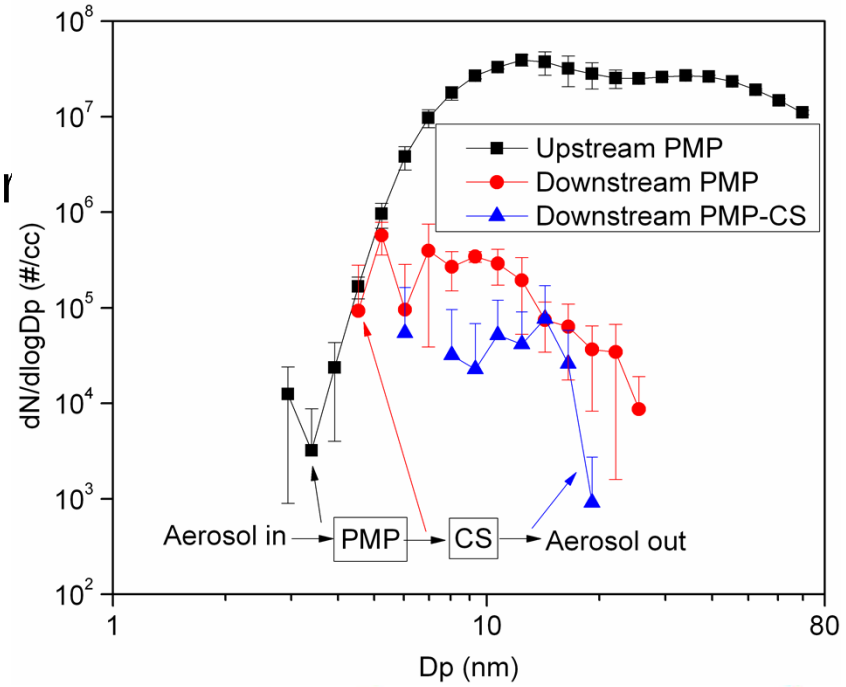
Lab test shows some residue particles exist downstream of the PMP system



Penetration efficiency by total particle number

	PMP	CS
H_2SO_4+HC	0.6%	0.55%
H_2SO_4	0.1%	0%
HC (C_{24} or C_{40})	1%	0%

Solid residue



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Conclusion

- Current PMP method regulates “solid” particles larger than 23 nm
  - For engines equipped with particle filters regulating to 23 nm effectively regulates all sizes
  - For engines without filters (advanced fuels, combustion modes, gasoline) there may be large concentrations of solid particles below 23 nm that are not counted by current method
  - The next generation of high efficiency direct injection gasoline engines are challenged by the current standard even with the 23 nm limit

Conclusion (continued)

- Extending solid PN (particle number) measurements to 10 nm
  - Significant semi-volatile particles downstream of PMP VPR often observed
  - No significant semi-volatile formation downstream of catalytic stripper in this size range
- Extending solid PN (particle number) measurements to below 10 nm – problematic
  - Particles as small as sub 3 nm formed in large concentrations downstream of PMP VPR
  - Some evidence of solid particle formation by VPR
  - Sub 10 nm particle formation observed downstream of CS under some conditions
  - Removal of sulfate or other low vapor pressure species critical

Acknowledgement

- **CARB**
  - For funding and instruments.
  - A. Ayala and J. Herner for encouraging this study.

- **AVL LIST GmbH Inc.**
  - Providing a PMP system (AVL particle counter) and technical support.
  - B. Giechaskiel, M. Linke, R. Frazee, S. Roeck, & W. Silvis

- **UCR/CE-CERT**
  - D. Pacocha, J. Valdez, and E. O' Neil
  - P. Ziemann and D. Cocker

- **University of Minnesota**
  - J. Swanson
- **Johnson Matthey**
  - M. Twigg (For catalysts to assemble the catalytic stripper)

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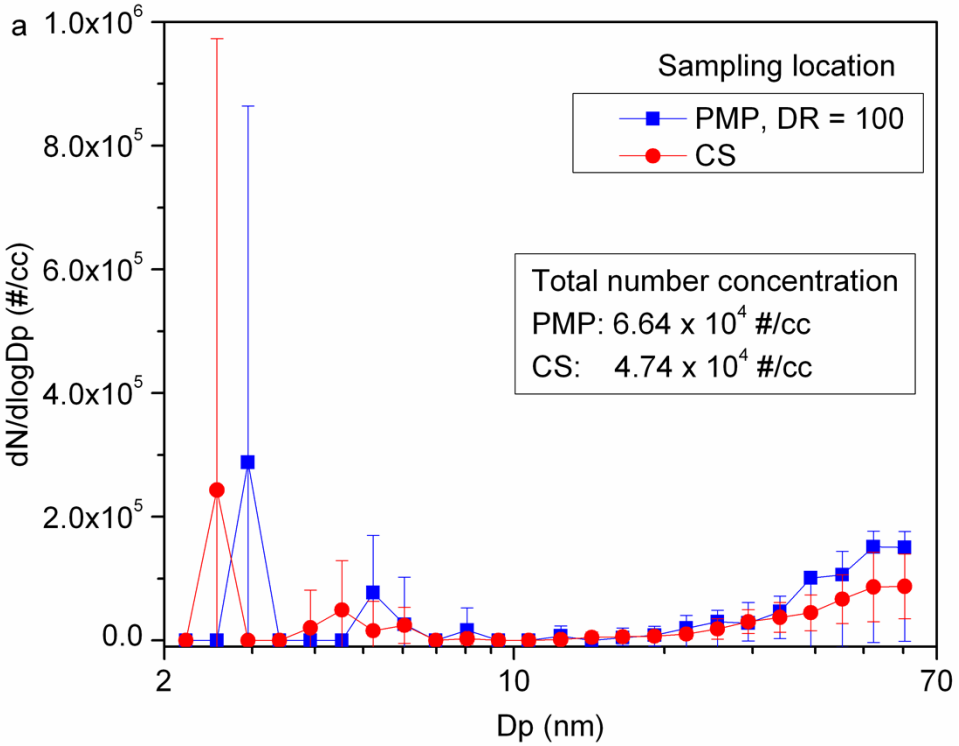
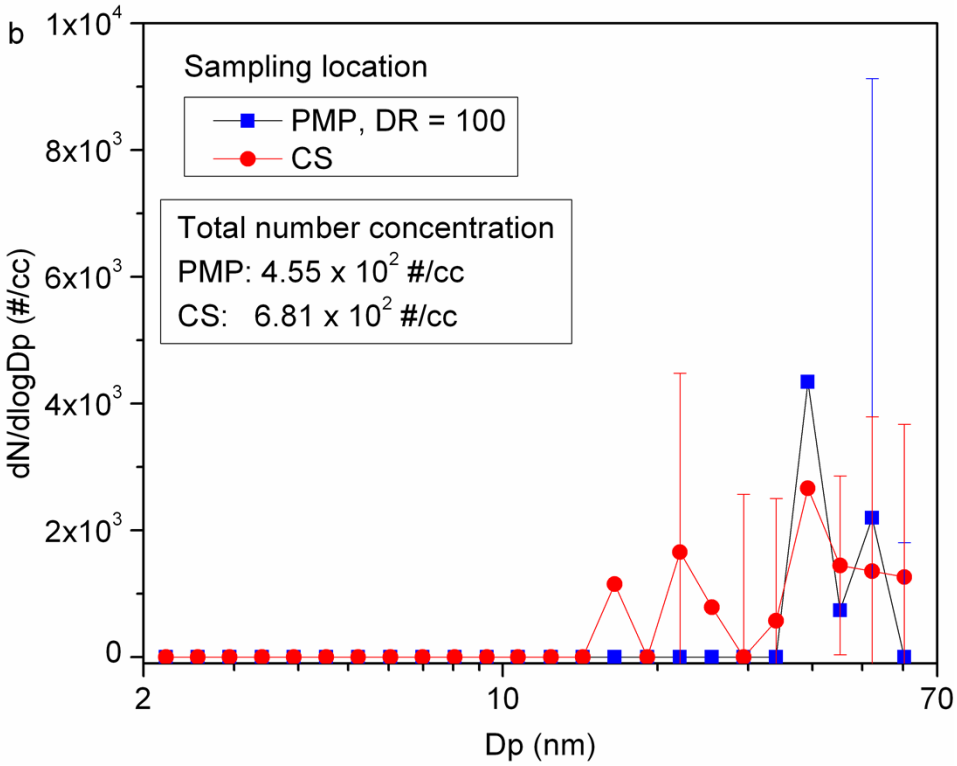
Thank You

Backup slide: nano-SMPS measurement

74% load



26% load



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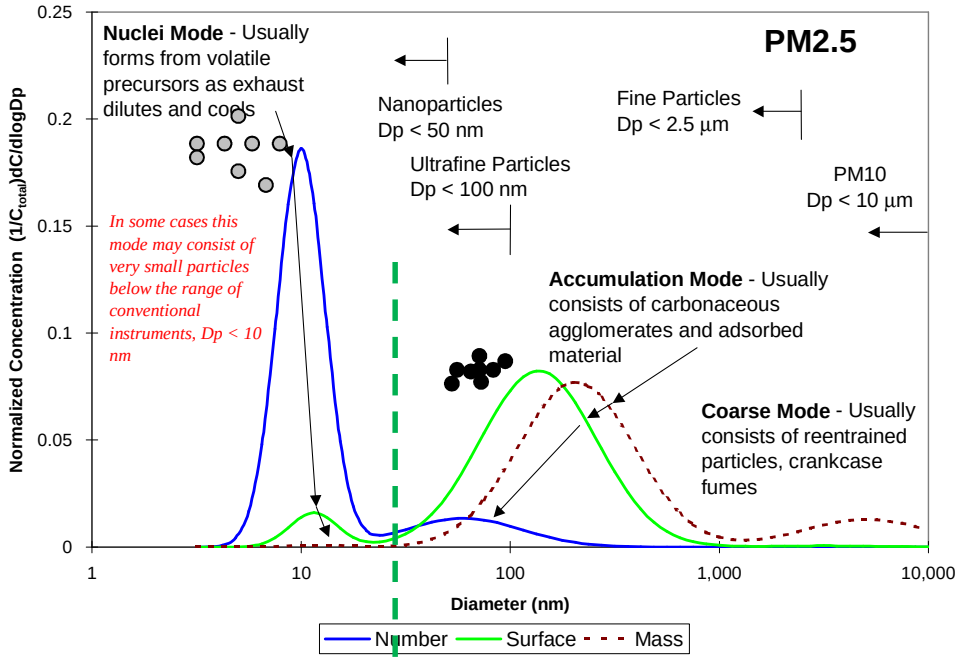
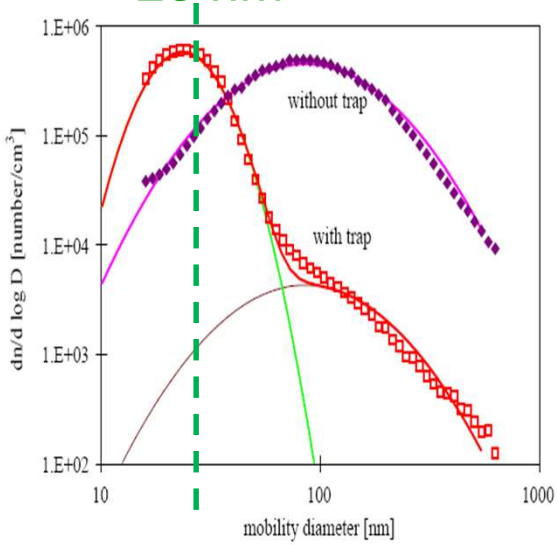
Why only particles larger than 23nm?



23 nm



- D50=23 ensures soot particles are measured but limits detection of any nucleation mode particles that escape the evaporation tube.

Giechaskiel et al. (2009) SAE 2009-01-1767

- Figures courtesy of D. Kittelson

- Sulfate>HC> Ammonium

Biswas et al. (2009)

- Figures courtesy of H. Burtscher (2005)

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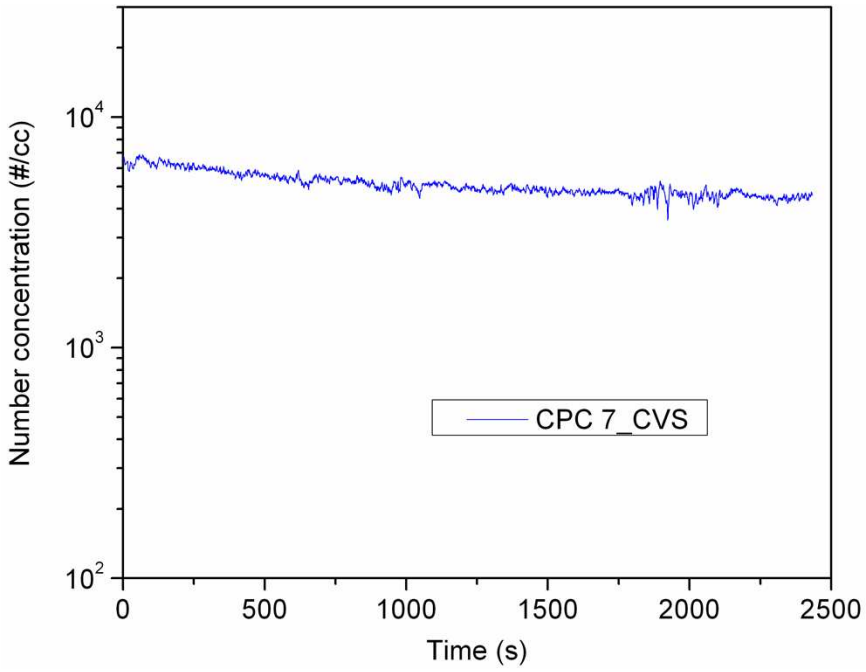
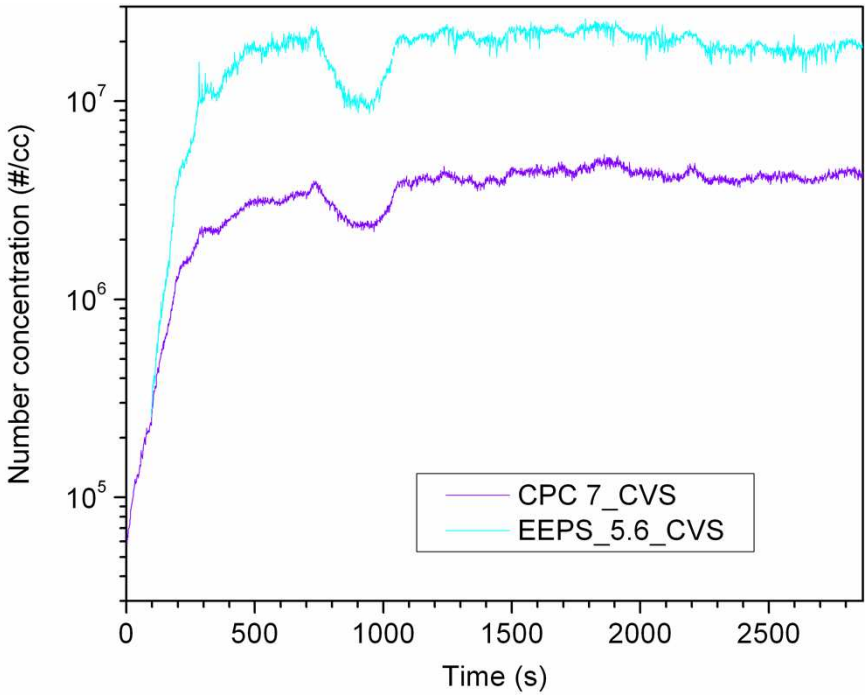
Steady state total particle number measurement

26% load



74% load



Instrument specifications

Table 1
Specifications of instruments used in this study.

Instrument	Cut off size (nm)	Max. conc. (#/cc)
CPC 3022A_CVS	7	9.99×10^6
EEPS	5.6	–
CPC 3790_APC	23	1×10^4
CPC 3772_CS	10	1×10^4
fast SMPS	3	–
CPC 3025 A	3	9.99×10^4
CPC 3772	10	1×10^4
CPC 3776	2.5	3×10^5
nanoSMPS	3	–