Laboratory and chassis dynamometer evaluation of an European PMP compliant particle number measurement system and catalytic stripper for measuring diesel solid nanoparticles

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Introduction

Progress in regulating diesel particle emissions by non-gravimetric means has been made in Europe. The United Nations Economic Commission for Europe-Group of Experts on Pollution and Energy (UNECE-GRPE) initiated the Particle Measurement Programme (PMP) working group to develop new particle measurement techniques to supplement or replace the current gravimetric method. The PMP protocol specifies measuring solid particles larger than 23 nm.

During previous California Air Resource Board (CARB)/UCR's studies of the PMP, a significant number of appeared-to-be solid sub-23 nm particles were found downstream of the PMP volatile particle remover under conditions that were thought to be unlikely to form sub-23 nm solid particles (1, 2). This study presents laboratory and vehicle experiments of diesel particle penetration/formation using the PMP system and CS.

Experimental

Laboratory Test Setup and Procedure

For the laboratory tests, aerosols with four different compositions were utilized to evaluate the response of the APC and CS systems under controlled conditions. The aerosol compositions included pure sulfuric acid, pure tetracosane (C_{24} n-alkane), a mixture of sulfuric acid and tetracosane, and a mixture of sulfuric acid and tetracontane (C_{40} n-alkane).

Chassis Dynamometer Test

For the chassis dynamometer tests, the APC and CS were tested with exhaust generated by driving a heavy-duty truck on a chassis dynamometer. Figure 1 shows the schematic of experimental setup.

Results and Discussions

Laboratory test

When aerosol composed of a mixture of sulfuric acid and tetracosane was used, the APC and CS removed 99.8% and 99.4% particles, respectively. For the APC-CS test, no particles were seen downstream of the APC-CS when aerosol composed of pure sulfuric acid or pure tetracosane were used. When using aerosol composed of a mixture of sulfuric acid and tetracosane for the APC-CS test, however, 14.2% of particles seen downstream the APC were observed downstream the APC-CS by number concentration, indicating at least 14.2% of those particles downstream of the APC were non-volatile.

Chassis dynamometer test

Negligible number of particles between 10 and 23 nm were present downstream the APC and CS. Due to thermophoretic loss, the CS reported ~40% less PN emissions than the APC for particles > 10 nm. PN emissions of particles between 3 and 10 nm downstream the APC were ~

2 and 7 times higher than the PN emissions of particles above 10 nm at the 74 and 26% engine load, respectively. At the 26% engine load, PN level of the 3 to 10 nm particles downstream the APC were even higher than that in the dilution tunnel, suggesting the APC was making 3 to 10 nm particles. Much less particles between 3 to 10 nm were seen downstream the CS for both engine loads. The PN emission of 3 to 10 nm particles downstream the APC was related to the heating temperature of the APC evaporation tube (Figure 2).

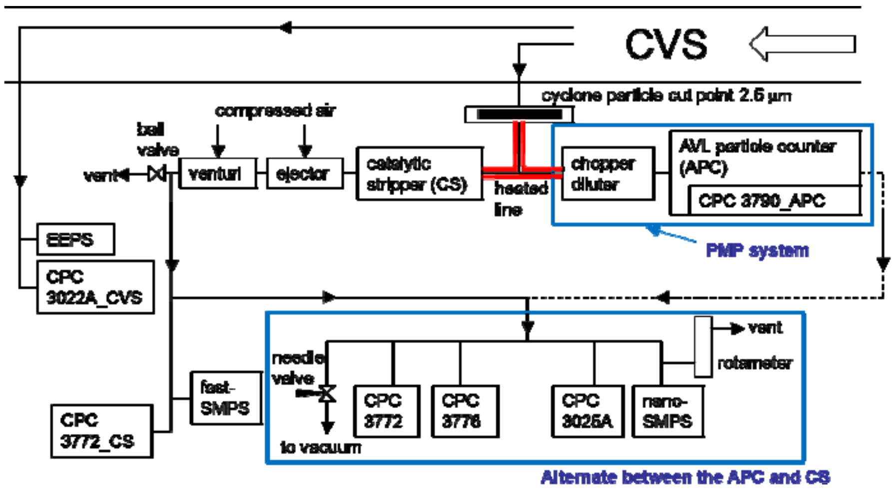

Figure 1 Schematic of chassis dynamometer test setup

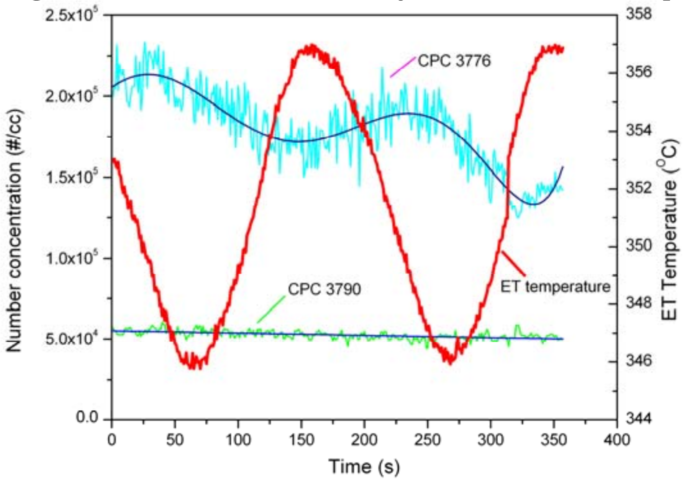

Figure 2 CPC concentrations vs ET temperature

References

(1) Johnson, K. C.; Durbin, T. D.; Jung, H.; Chaudhary, A.; Cocker, D. R.; Herner, J. D.; Robertson, W. H.; Huai, T.; Ayala, A.; Kittelson, D. Evaluation of the european pmp methodologies during on-road and chassis dynamometer testing for dpf equipped heavy-duty diesel vehicles. *Aerosol Science and Technology* **2009,** *43,* (10), 962 - 969.

(2) Herner, J. D.; Robertson, W. H.; Ayala, A. Investigation of ultrafine particle number measurements from a clean diesel truck using the european pmp protocol. *SAE International* **2007**.

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Measurement of diesel solid nanoparticle emissions using a catalytic stripper for comparison with Europe's PMP protocol

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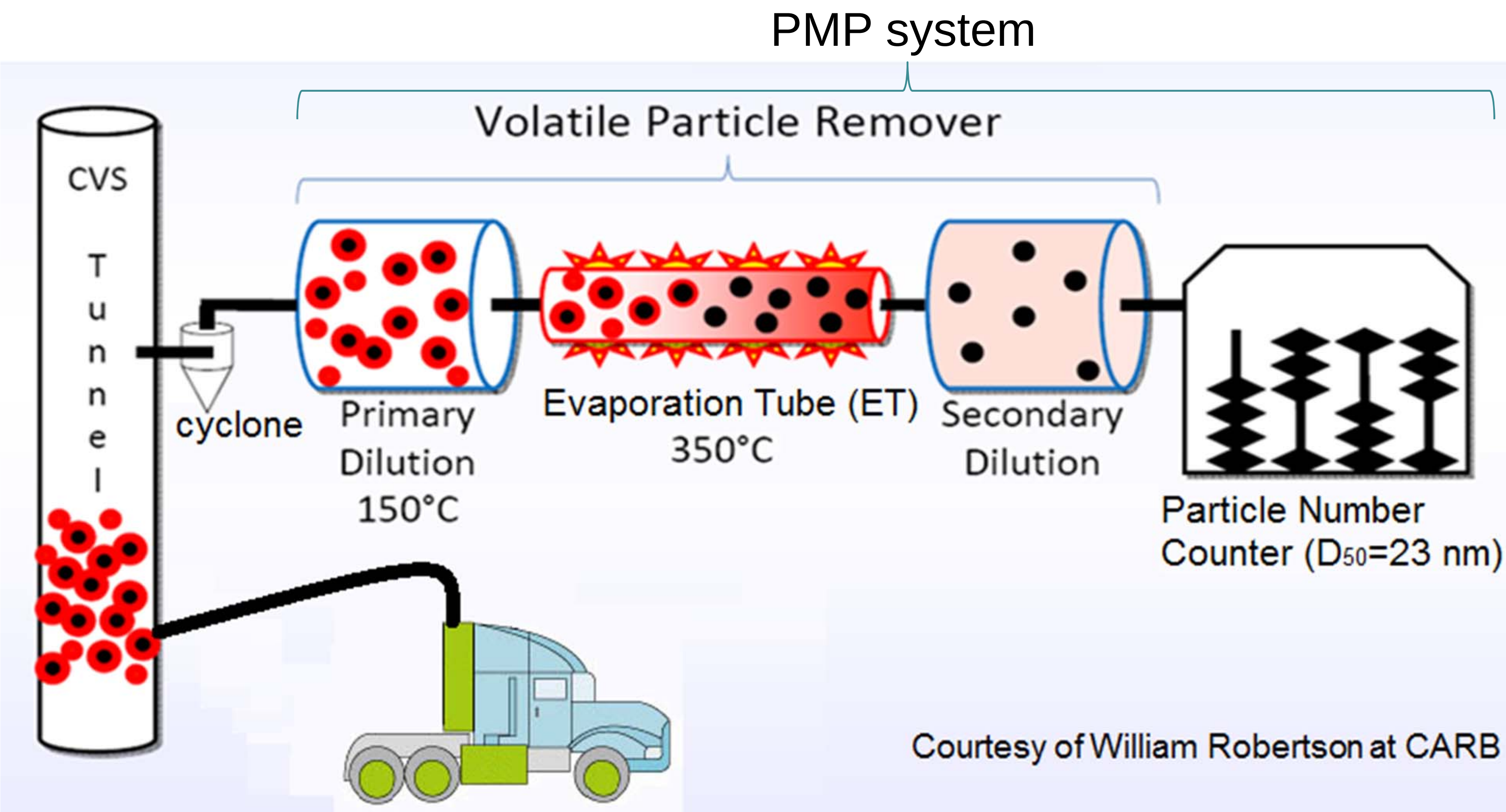
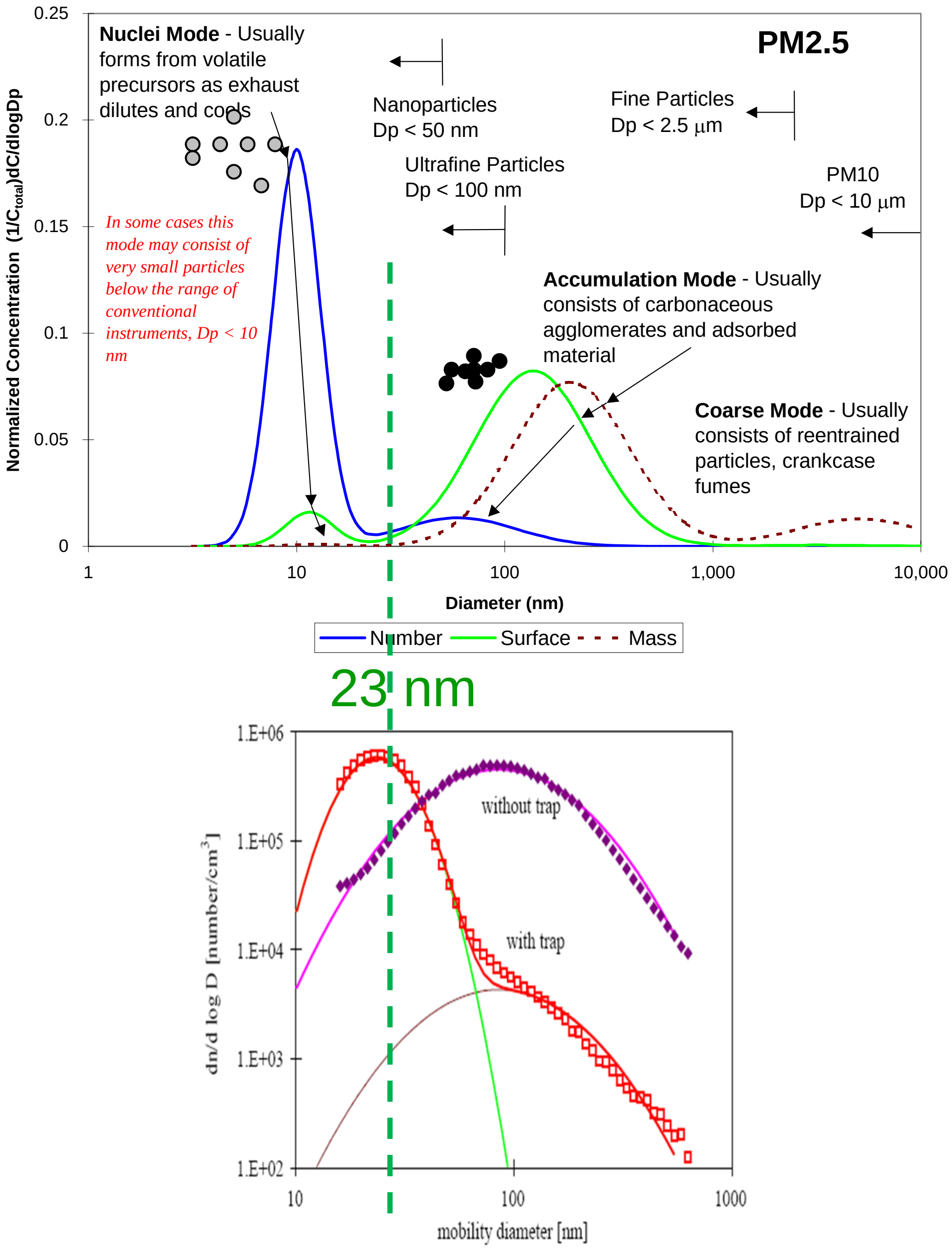
Particle measurement programme



Red: Semivolatile particles
Black: Solid (mostly soot) particles

Why only particles larger than 23nm?



•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

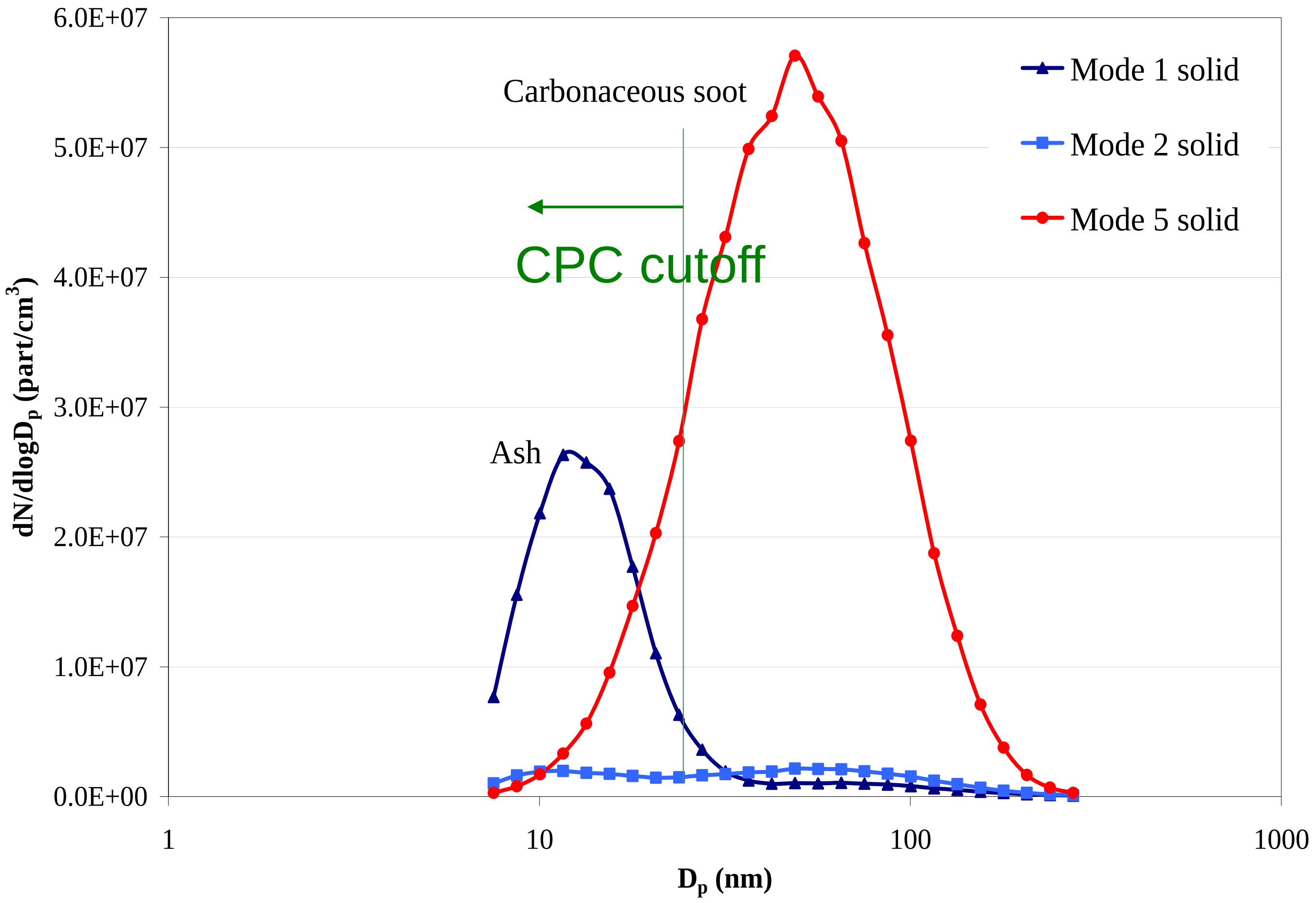
•Sulfate>HC> Ammonium

Biswas et al. (2009)

- Figures courtesy of H. Burtscher (2005)

Issues with not counting sub 23nm particles

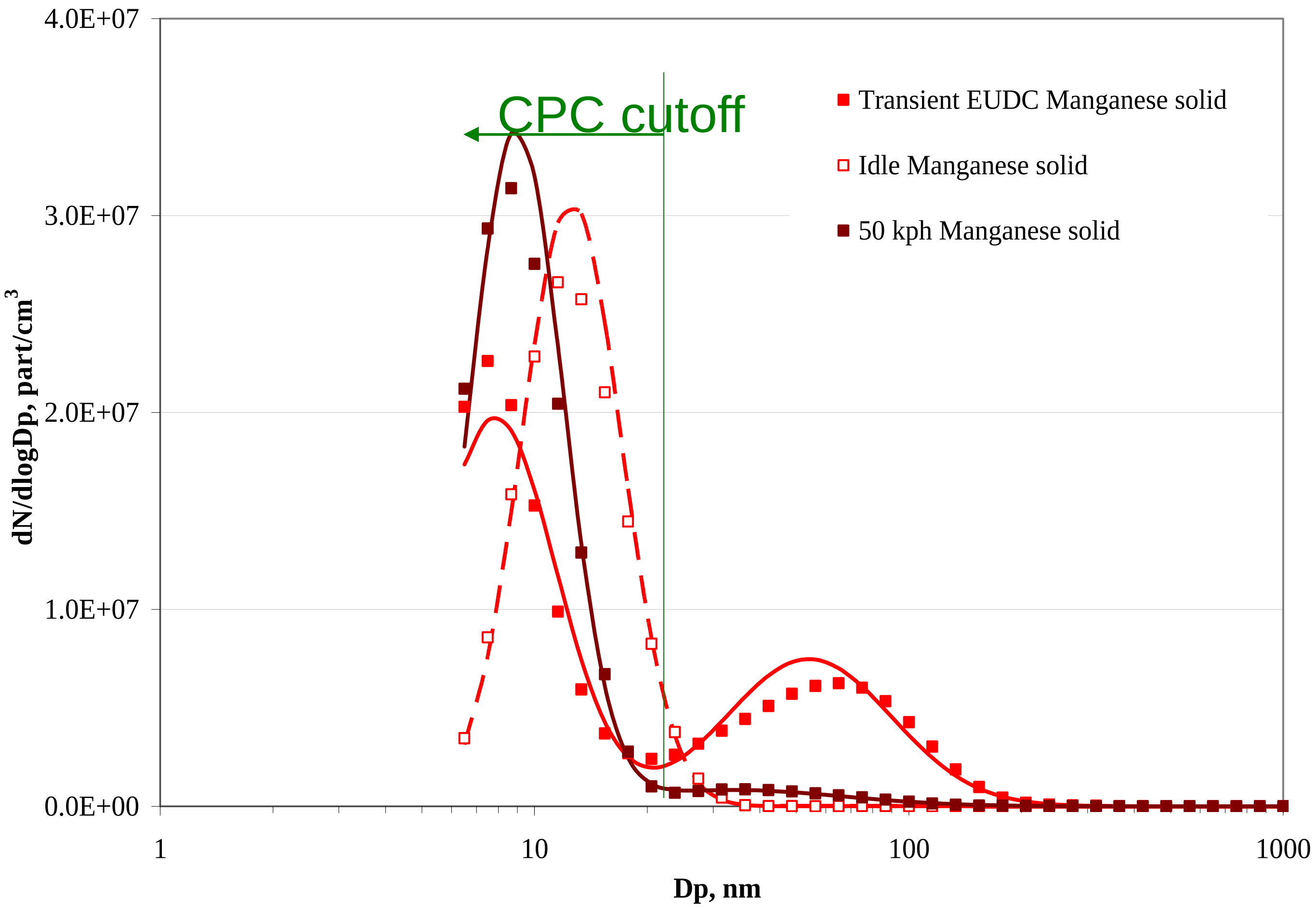
Engine out, light-load, low soot conditions: Most of the number emissions are solid with Dp < 23 nm



Cummins 2004 ISM engine, BP 50 fuel, AVL modes

Courtesy of Dr. Kittelson

Spark ignition engines can also produce tiny solid nanoparticles, especially with metal additives



Euro 3 passenger car, 10 ppm Mn in fuel, data courtesy Johnson-Matthey

Courtesy of Dr. Kittelson

Objective

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

Results

Test conditions

- Comparisons of fully compliant PMP system with measurement system using catalytic stripper for volatile particle removal
  - 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
  - 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

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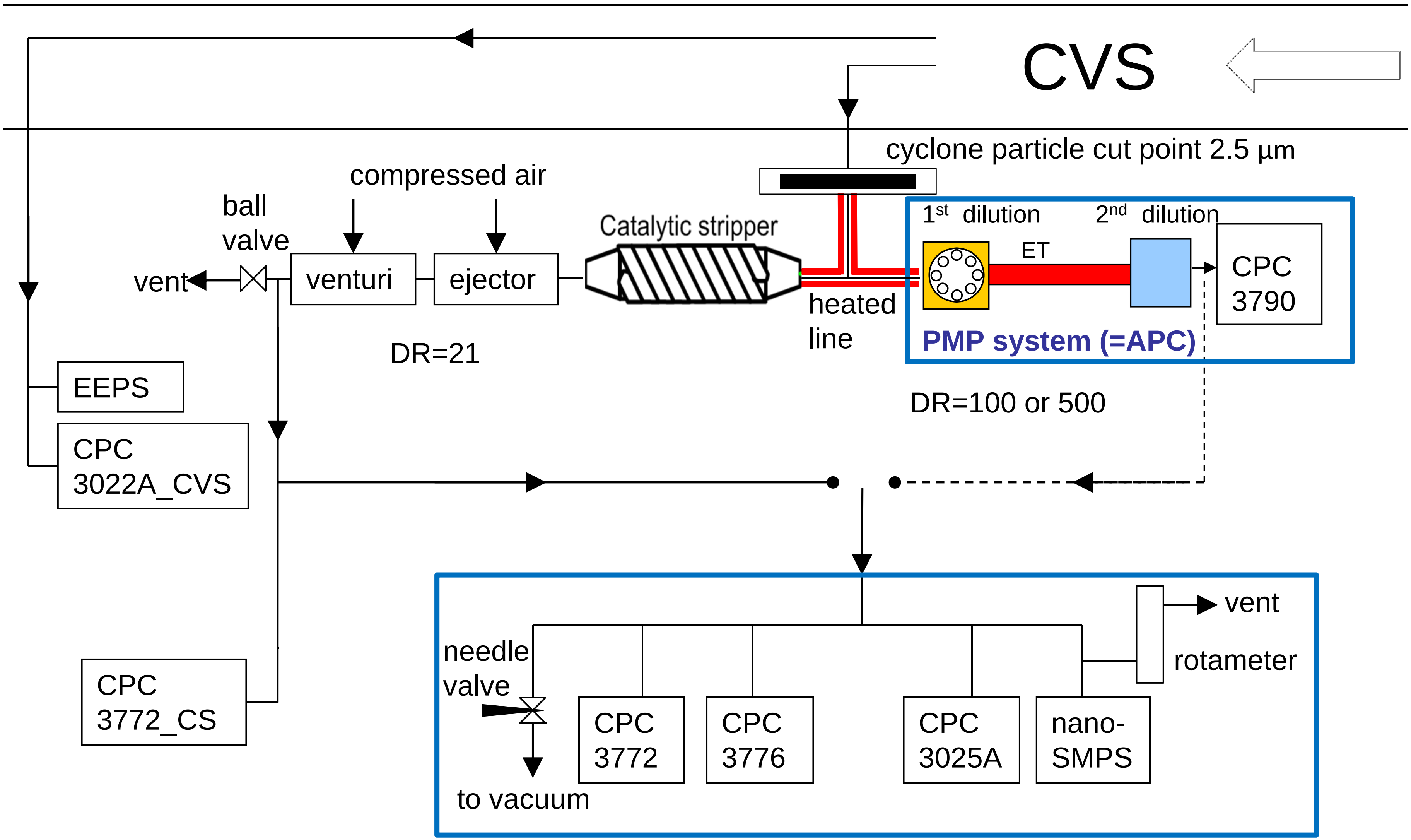
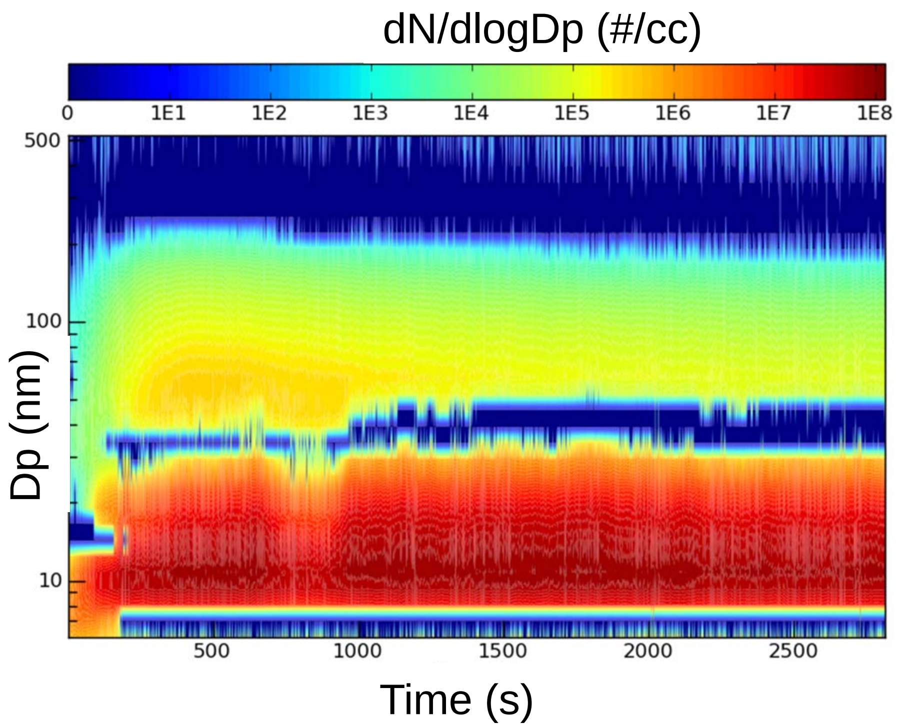
Chassis test



Alternate between the APC and CS

CVS particle size dist. measured by EEPS

74% engine load

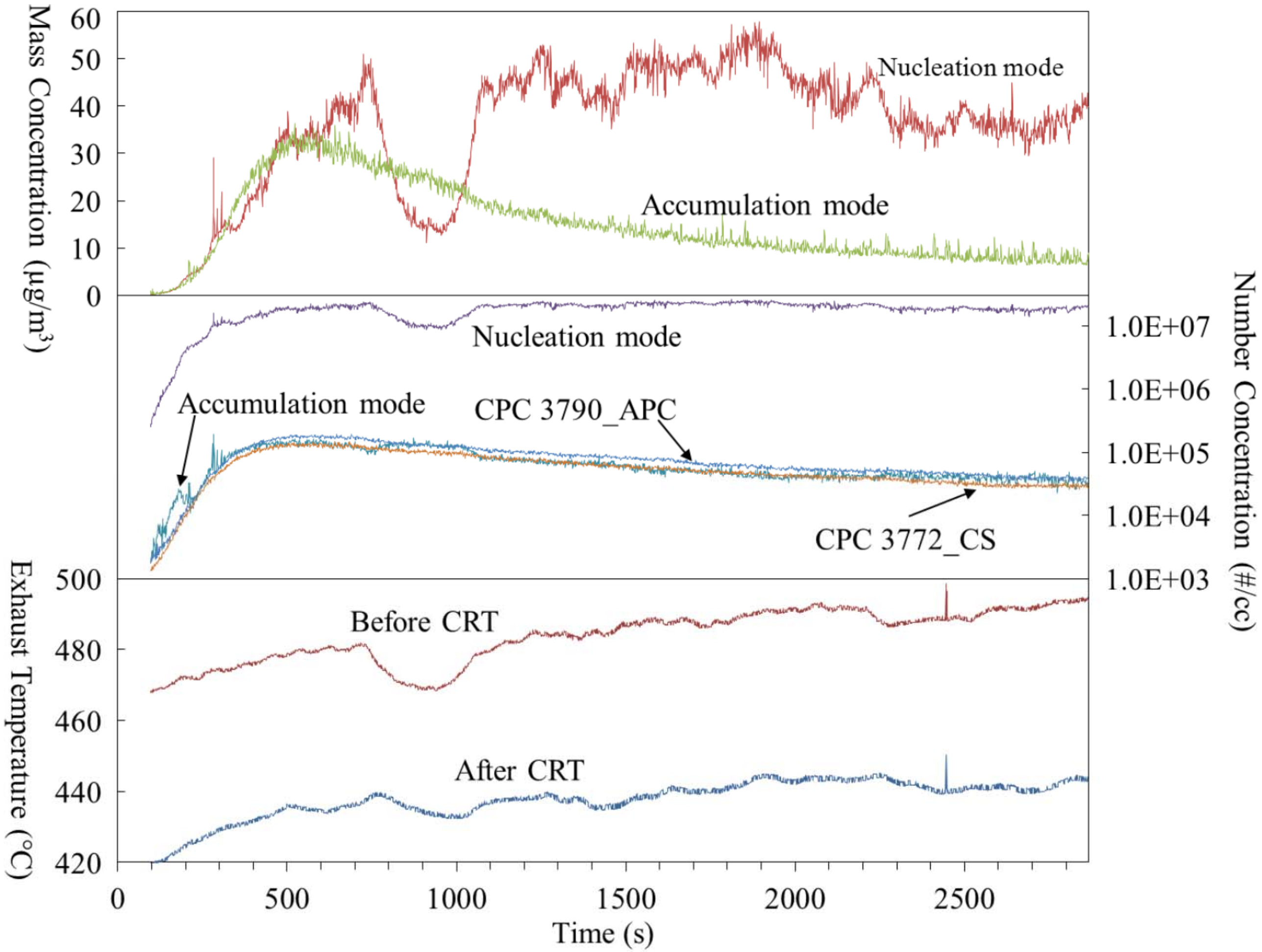


26% engine load

Dp (nm)

EEPS data near noise level at 26% engine load

The PMP compliant system closely tracks the accumulation mode (74% load)



CPC	D_{50} (nm)
3790_APC	23
3772_CS	10
3025A	3
3772	10
3776	2.5

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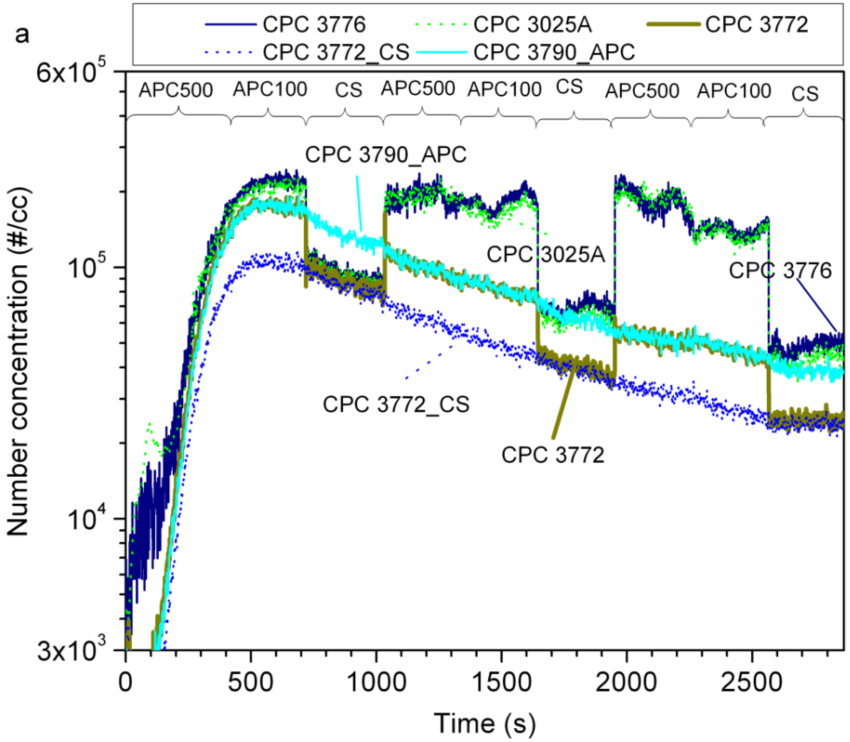
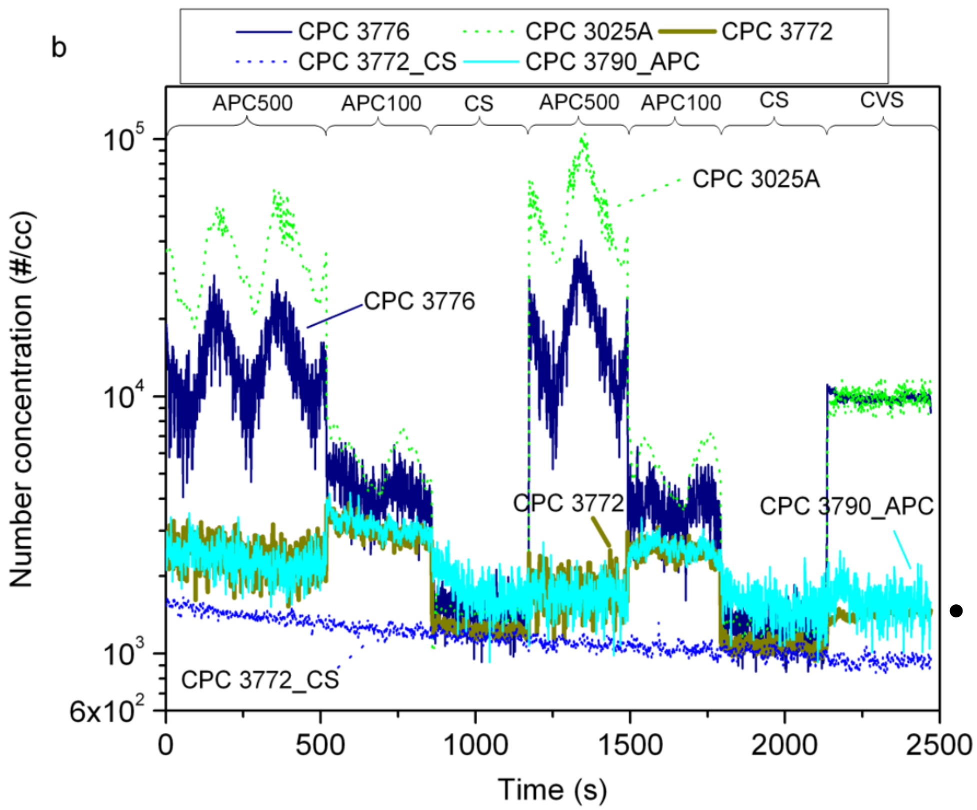
Comparison of instruments at 74% load cruise



CPC	D_{50} (nm)
3790_APC	23
3772_CS	10
3025A	3
3772	10
3776	2.5

- **Downstream of PMP system**
  - 3790 and 3772 agree – no particles between 10 and 23 nm
  - 3025A and 3776 agree and read progressively higher than 3772 and 3790 as time goes on – particles forming between 3 and 10 nm
  - Same trend at 100 and 500 dilution ratio
- **Downstream of CS**
  - In first time window all instruments agree – no particle below 23 nm
  - In second and third time windows 3776 and 3025A read higher than 3772 – particle formation between 3 and 10 nm

Comparison of instruments at 26% load cruise



- Much lower concentrations than at 74%
  - Downstream of PMP system
    - In first time window, DR = 500
      - 3790 and 3772 agree – no particles between 10 and 23 nm
      - 3776 and 3025A 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
      - 3790 and 3772 read higher but agree – no particles between 10 and 23 nm but formation above 23 nm
      - 3776 and 3025A agree but read only slightly higher than 3790 and 3772 – 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 APC, clear evidence of particle formation by APC

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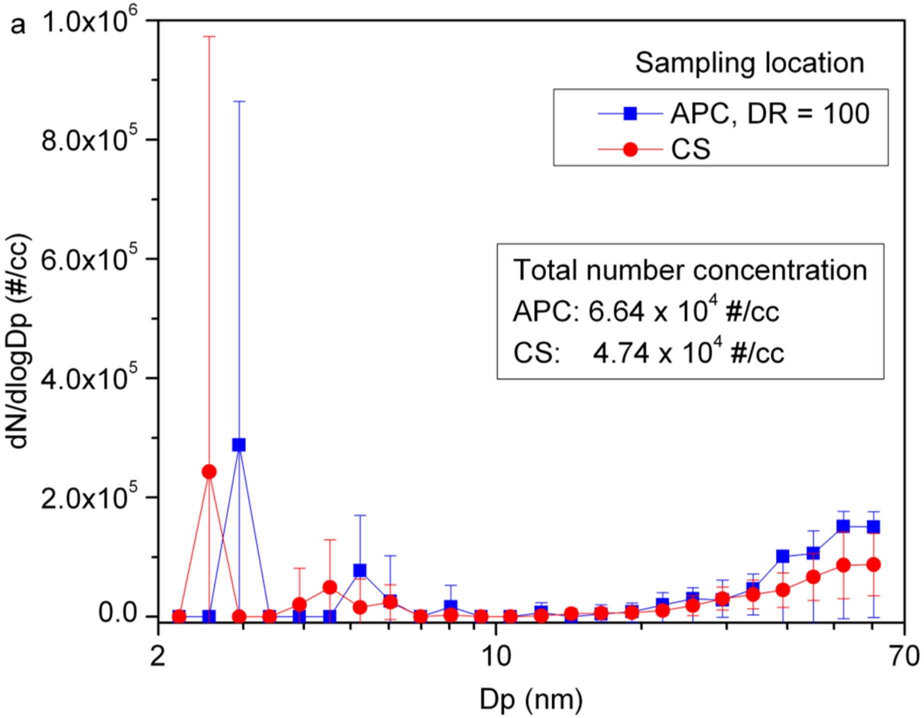
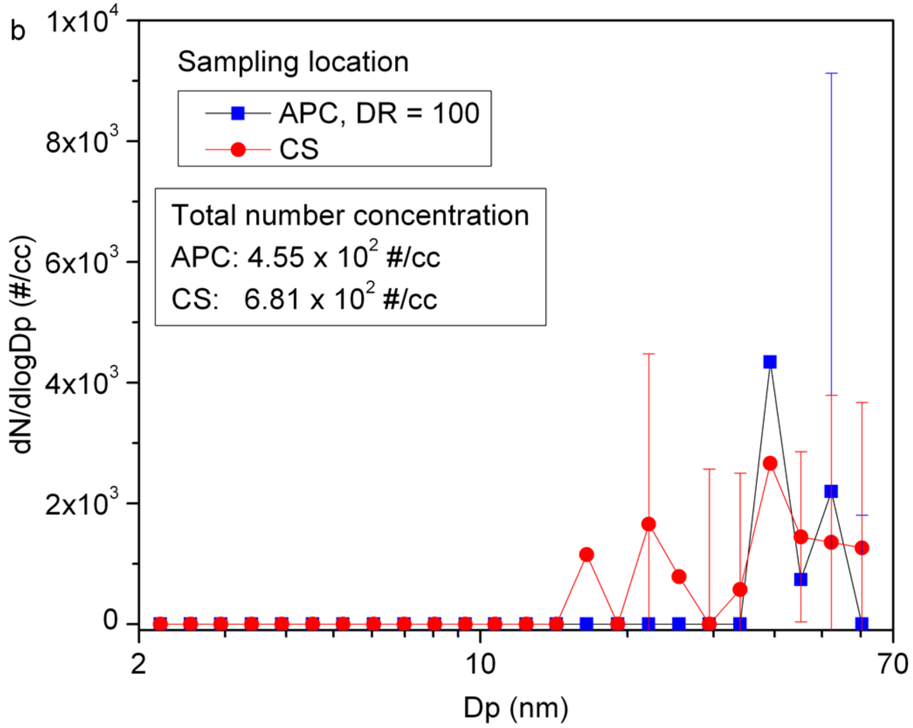
Nano SMPS measurement

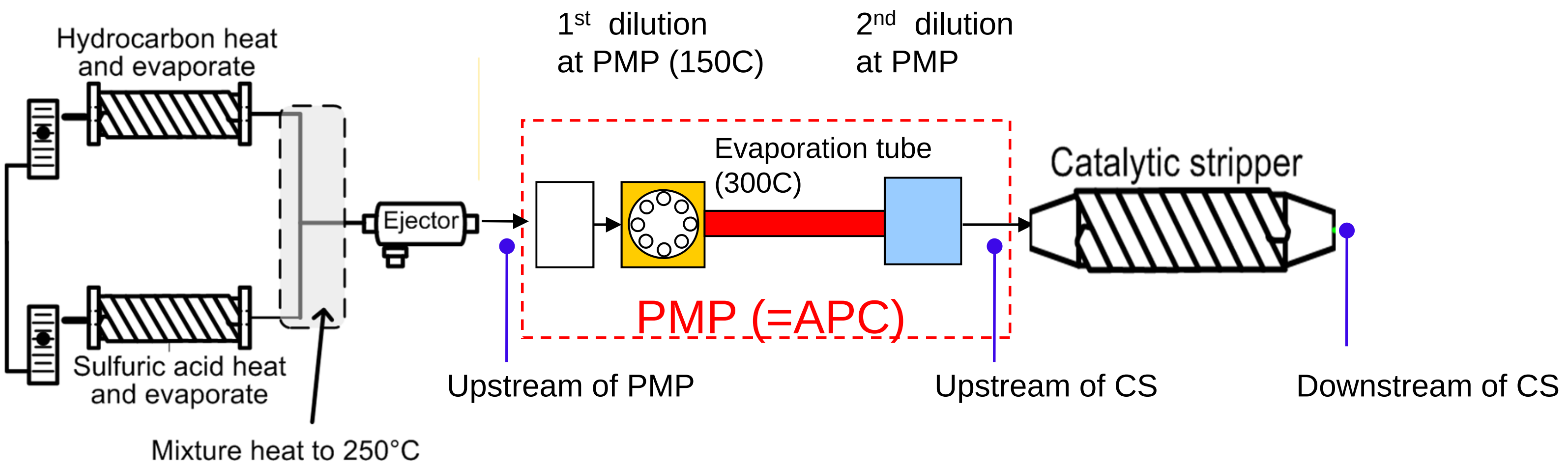
74% load



26% load

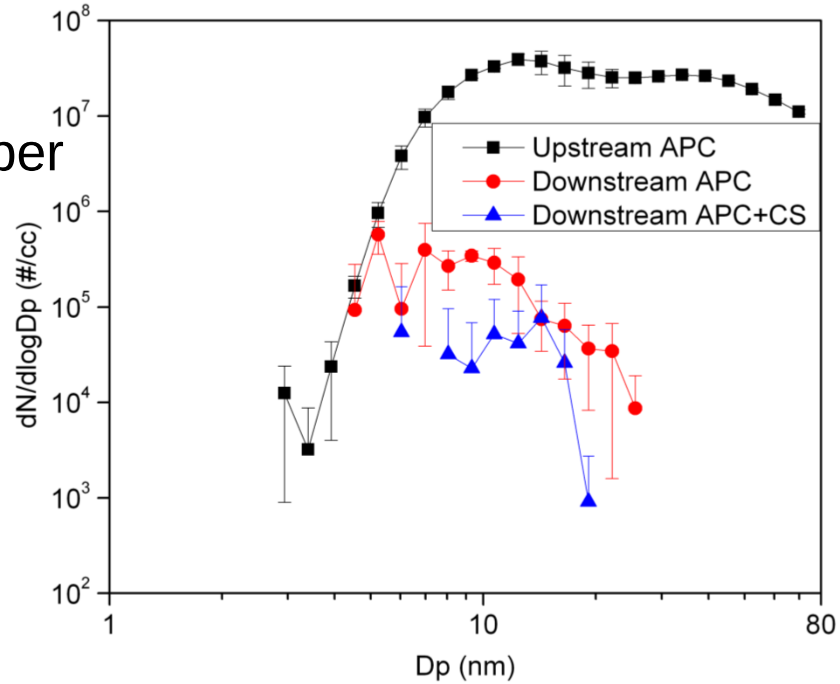


Lab test (smilar to Swanson and Kittelson)



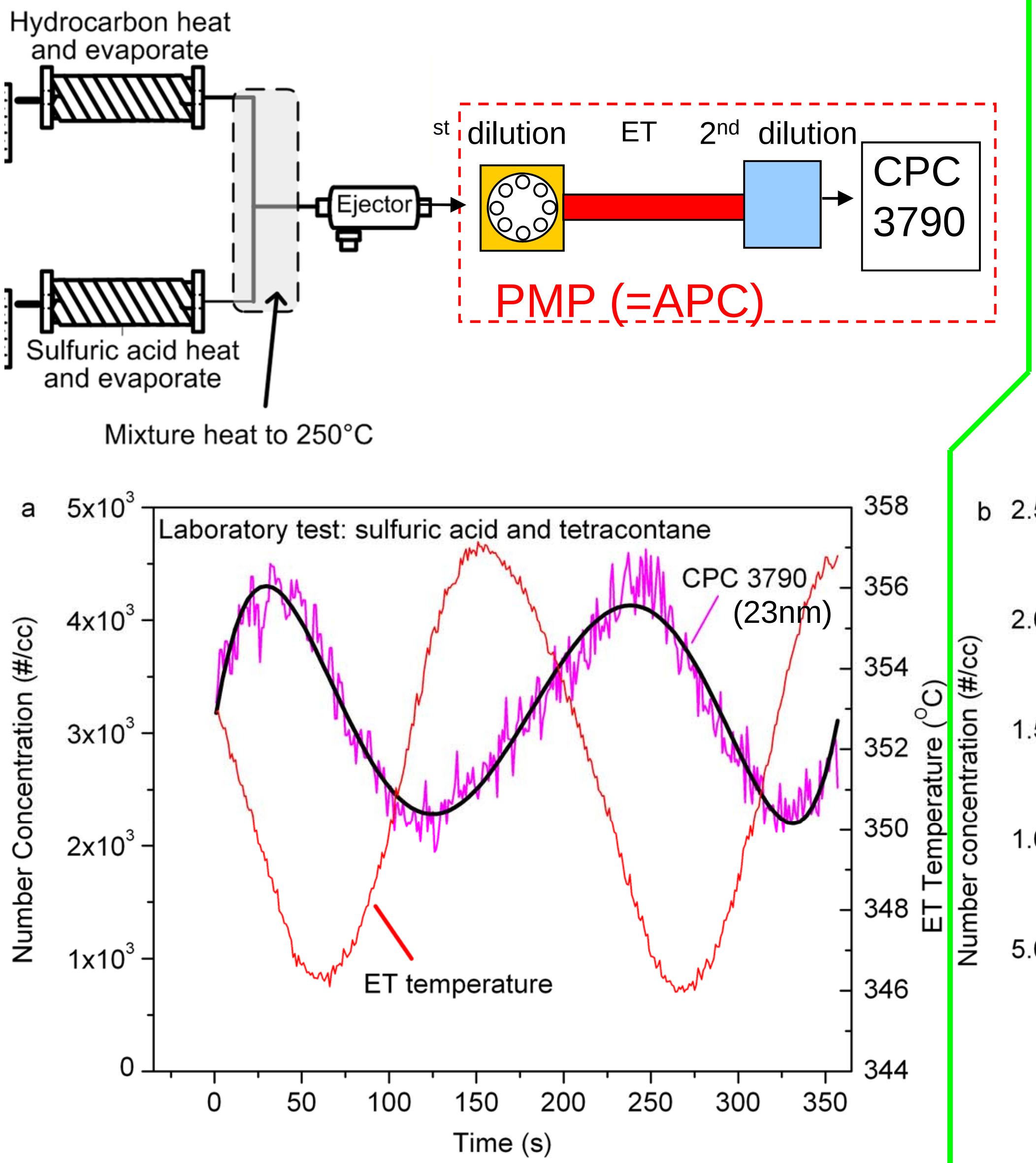
Penetration efficiency by total particle number

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

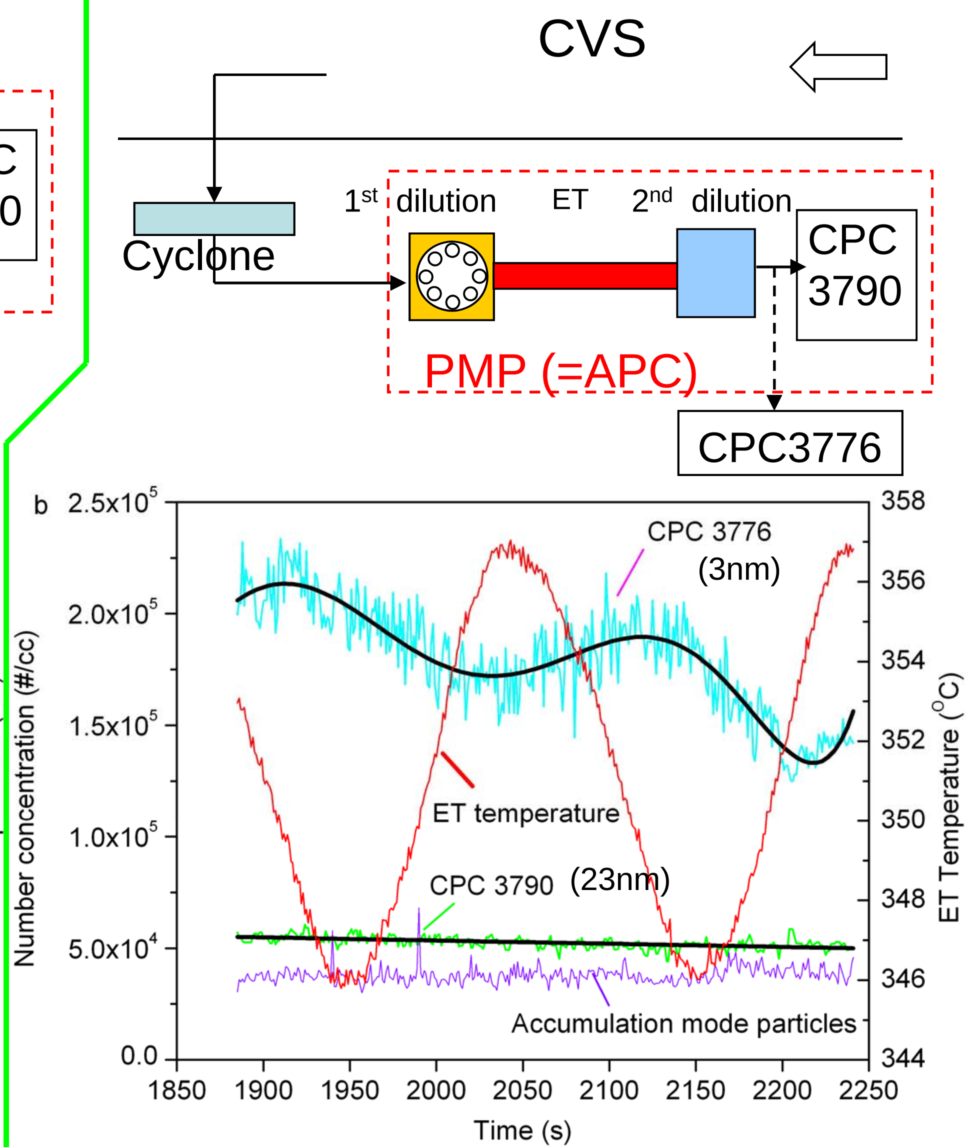


APC ET temperature oscillation

Lab test



Chassis test (74% load)



Conclusion

- Volatile remover such of the PMP system and the CS makes substantial number of sub 10nm particles.
- The sub 10 nm particles downstream the PMP were formed in the PMP system, because:
  - Particle concentration of those sub 10 nm particles oscillated in relation with the oscillation of the PMP ET temperature.
  - Some of these appeared to be solid as they could not be removed by the CS in the lab experiment others appear to be semivolatile as they fluctuate along with ET temperature.

Implication and future work

- The PMP works fine with D_{50}=23nm, but if PMP needs to measure ash particles and be applied more widely with a lower or no cutoff diameter then the PMP needs to be improved not to make artifact particles.
- New D_{50} for PMP=10nm?
- Do sub 10nm particles exist in other vehicles and cycles?
  - e.g. HD 2010 compliant OEM, GDI, & transient cycles
  - More experiments are needed.
- More controlled study (e.g. lab study) is needed to better understand the particle formation process.

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  - For funding and instruments.
  - A. Ayala and J. Herner for encouraging this study.
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  - J. Swanson
- **Johnson Matthey**
  - M. Twigg (For catalysts to assemble the catalytic stripper)

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Four papers raise issues about solid particle measurements, especially when applied to particles smaller than 23 nm

- 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). Laboratory and chassis dynamometer evaluation of an European PMP compliant particle number measurement system and catalytic stripper for measuring diesel solid nanoparticles, submitted to *Journal of Aerosol Science*.
- 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*, Volume 41, Issue 12, Pages 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

Thank You

Backup slides

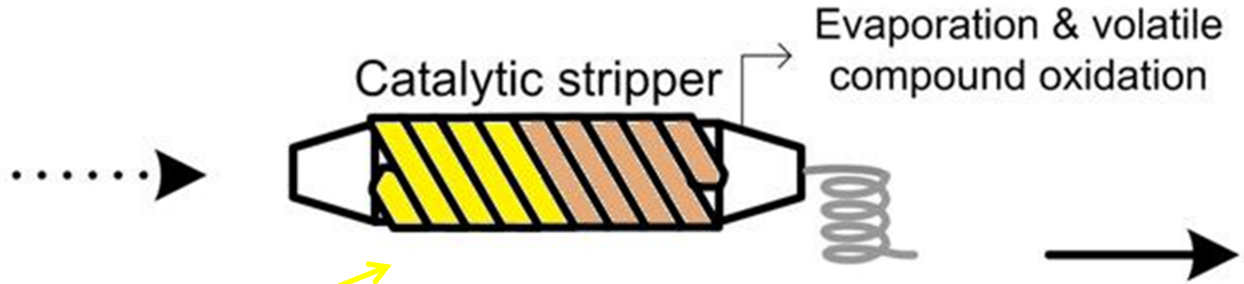
Conclusions

- Current PMP method regulates “solid” particles larger than 23 nm
  - For engines equipped with particle filters regulating to 23 nm effectively regulates all sizes
  - Under extreme conditions false counts of nucleated semi-volatile have been observed
  - 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
- Extending solid PM measurements to 10 nm
  - No significant semi-volatile formation downstream of catalytic stripper in this size range
- Extending solid PM 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 thermal denuder
  - Sub 10 nm particle formation observed downstream of CS under some conditions

Experimental conditions

Base	CE-CERT HD Chassis dynamometer
Vehicle	Freightliner class 8
Engine	Caterpillar C-15 (14.6L)
Fuel	ULSD (8ppm S)
Lubricating oil	SAE 15W-40 (2900 ppm S)
DPF	JM CRT
Vehicle weight	65,000 lb
Truck mileage	41442 miles
Cycles	(a) 56 mph cruise at 74% engine load; (b) 56 mph cruise at 26% engine load.

Catalytic stripper (CS)



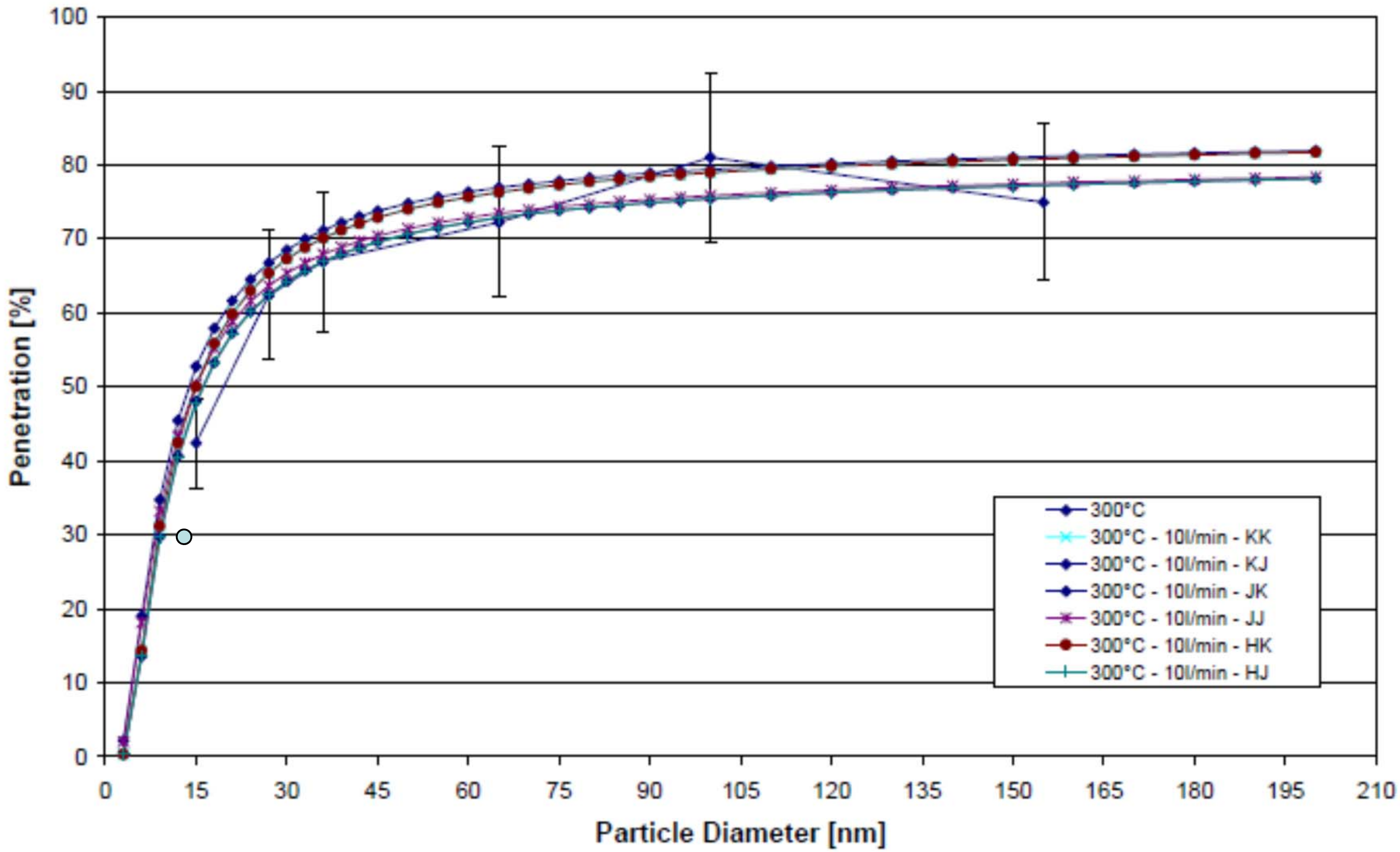
- Sulfur-trap (S-Trap):
  - Wall temperature: 300°C
  - Length: 11 cm
  - Diameter: 3.2 cm
  - $BaO + SO_3 \rightarrow BaSO_4$

- Particle penetration
  - 5% at 3 nm
  - 75% at 100 nm

- Oxidation catalyst:
  - Wall temperature: 300°C
  - Length: 11 cm
  - Diameter: 3.2 cm
  - 75 g/ft^3 of Pt

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

Penetration efficiency



Integrated particle number emissions