UCR | College of Engineering- Center for Environmental Research & Technology

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

Heejung Jung, Zhongqing Zheng, Kent C. Johnson, Zhihua Liu, and Thomas D. Durbin
University of California, Riverside

David B. Kittelson
University of Minnesota

Shaohua Hu and Tao Huai
California Air Resources Board

Background

- Gravimetric method reaches its limit to accurately measure diesel particle emissions.
- One cannot take advantage of DPF technology.
- Europeans recognized this problem and came up with a solid particle counting method a.k.a European PMP method, which counts particles larger than 23 nm (due to repeatability).

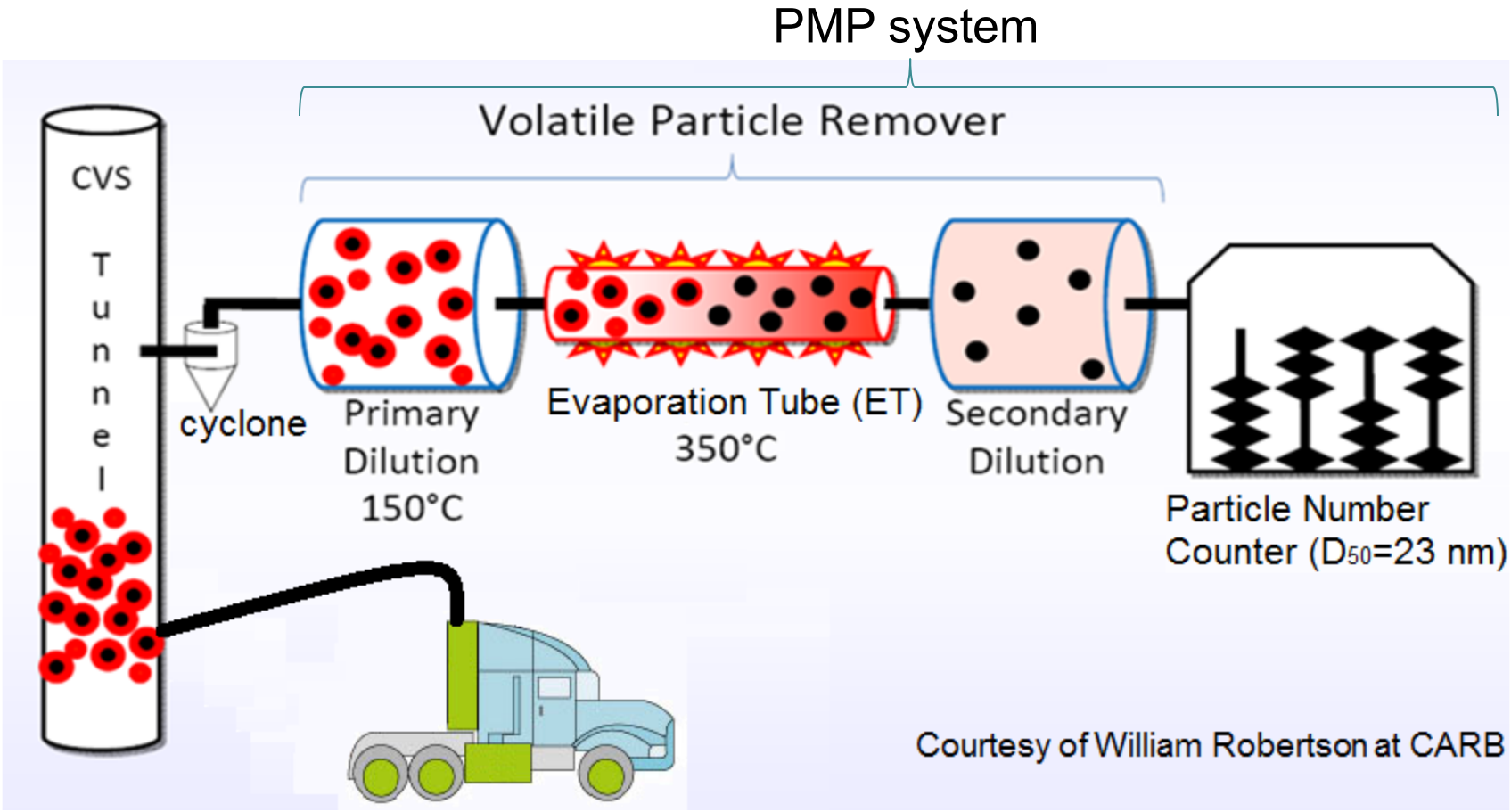
Background

- Issues with excluding sub 23nm particles in solid particle number counting.
  - Exclusion of ash particles.
- Issues with including sub 23nm particle in solid particle number counting.
  - Artifact particles can exist in this size range.

Objective

- Investigation of the nature of sub 23nm particles downstream the PMP system.
  - Existence and nature of sub 23nm particles
- Evaluation and comparison of the PMP system and catalytic stripper.

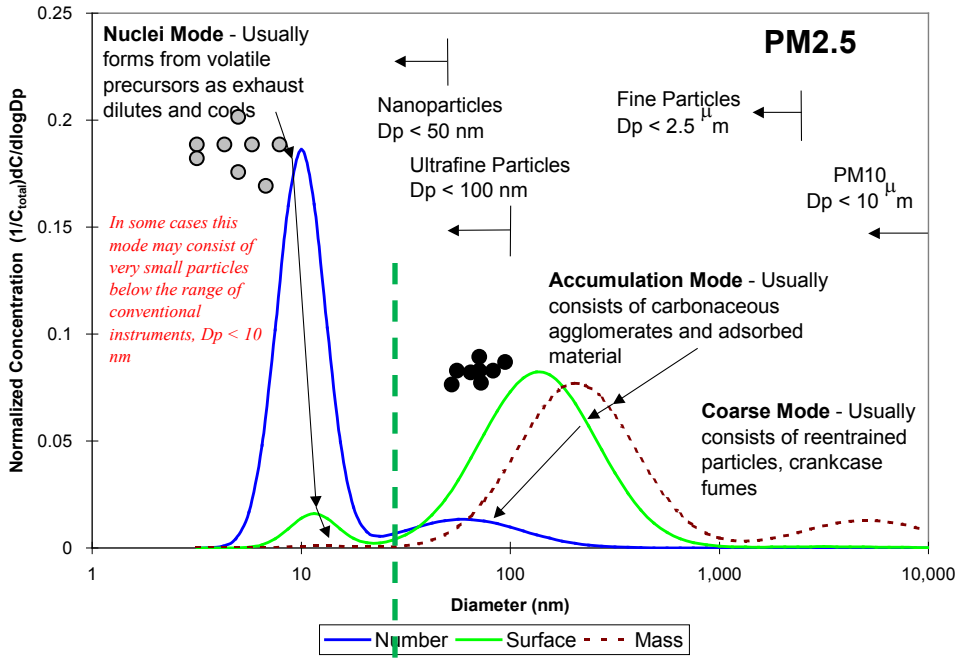
Particle measurement programme (PMP)



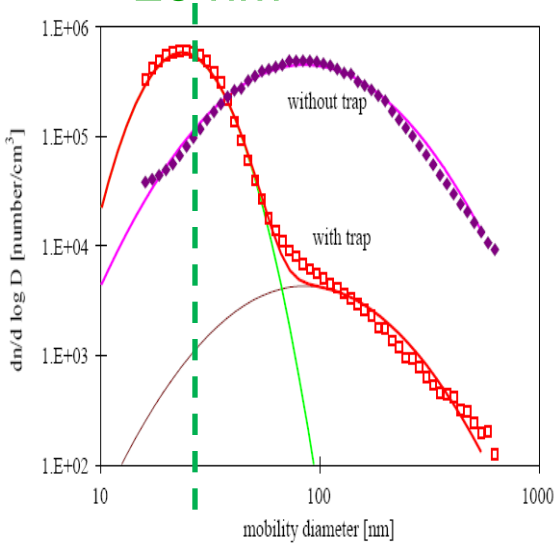
Red: Semivolatile particles

Black: Solid (mostly soot) particles

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

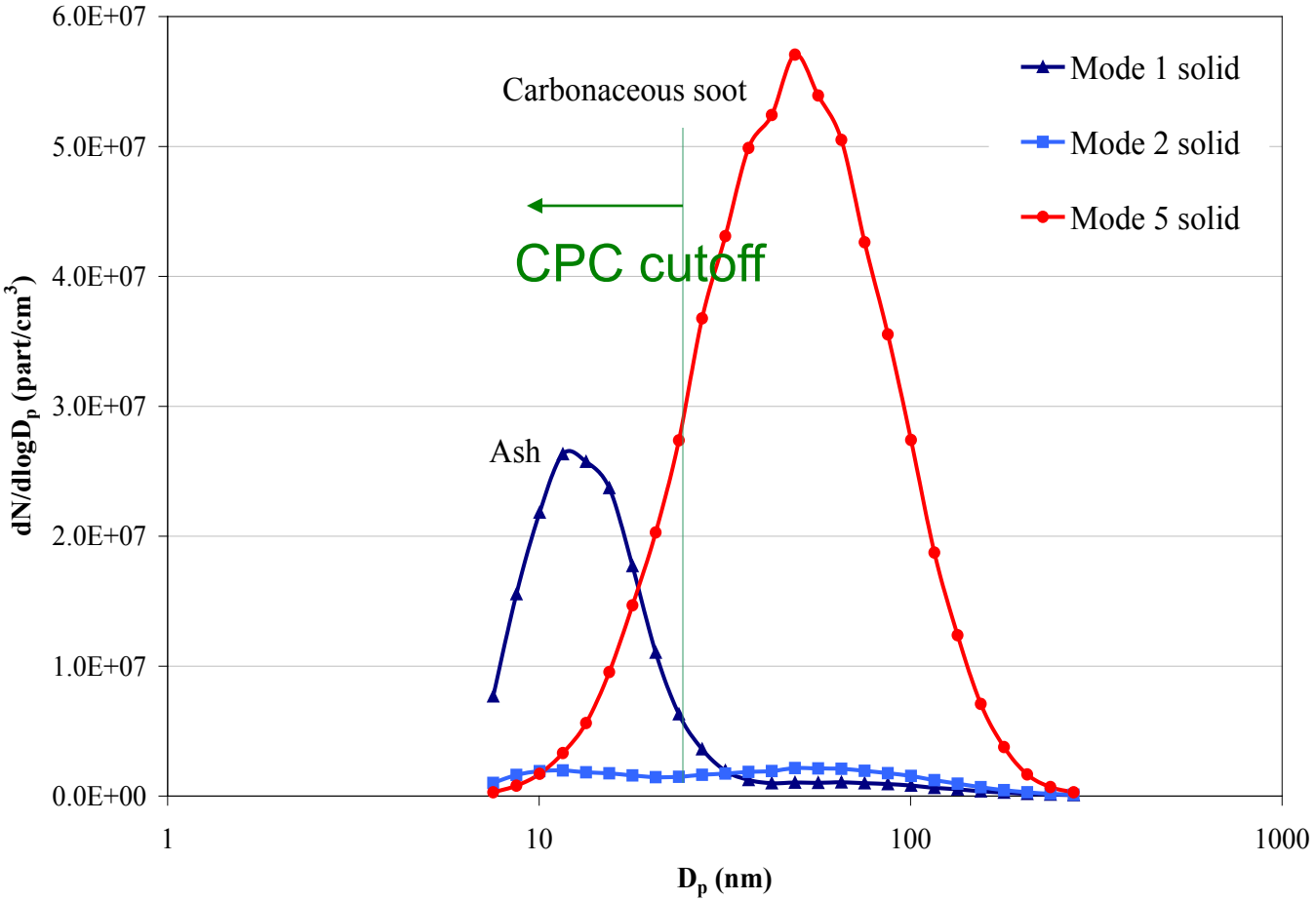
•Sulfate>HC> Ammonium

Biswas et al. (2009)

Figures courtesy of H. Burtscher (2005)

Issues with not counting sub 23nm particles

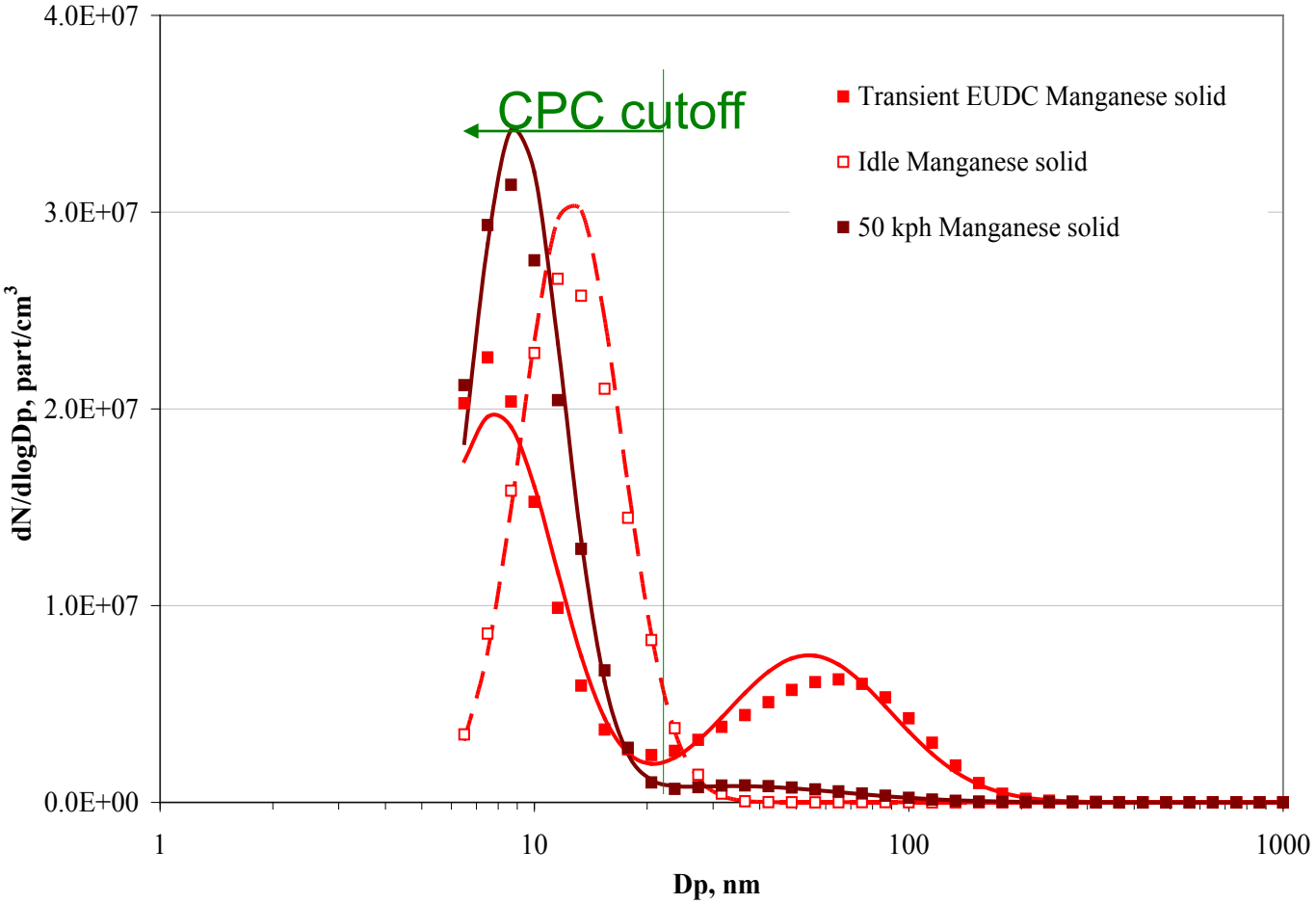
Engine out, light-load, low soot conditions: Most of the number emissions are solid with Dp < 23 nm



Cummins 2004 ISM engine, AVL modes

Courtesy of Dr. Kittelson

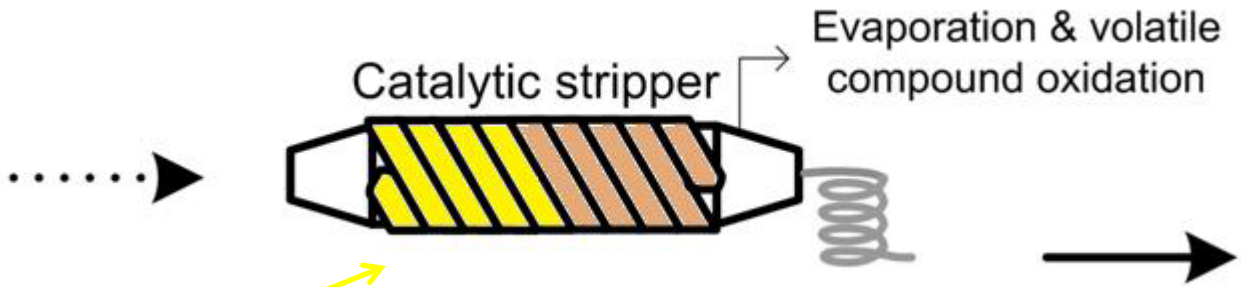
Spark ignition engines can also produce tiny solid nanoparticles, especially with metal additives



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

Courtesy of Dr. Kittelson

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

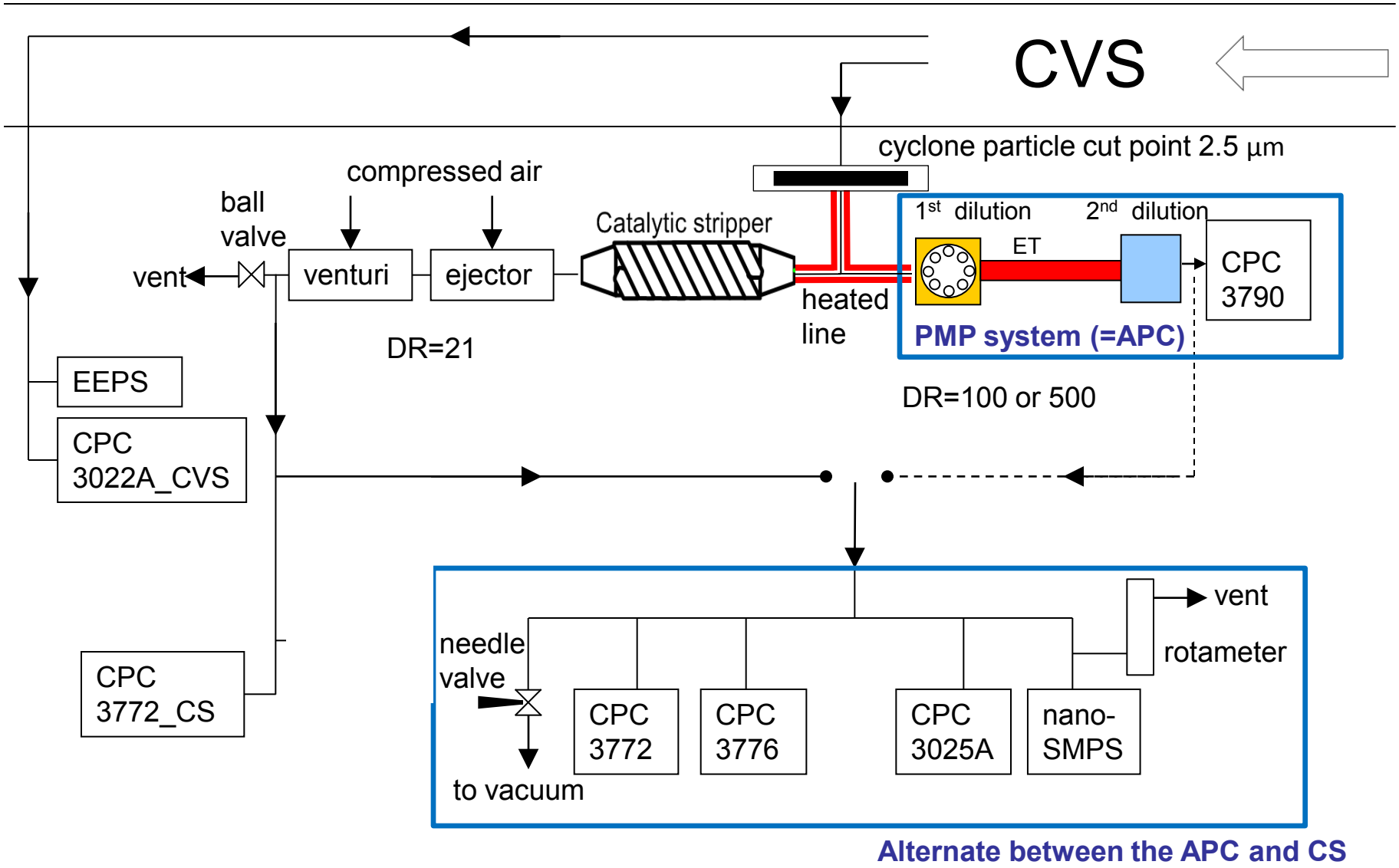
- Oxidation catalyst:
  - Wall temperature: 300°C
  - Length: 11 cm
  - Diameter: 3.2 cm
  - 75 g/ft^3 of Pt

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

Test conditions

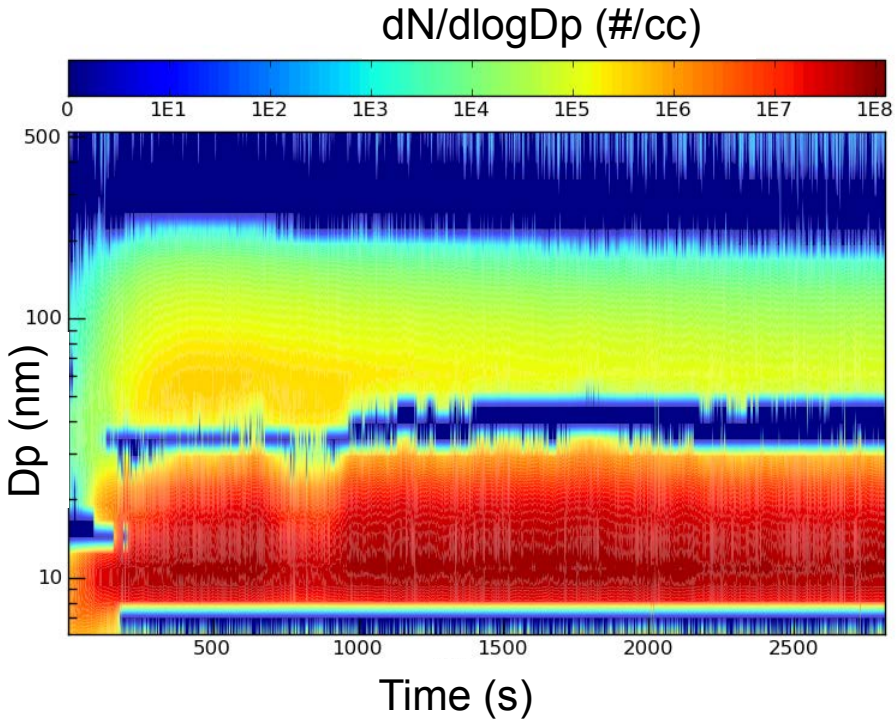
- Tests with exhaust aerosols from heavy-duty vehicle operating on chassis dynamometer.
  - Freightliner class 8 truck with 14.6 liter, 2000 Caterpillar C-15 engine, equipped with Johnson Matthey Continuously Regenerating Trap (CRT™)
  - Two steady state cruise conditions, constant speed 56 mph at 26% and 74% of full load
- Tests with laboratory-made challenge (or surrogate) aerosols without using an engine.

Measurement Diagram for Chassis Test



CVS particle size dist. measured by EEPS

74% engine load

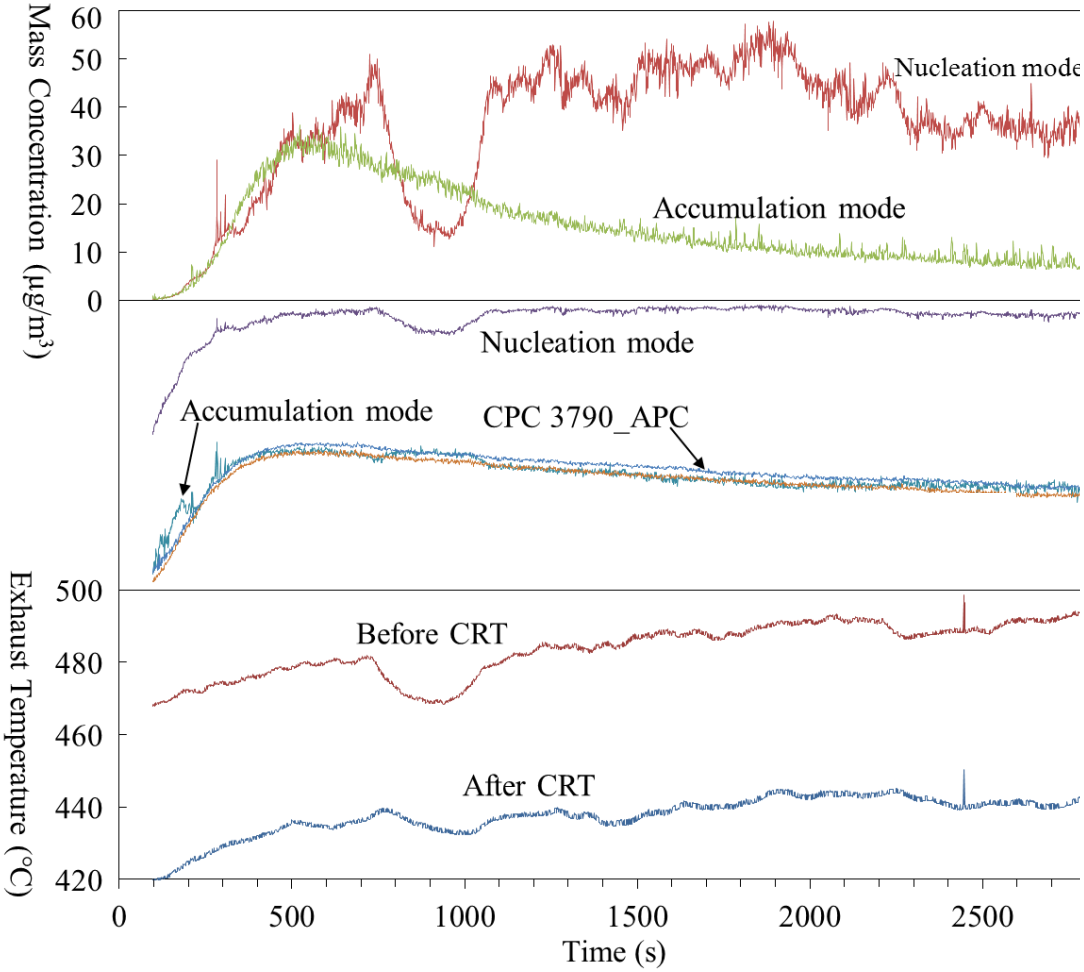


Dp (nm)

26% engine load

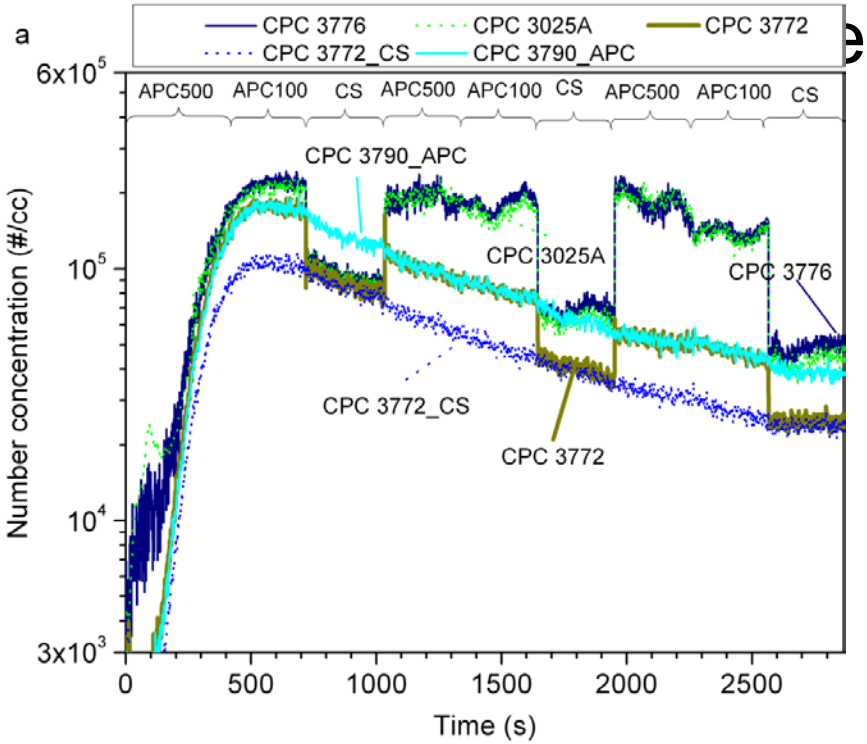
EEPS data near noise level at 26% engine load

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

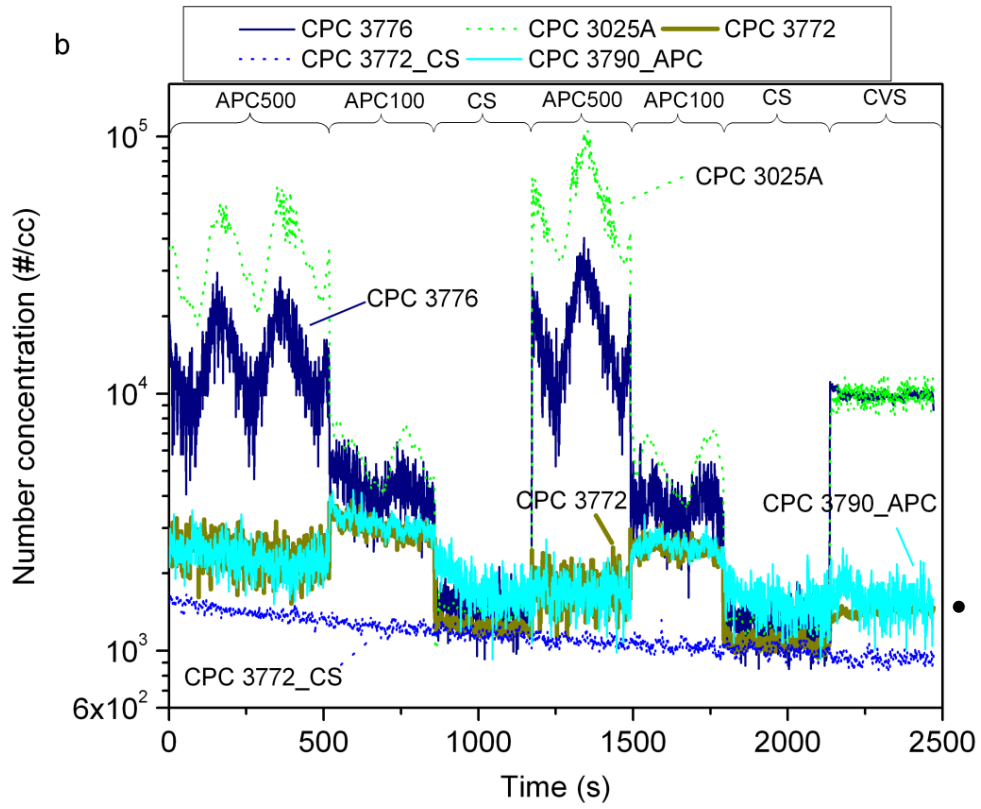
Comparison of particle concentrations at 74% load



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

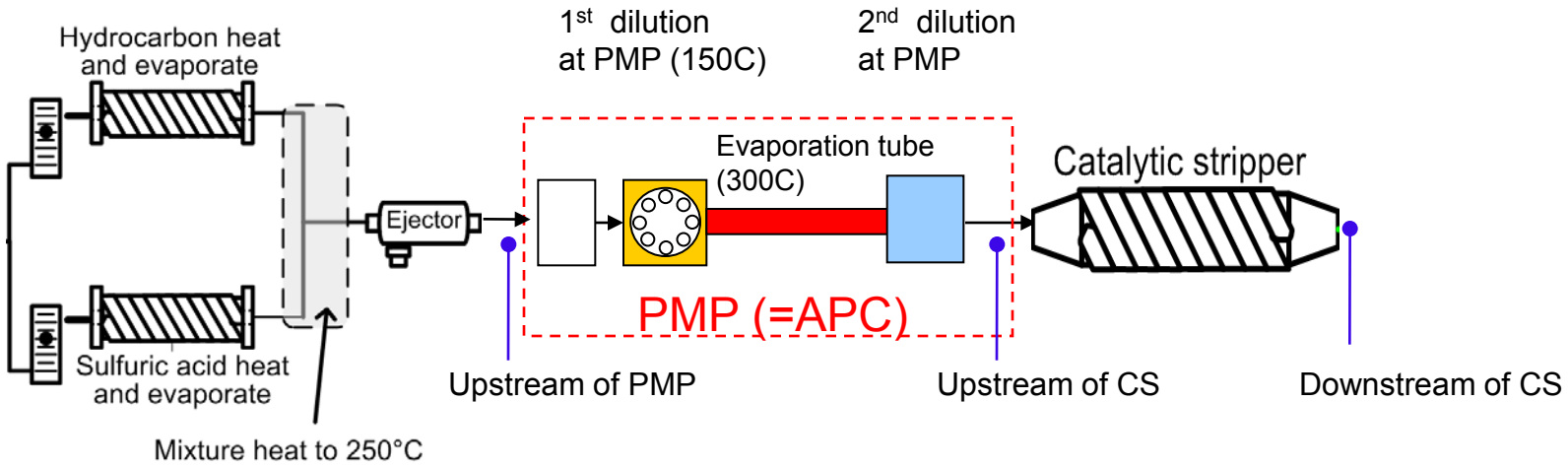
- **Downstream of PMP system**
  - 3790 and 3772 agree – no particles between 10 and 23 nm
  - 3025A and 3776 agree and read progressively higher than 3772 and 3790 as time goes on – particles forming between 3 and 10 nm
  - Same trend at 100 and 500 dilution ratio
- **Downstream of CS**
  - In first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



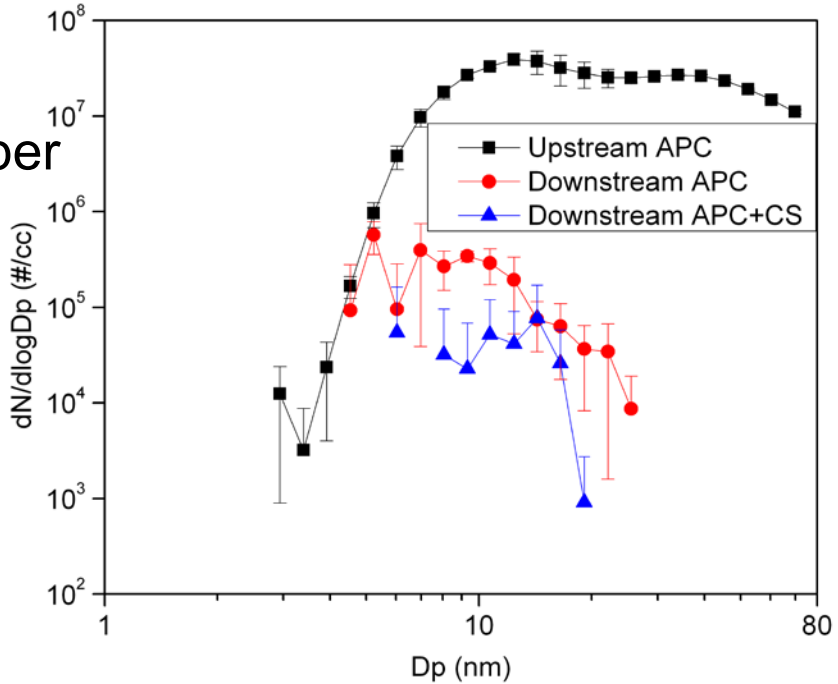
- Much lower concentrations than at 74%
  - Downstream of PMP system
    - In first time window, DR = 500
      - 3790 and 3772 agree – no particles between 10 and 23 nm
      - 3776 and 3025A read much higher and disagree – many particles below lower cutoff size of these instruments, 2.5 to 3 nm
    - 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

Lab test (smilar to Swanson and Kittelson)



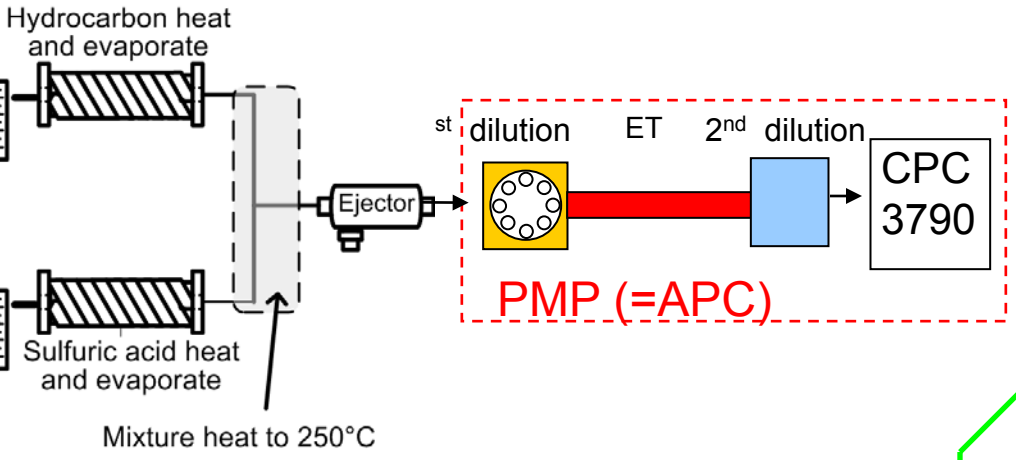
Penetration efficiency by total particle number

	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%

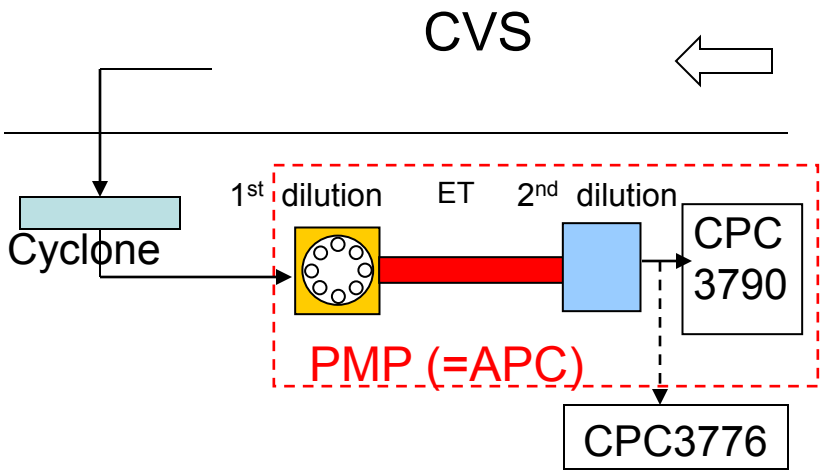


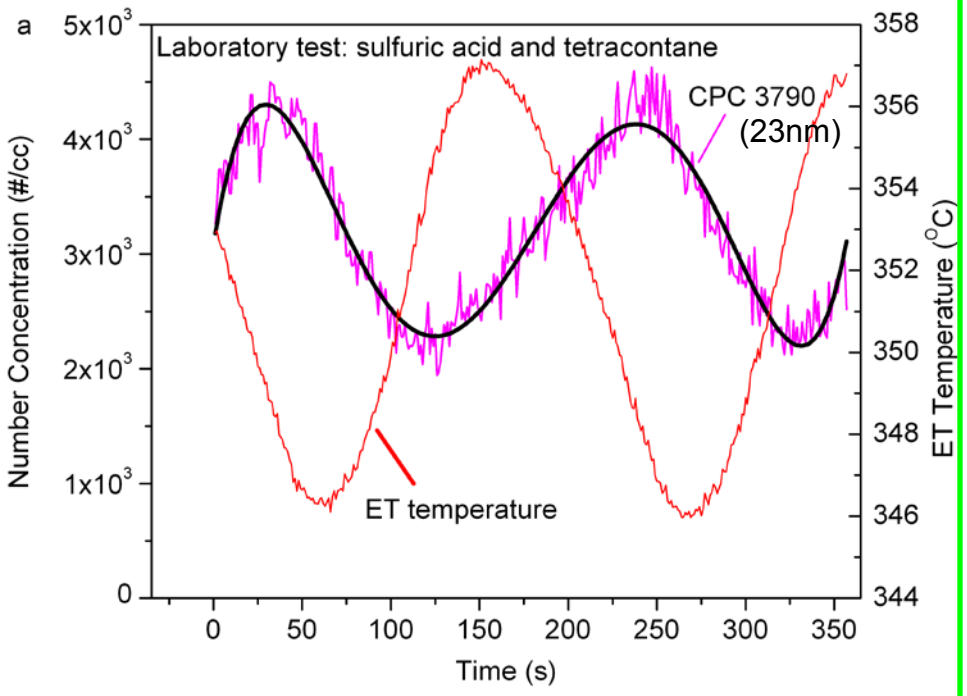
APC ET temperature oscillation

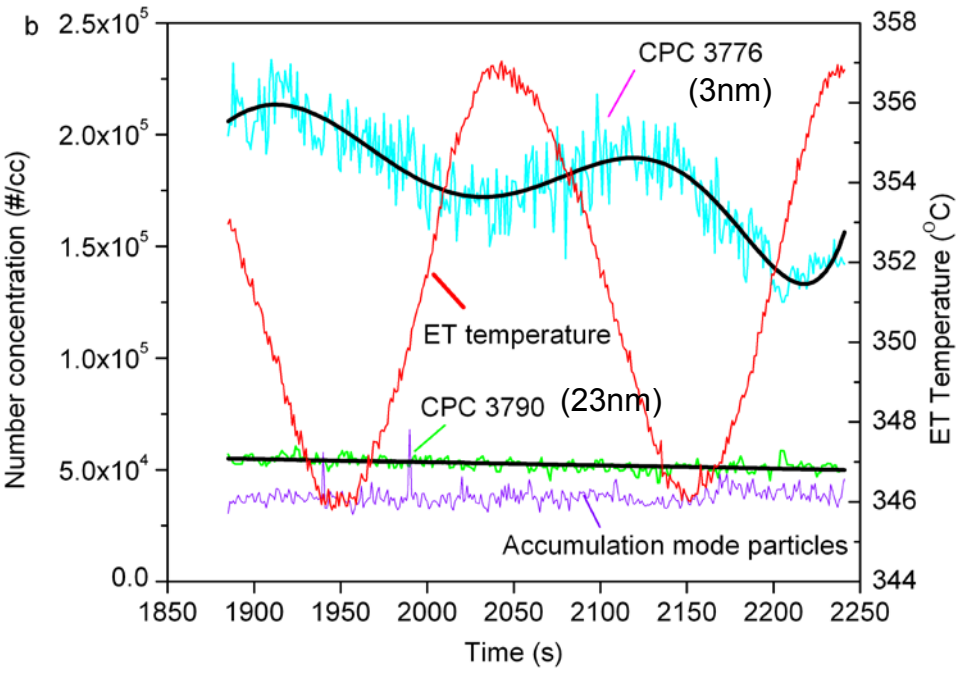
Lab test



Chassis test (74% load)







Conclusion

- Volatile remover such as 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 fluctuated 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.

Acknowledgements

- **CARB**
  - For funding and instruments.
  - A. Ayala and J. Herner for encouraging this study.
- **AVL LIST GmbH Inc.**
  - Providing an 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)

Five 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). 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). Evaluation of the European PMP Methodologies during On-Road Testing: Focus on Real Time Data Analysis, *Aerosol Science and Technology*, 2011, submitted
- 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

Thank You