



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

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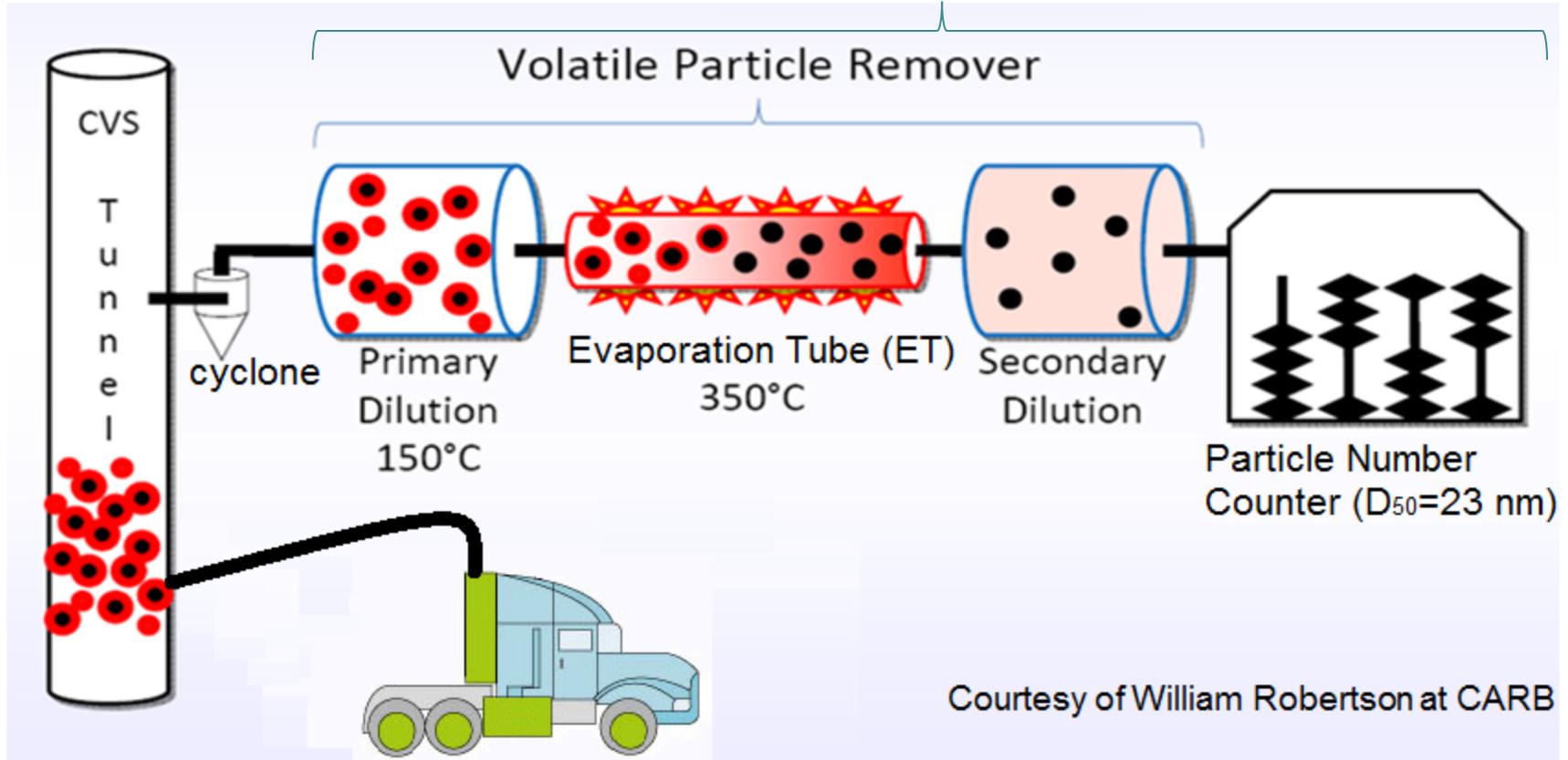
David B. Kittelson  
[University of Minnesota](#)

Shaohua Hu and Tao Huai  
[California Air Resources Board](#)



# Particle measurement programme

## PMP system

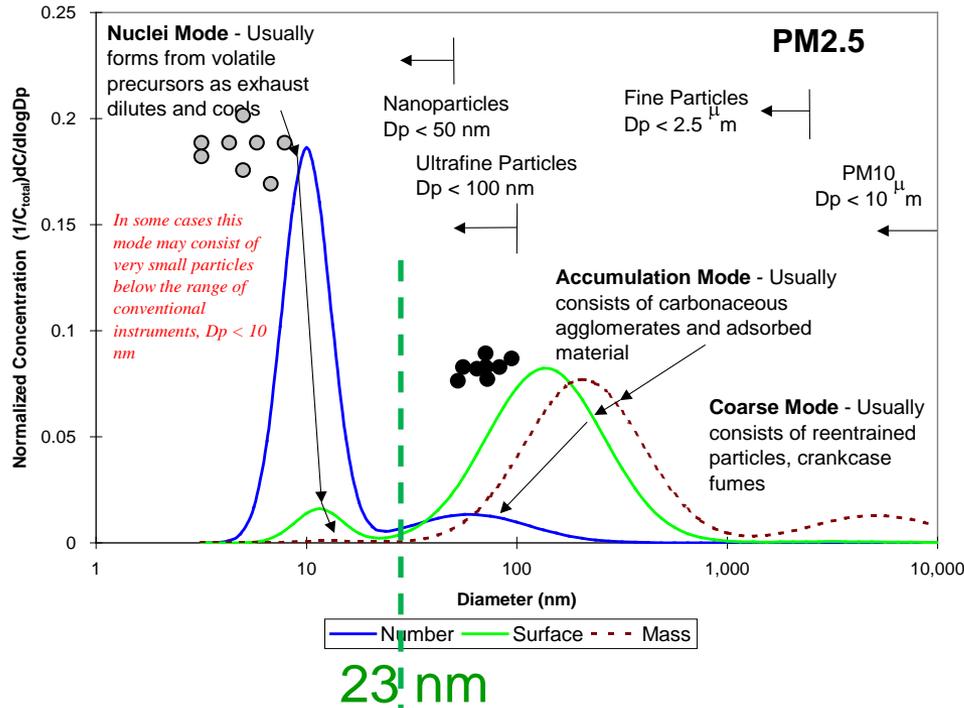


Courtesy of William Robertson at CARB

Red: Semivolatile particles

Black: Solid (mostly soot) particles

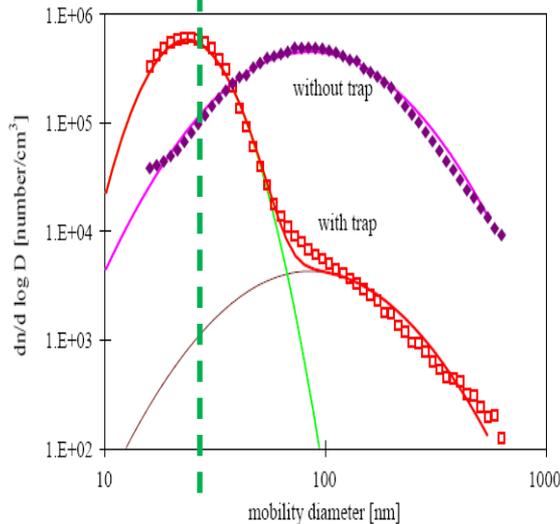
# Why only particles larger than 23nm?



- $D_{50}=23$  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)

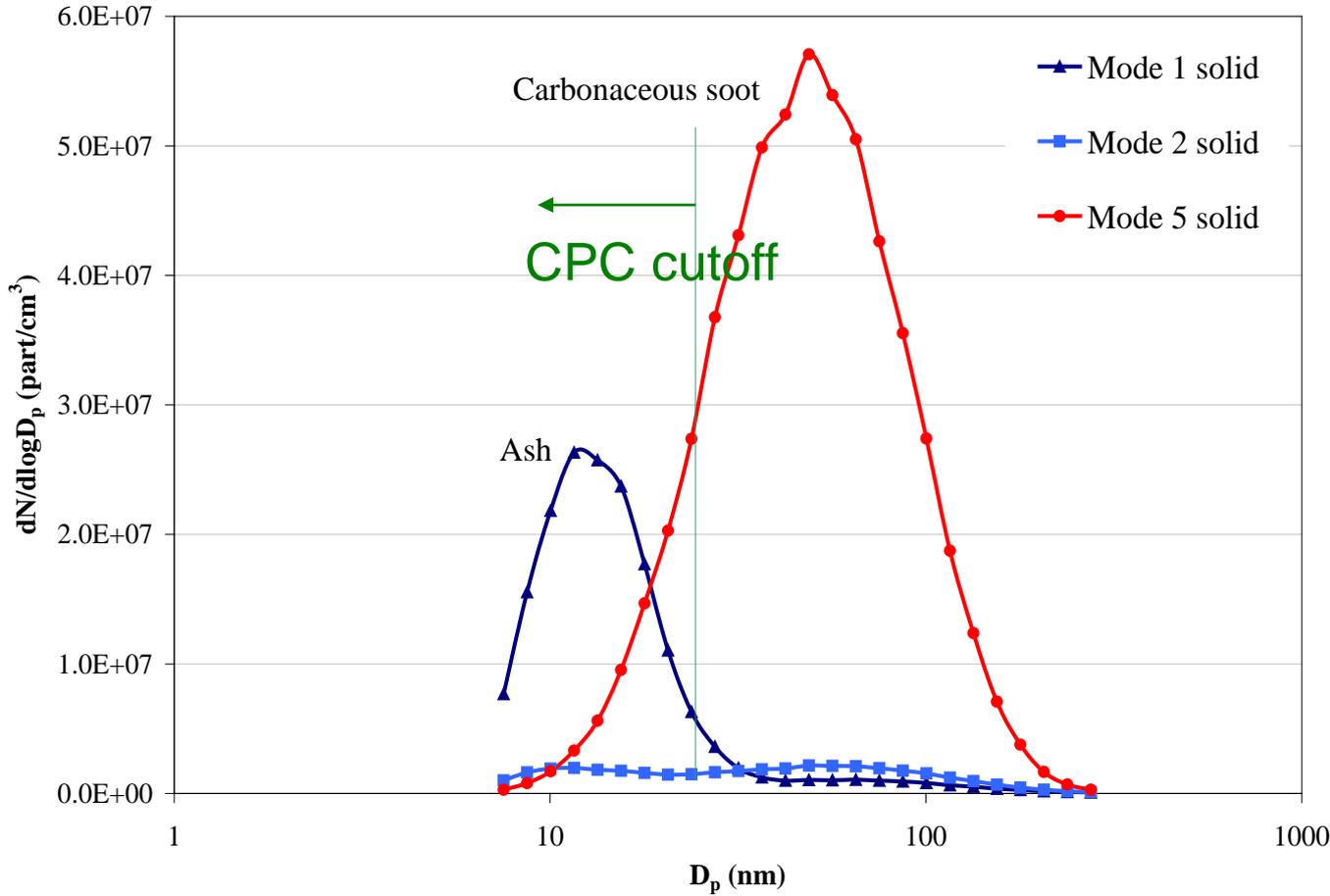
Figures courtesy of H. Burtscher (2005)



# Issues with not counting sub 23nm particles



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

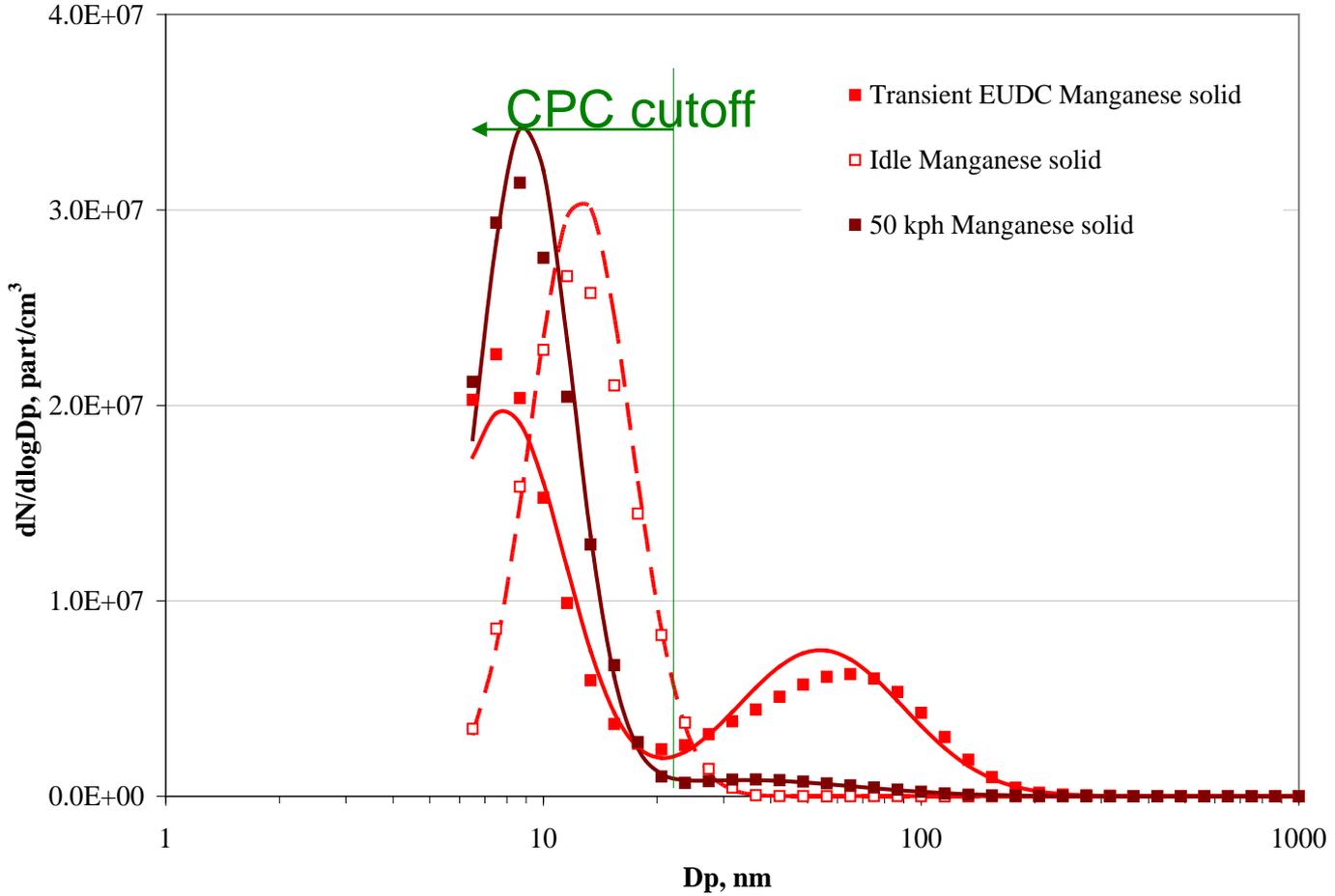


Cummins 2004 ISM engine, BP 50 fuel, AVL modes

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

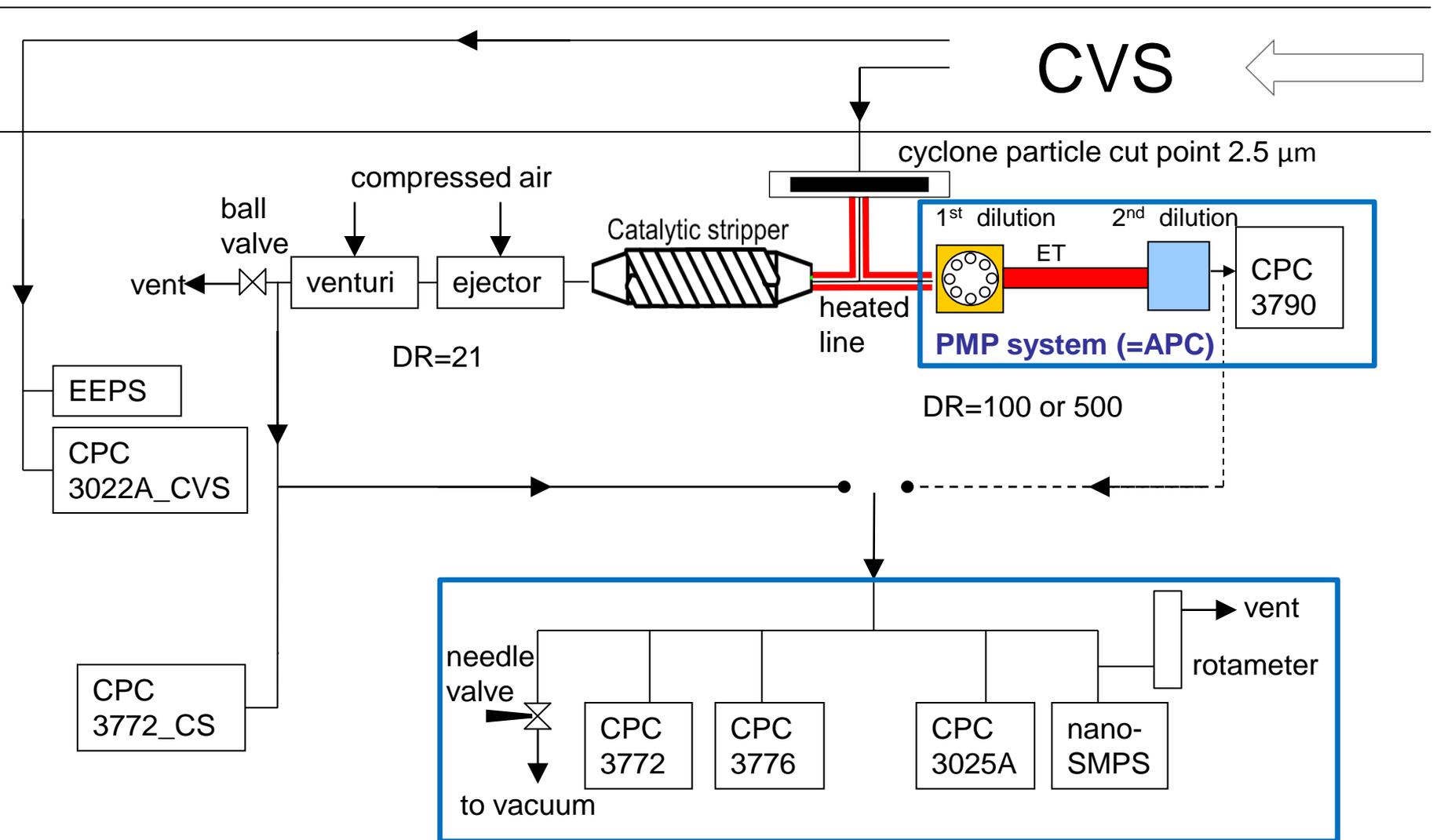


# Test conditions

- 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



# Chassis test

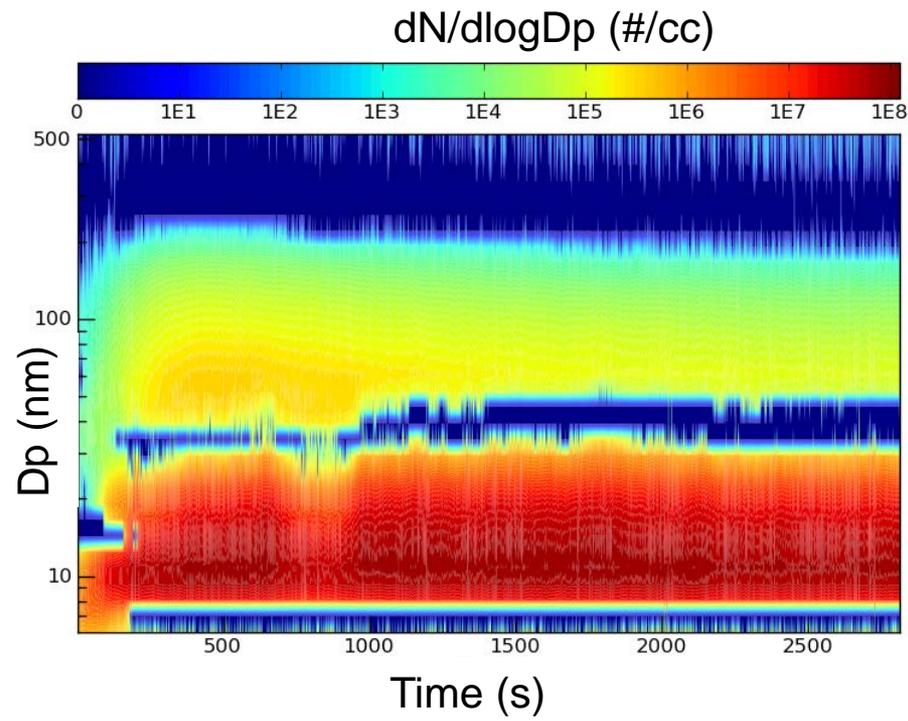


Alternate between the APC and CS



# CVS particle size dist. measured by EEPS

74% engine load

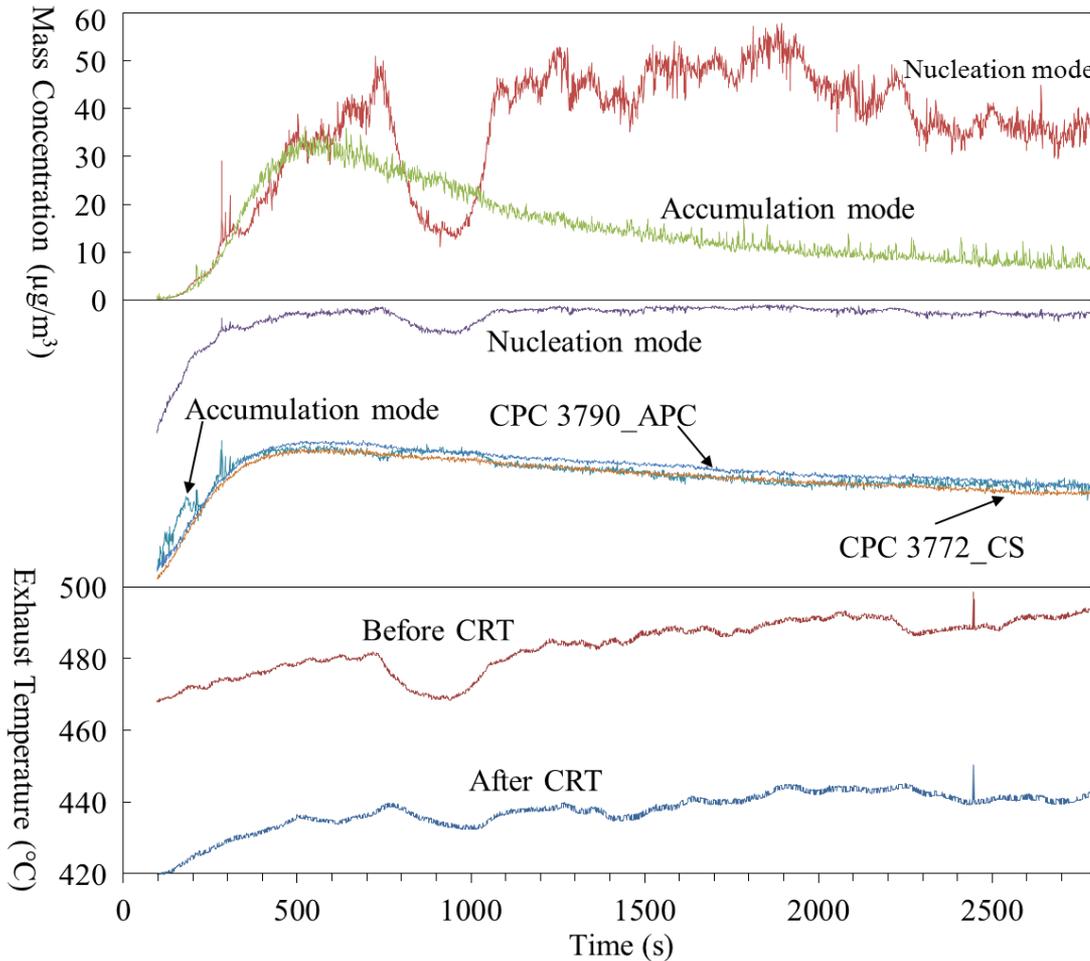


26% engine load

EEPS data near noise level at 26% engine load



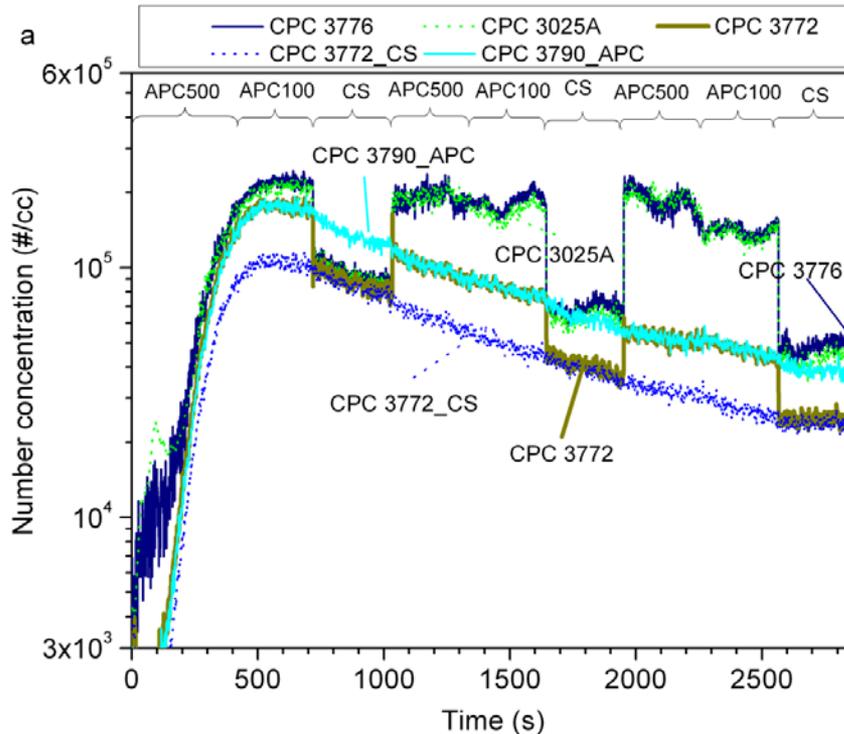
# The PMP compliant system closely tracks the accumulation mode (74% load)



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



# Comparison of instruments at 74% load cruise

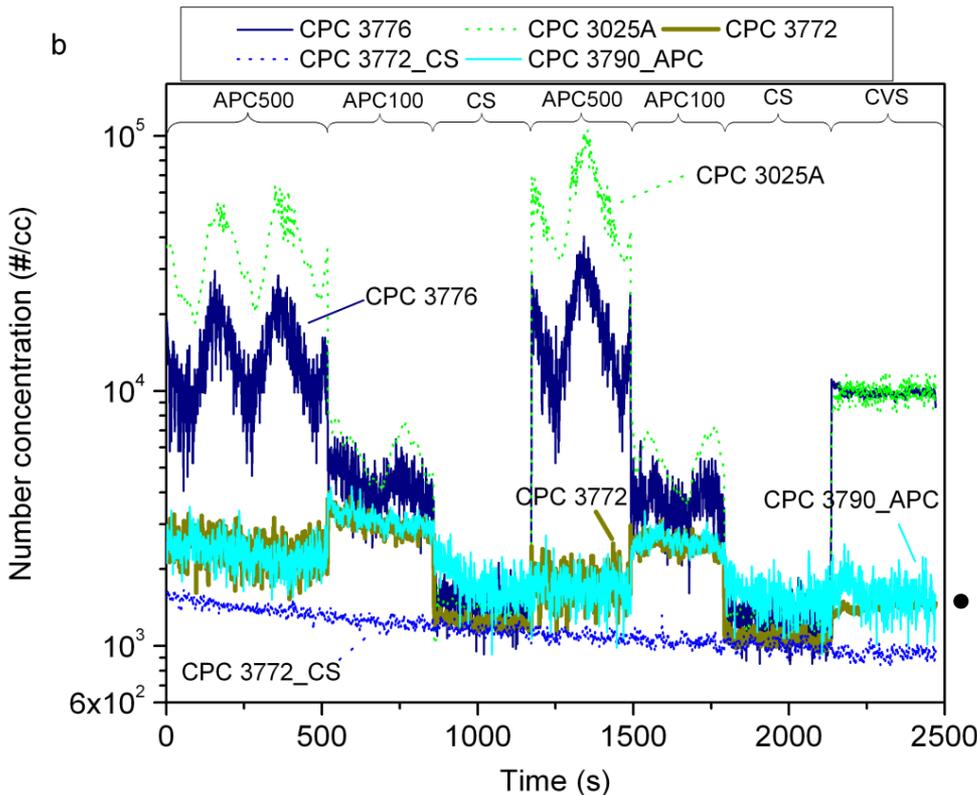


CPC	D <sub>50</sub> (nm)
3790_APC	23
3772_CS	10
3025A	3
3772	10
3776	2.5

- 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



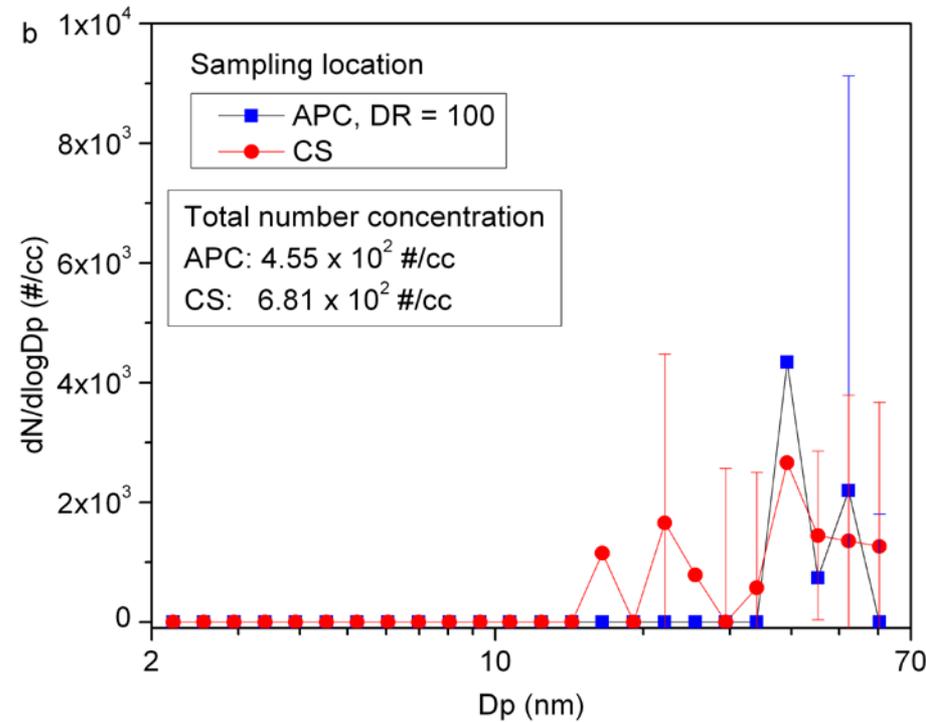
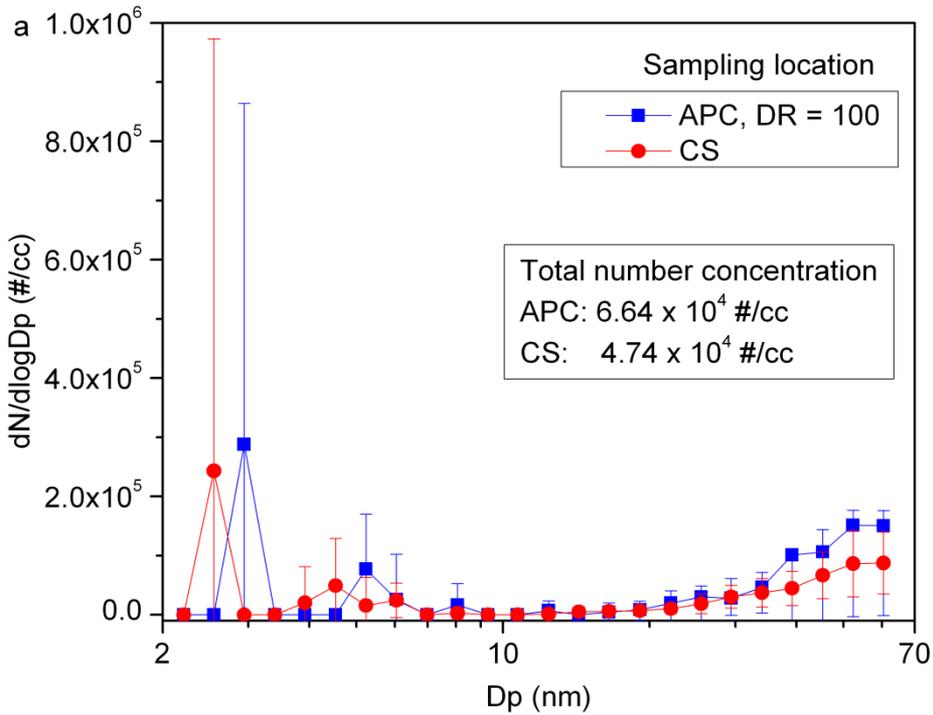
- Much lower concentrations than at 74%
  - Downstream of PMP system
    - In first time window, DR = 500
      - 3790 and 3772 agree – no particles between 10 and 23 nm
      - 3776 and 3025A read much higher and disagree – many particles below lower cutoff size of these instruments, 2.5 to 3 nm
  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



# Nano SMPS measurement

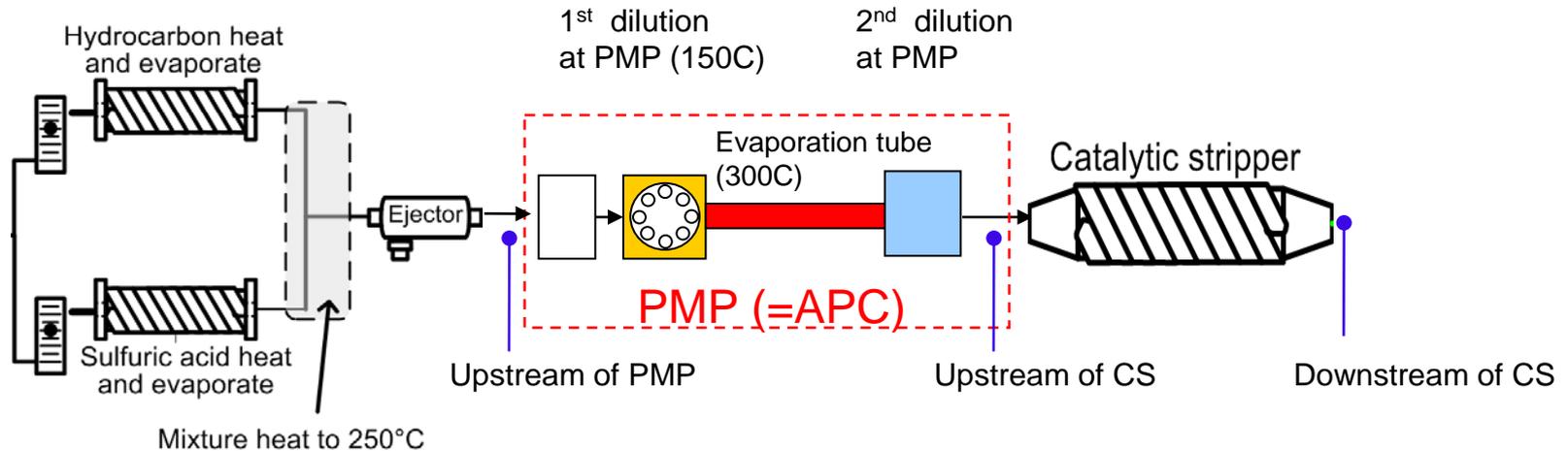
74% load

26% load



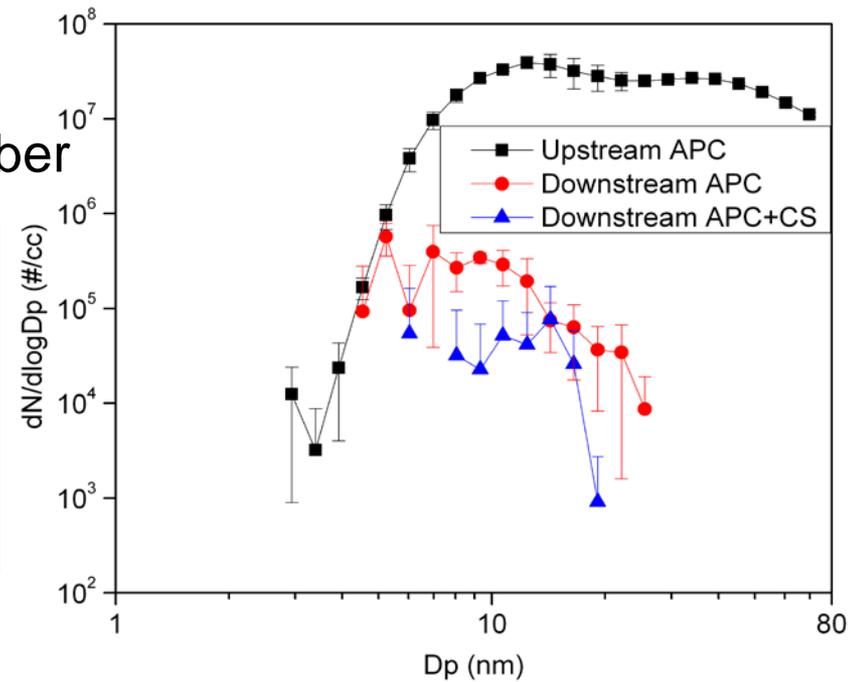


# Lab test (similar to Swanson and Kittelson)



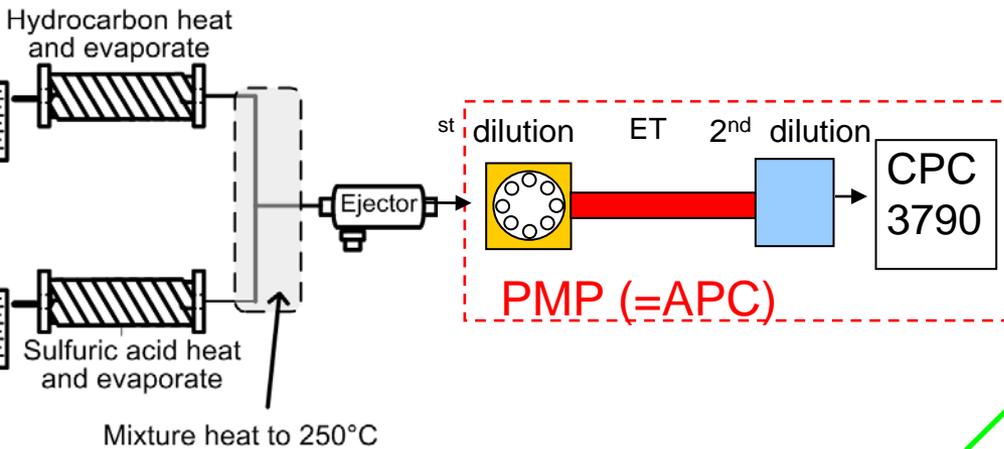
## Penetration efficiency by total particle number

	PMP(=APC)	CS
<b>H<sub>2</sub>SO<sub>4</sub>+HC</b>	0.6%	0.55%
H <sub>2</sub> SO <sub>4</sub>	0.1%	0%
HC (C <sub>24</sub> or C <sub>40</sub> )	1%	0%

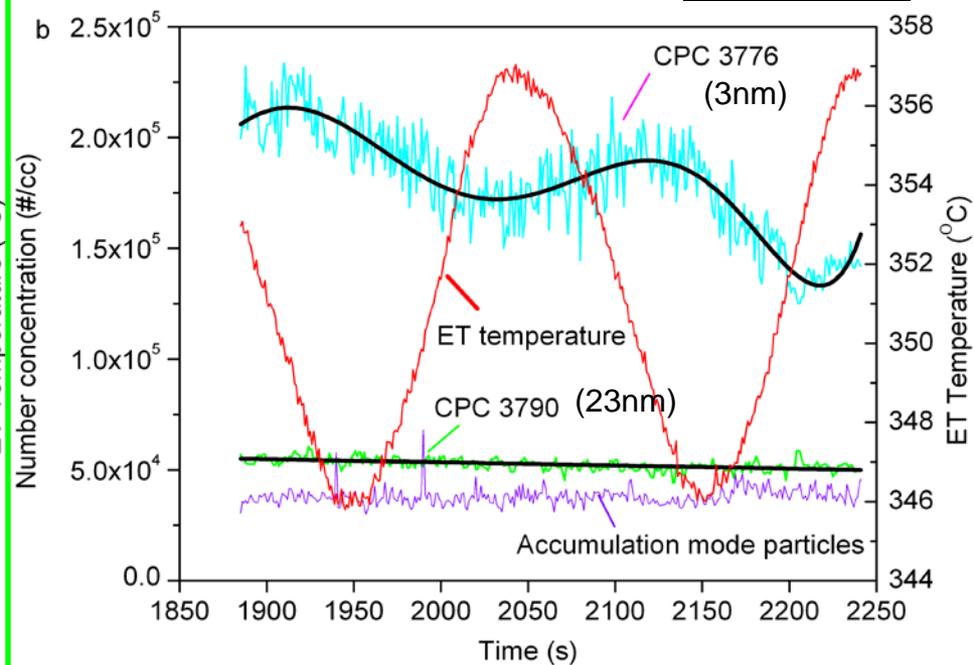
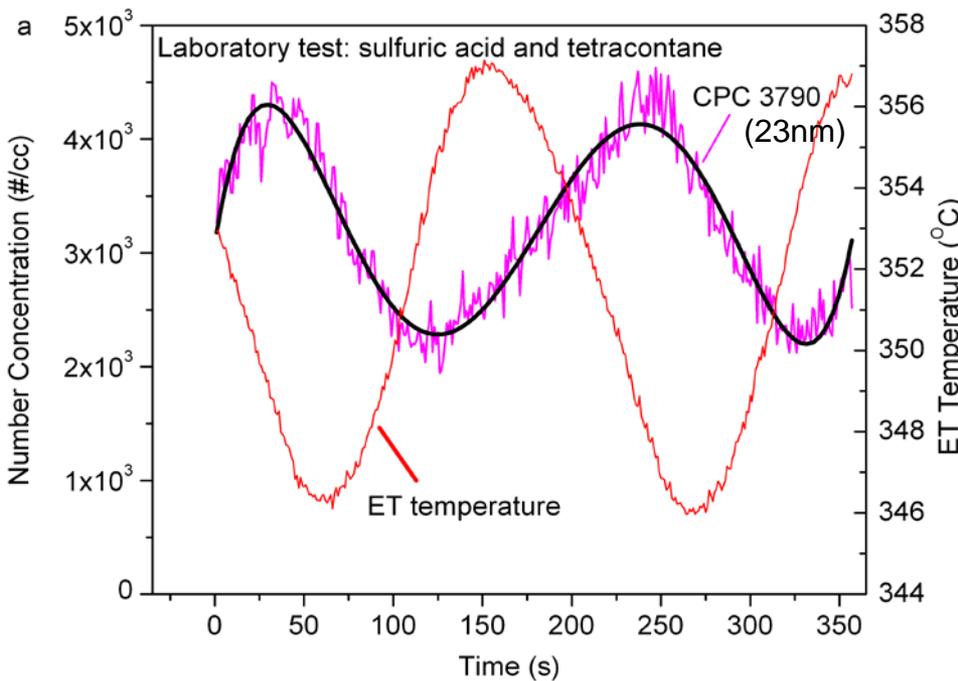
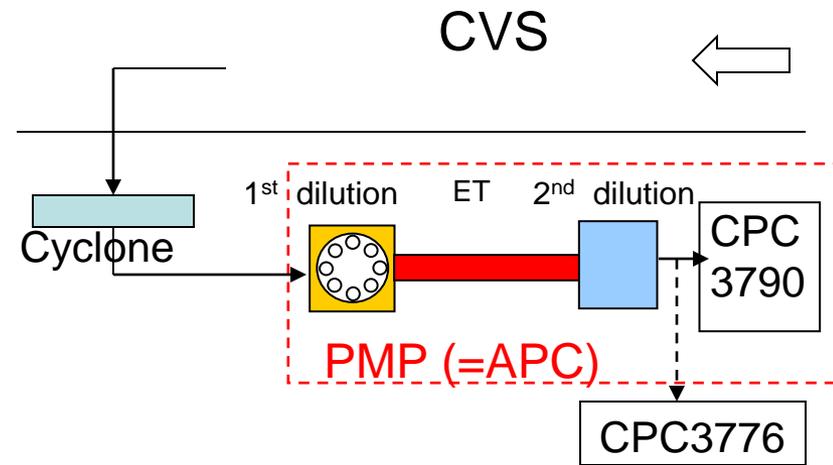


# APC ET temperature oscillation

## 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  $D_{50}=23\text{nm}$ , 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= $10\text{nm}$ ?
- 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.
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  - 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)



## 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