Issues associated with solid particle measurement

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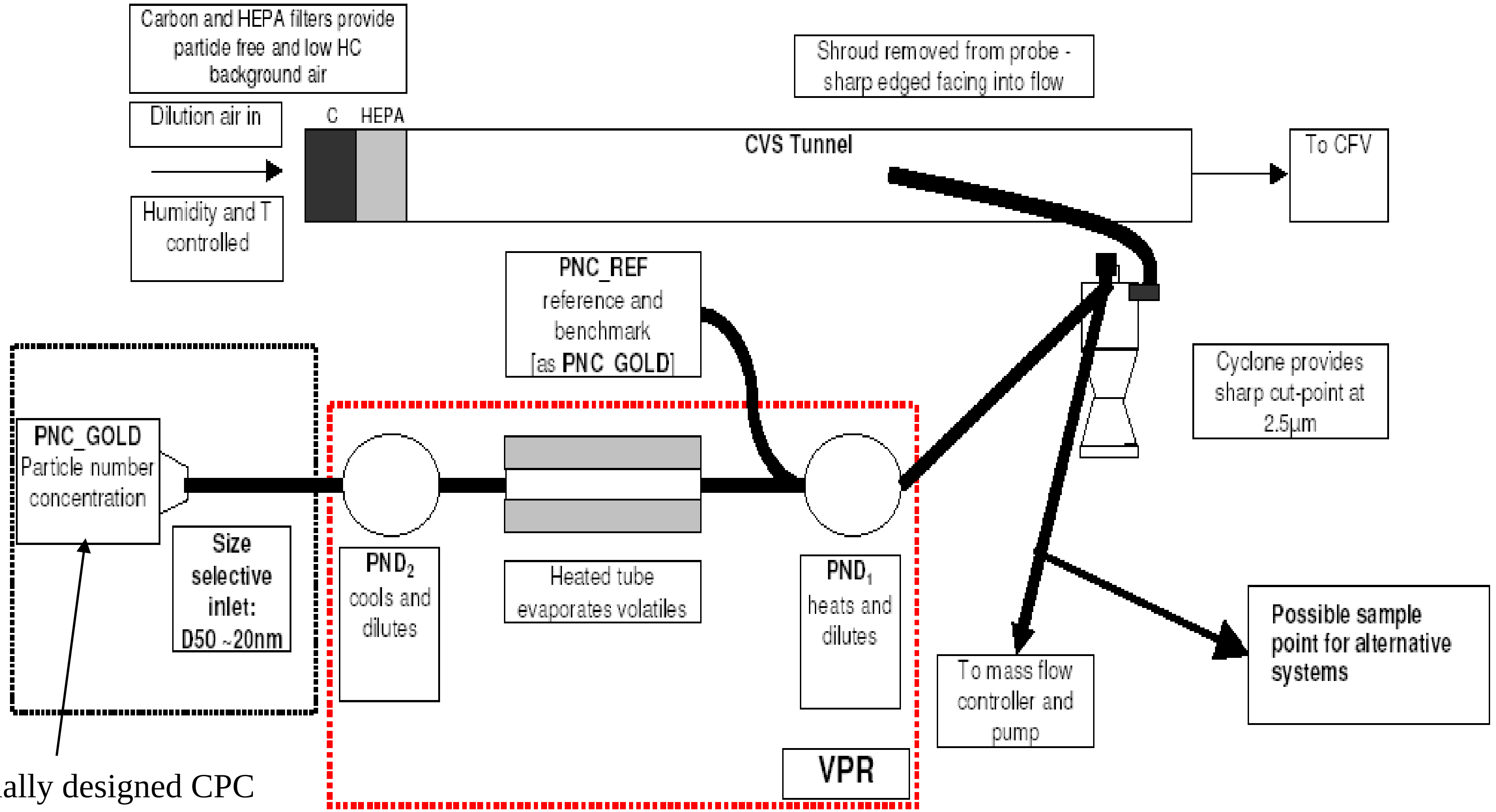
Conclusions

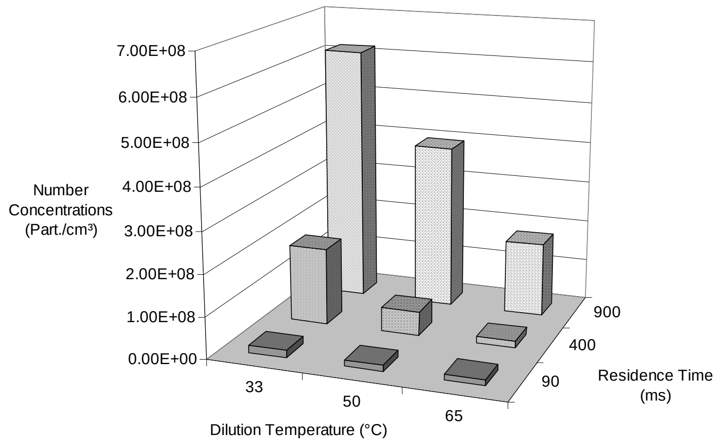
- Current PMP method regulates "solid" particles larger than 23 nm
  - For engines equipped with particle filters regulating to 23 nm effectively regulates all sizes
  - Under extreme conditions false counts of nucleated semi-volatile have been observed
  - For engines without filters (advanced fuels, 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
  - 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 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

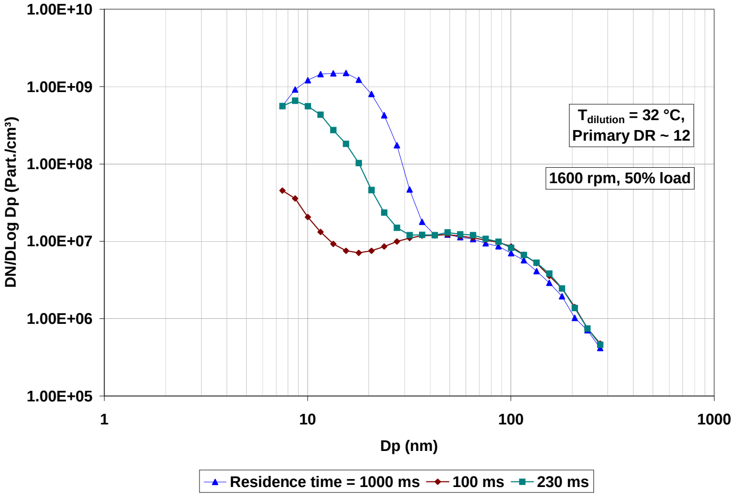
PMP number measurement system

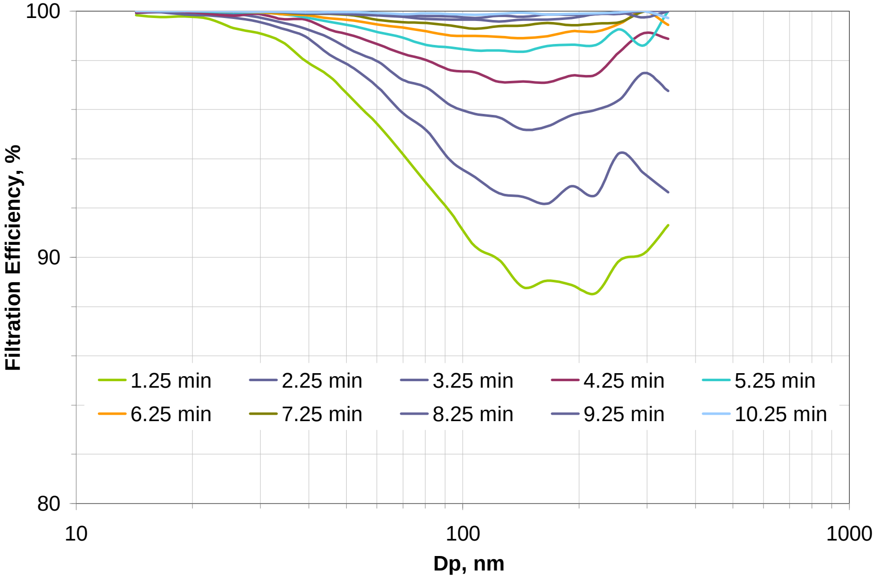


A specially designed CPC with a lower size cutoff of 23 nm is used

Why solid, why only larger than 23 nm?

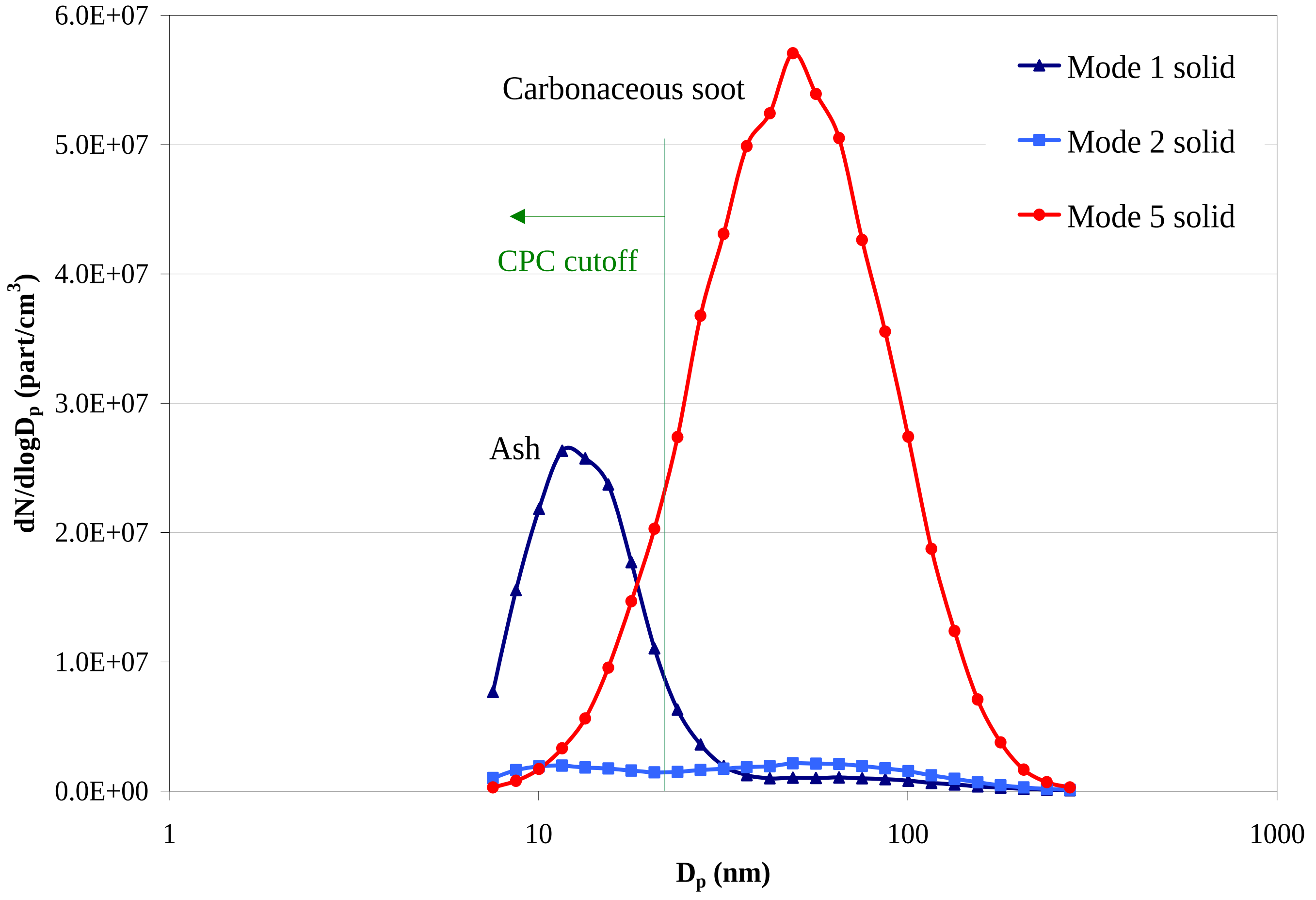






- The concentration of volatile nucleation mode particles is very dependent on sampling conditions
- Most of these particles are smaller than 23 nm
- If the engine is fitted with a particle filter particles below 50 nm or so are very effectively removed
- Thus regulating solid particles above 23 nm is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

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

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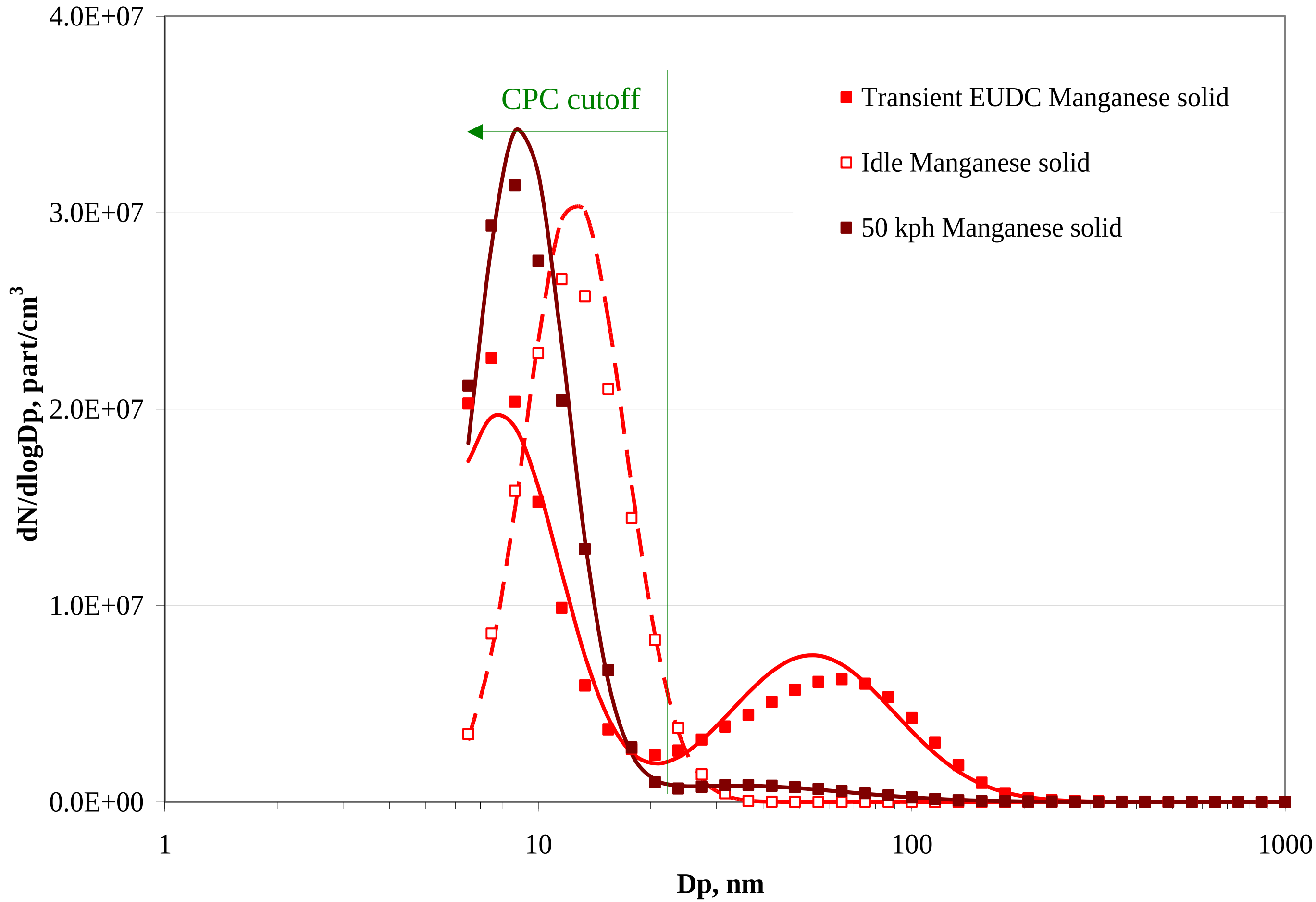
Spark ignition engines can also produce tiny solid nanoparticles, especially with metal additives



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

Three recent 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, Kent C., Thomas D. Durbin, Heejung Jung, Ajay Chaudhary, David R. Cocker III, Jorn D. Herner, William H. Robertson, Tao Huai, Alberto Ayala, and David Kittelson, 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.

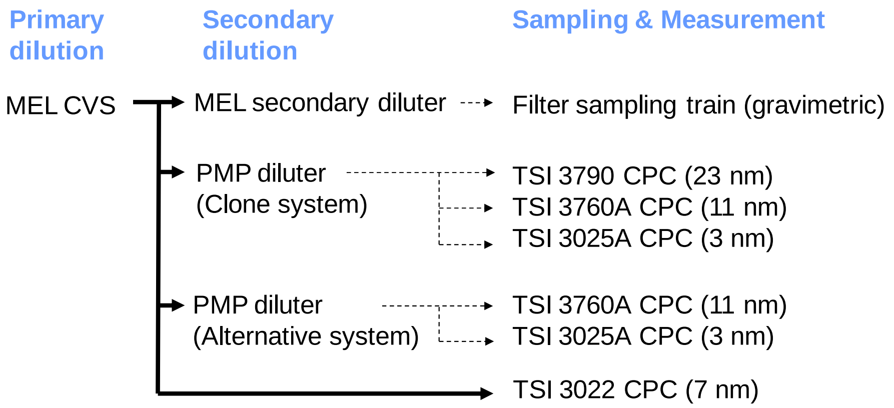
  - Zheng, Zhongqing, Kent C. Johnson, Zhihua Liu1 Thomas D. Durbin, Shaohua Hu, Tao Huai, David B. Kittelson, Heejung S. Jung, 2011. Laboratory and chassis dynamometer evaluation of an European PMP compliant particle number measurement system and catalytic stripper for measuring diesel solid nanoparticles, submitted to *Aerosol Science and Technology*.

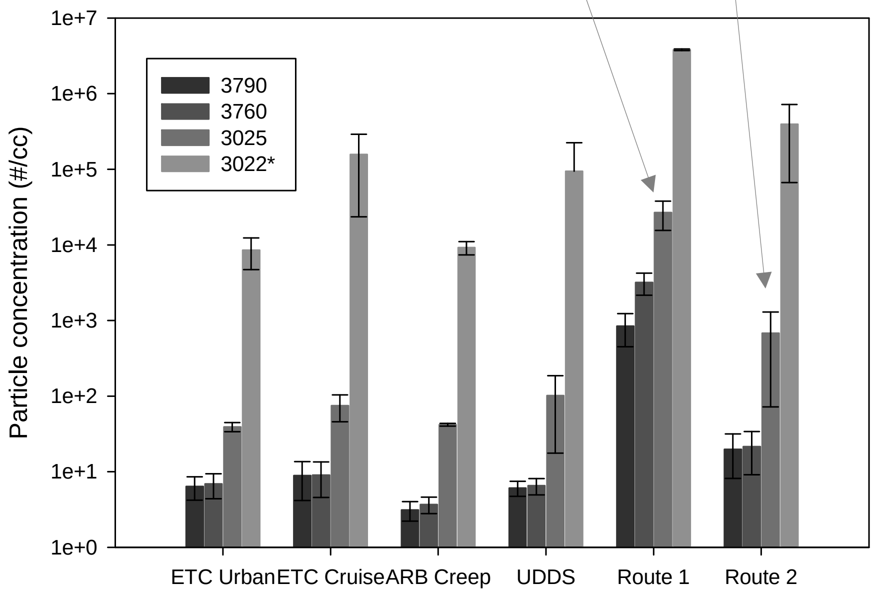
- Work done at the University of Minnesota, CDR
  - Swanson, Jacob and David Kittelson, 2010. Evaluation of thermal denuder and catalytic stripper methods for solid particle measurements, *Journal of Aerosol Science*, Volume 41, Issue 12, Pages 1113-1122.

On road tests using PMP protocol show unexpected "solid" particles and many particles below 23 nm

A heavy-duty truck equipped with a CRT was tested on road and on a chassis dynamometer

- It showed large concentrations of "solid" particles below 23 nm at high load conditions
- These conditions favor sulfate particle formation.
- Filtration efficiency for particles below 23 nm should be very high.





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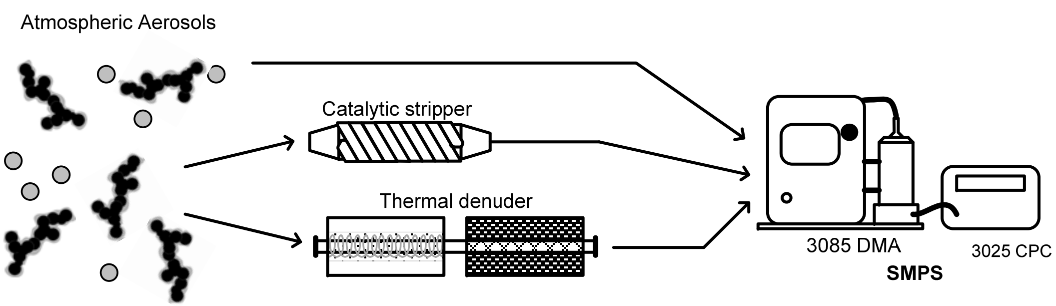
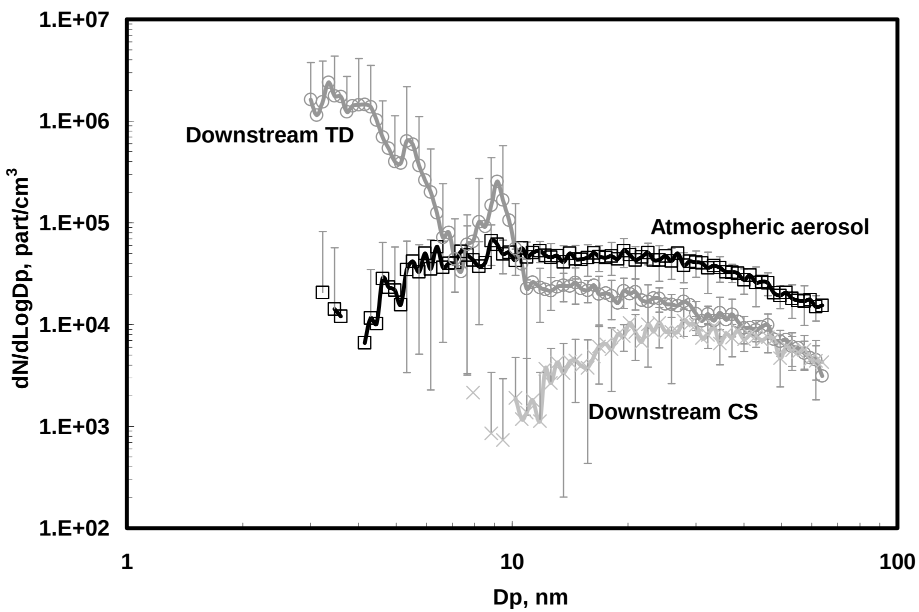
Performance of thermal denuder and catalytic stripper with ambient aerosol





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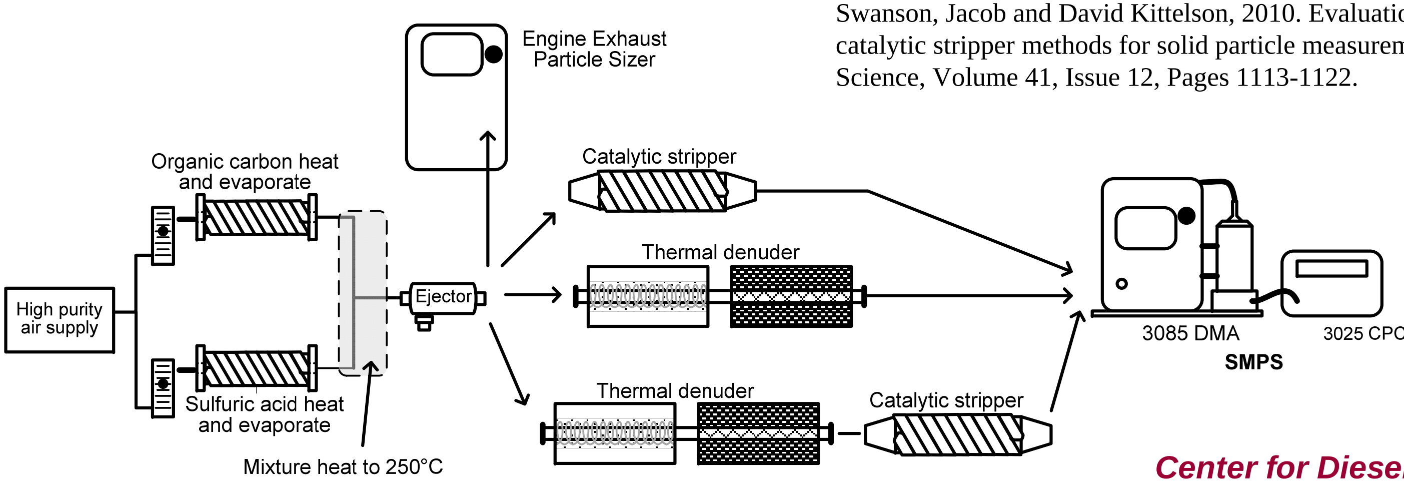
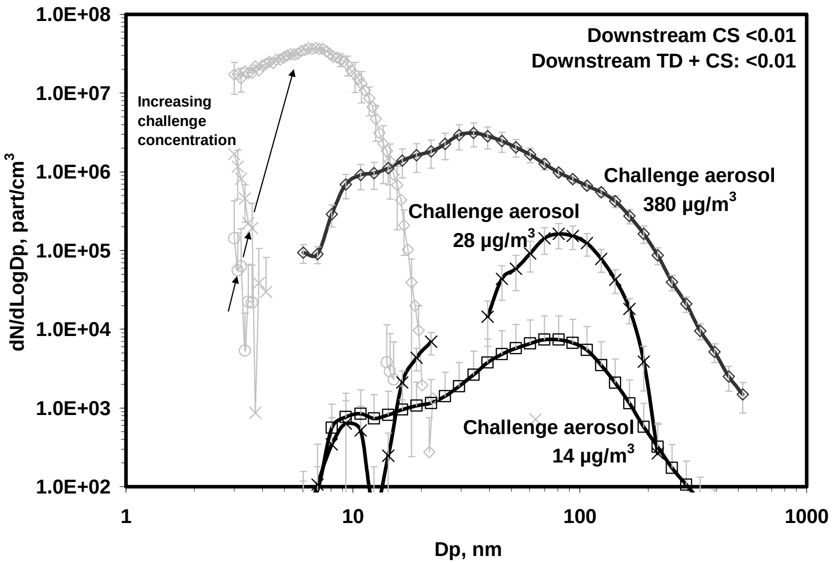
Evaluating thermal denuder and catalytic stripper with pure semi-volatile challenge aerosols

- The test compounds
  - Sulfuric acid (reagent grade 99.9% pure, 18 M)
  - Solid tetracosane ($C_{24}H_{50}$) flakes (reagent grade 99.9% pure)
  - Dioctyl sebacate liquid ($C_{26}H_{50}O_4$) (technical grade 90% pure)
- An evaporation and condensation technique was used to generate nanometer sized particles.
  - Test compounds were heated in an alumina combustion boat to various temperatures ranging from 120°C to 250°C.
  - Temperatures were chosen such that the saturation vapor pressure above each compound was roughly the same, so that the evaporation rates would be similar and they would be similar mole fractions of each in the carrier gas stream at the time they were mixed.
  - The vapor(s) were entrained with hot dry air, mixed and heated to 250°C, and then cooled by dilution with a dilution ratio of ~20:1.
  - The cooling causes the vapors to nucleate, forming a high concentration of nanoparticles composed of the evaporated compounds.

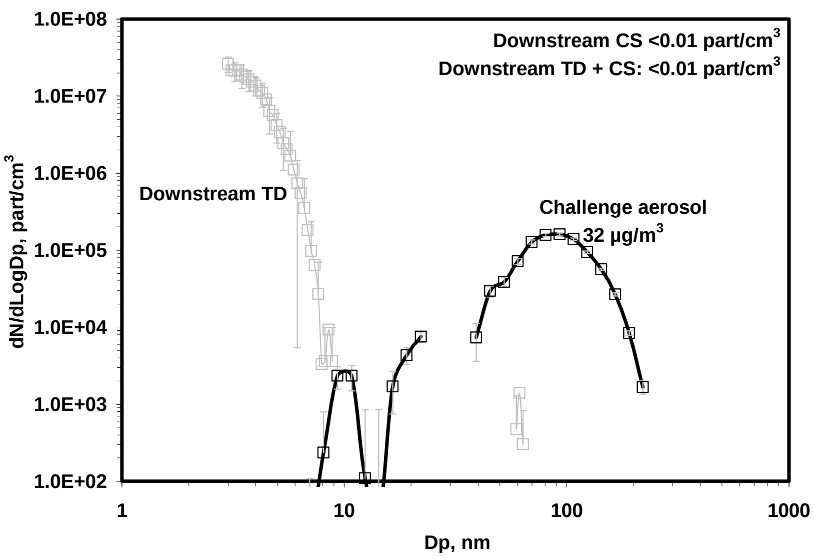
Swanson, Jacob and David Kittelson, 2010. Evaluation of thermal denuder and catalytic stripper methods for solid particle measurements, Journal of Aerosol Science, Volume 41, Issue 12, Pages 1113-1122.



Test of TD and CS with laboratory generated semi-volatile particles



- Pure tetracosane challenge aerosol
  - Wide range of concentrations
  - Particles form downstream of TD
  - No particle downstream of CS
  - No particles downstream of TD + CS – particles formed by TD volatile



- Tetracosane plus sulfuric acid challenge aerosol
  - Significant particle formation downstream of TD
  - No particle downstream of CS
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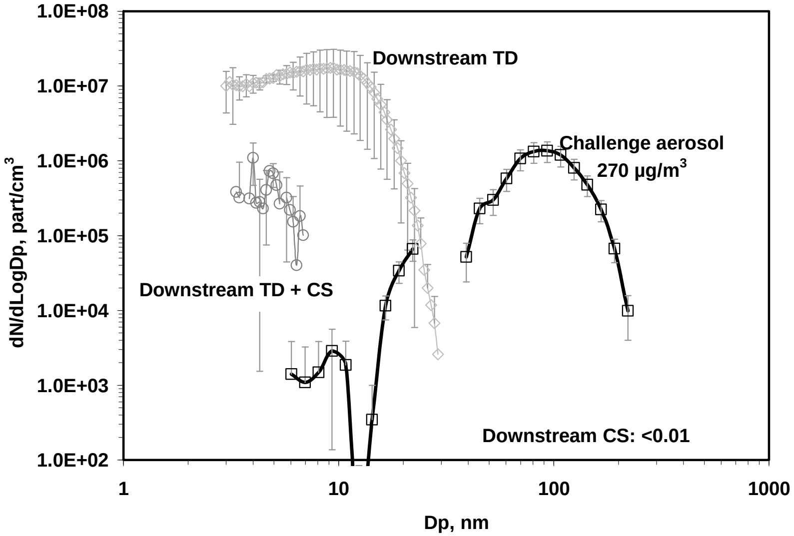

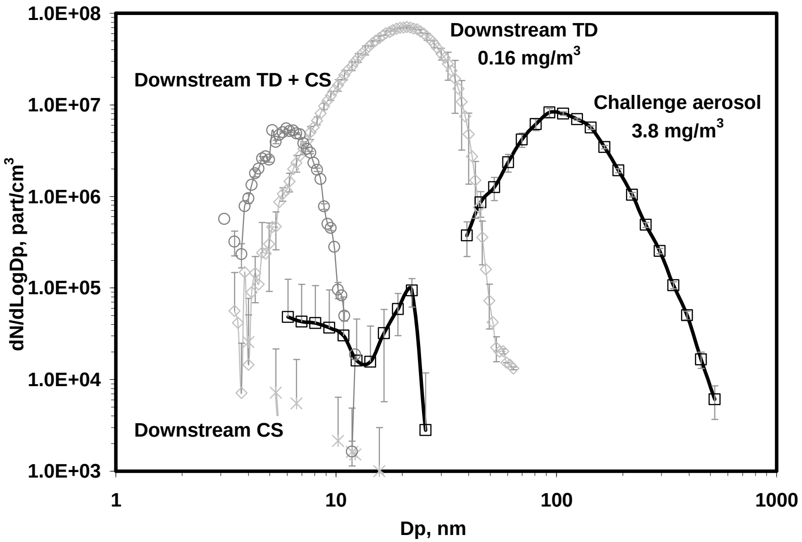

- Tetracosane plus sulfuric acid challenge aerosols
  - Higher challenge aerosol concentrations
  - Significant particle formation downstream of TD
  - A few particles downstream of CS at highest challenge aerosol concentrations
  - Particles downstream of TD + CS – particles suggesting solid particle formation by TD

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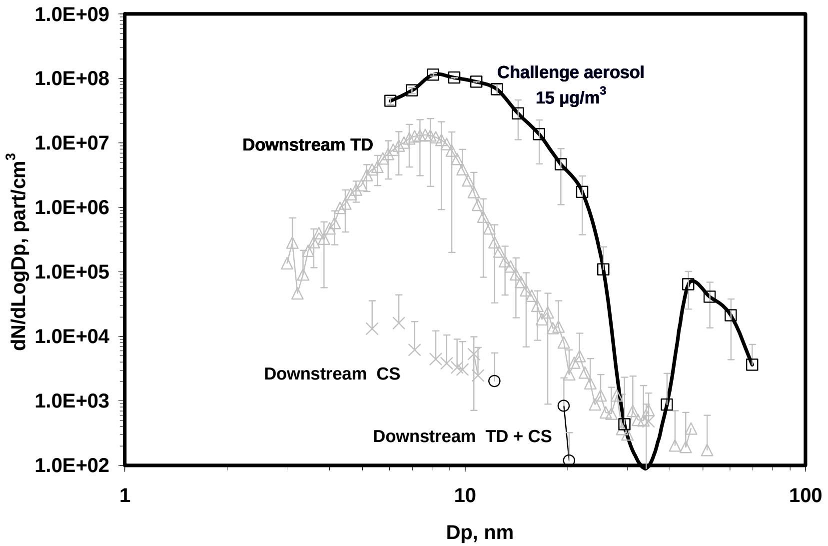
Acknowledgements

- All catalytic strippers used in this work were supplied by Martyn Twigg of Johnson-Matthey

Behaviour of oxygenated hydrocarbon in TD and CS



– Dioctyl sebacate ($C_{26}H_{50}O_4$) aerosol at low concentrations
– Particles formed downstream of TD
– Particles formed downstream of CS, but lower concentrations
– No significant evidence if particles downstream of TD + CS