Issues associated with solid particle measurement

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Outline

- Background
- UCR on-road and laboratory tests
- UMN laboratory tests
- Conclusions

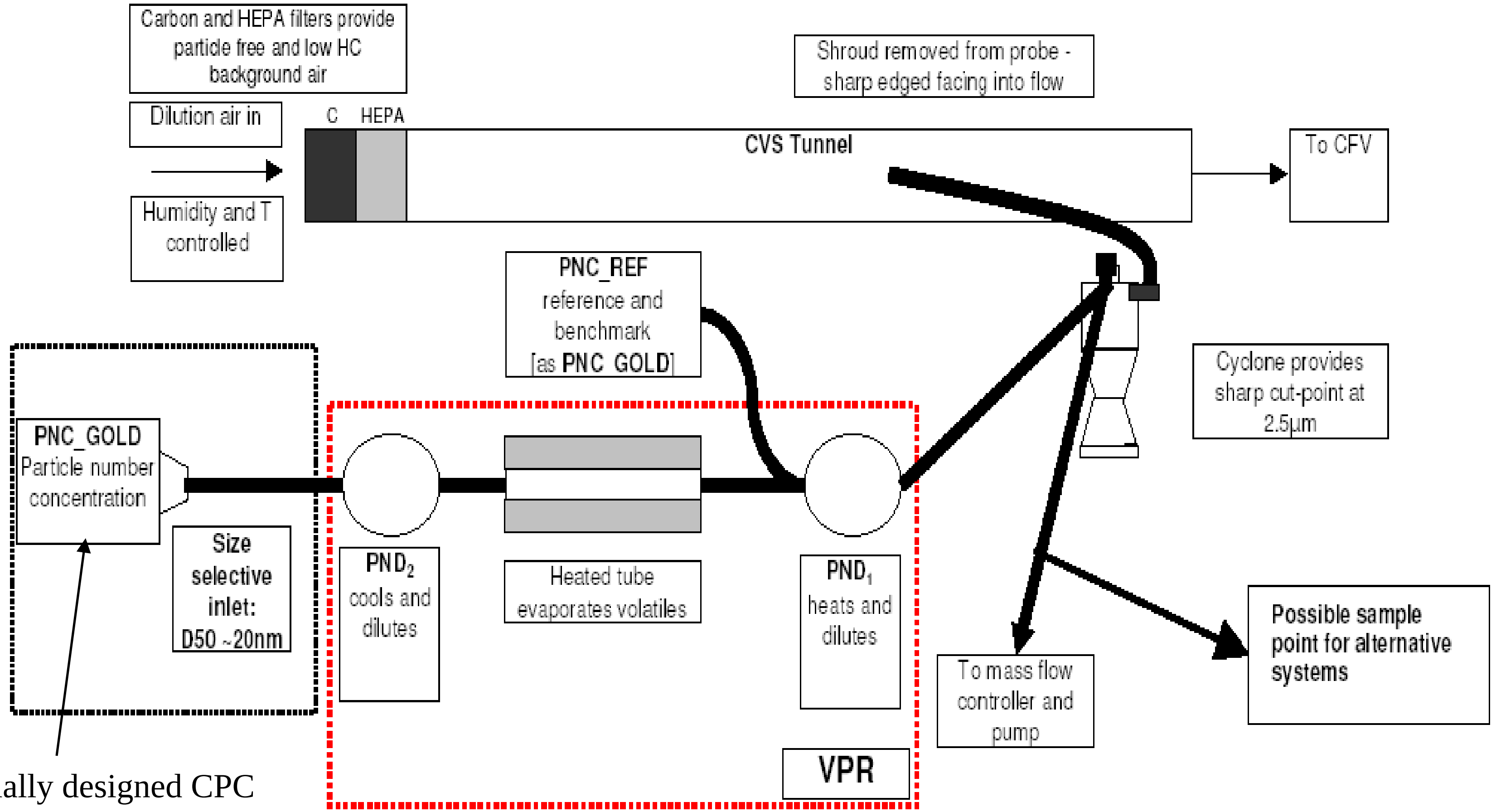
At very low emission levels number measurements have much better resolution than mass but..

- 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.
  - The next generation of high efficiency direct injection gasoline engines are challenged by the current standard even with the 23 nm limit
- An international solid number standard for aircraft emissions is being considered and is likely use a lower counting limit to 10 nm
- 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
  - Downstream nucleation and solid particle losses greatly reduced in new mini CS
  - Removal of sulfate or other low vapor pressure species critical

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

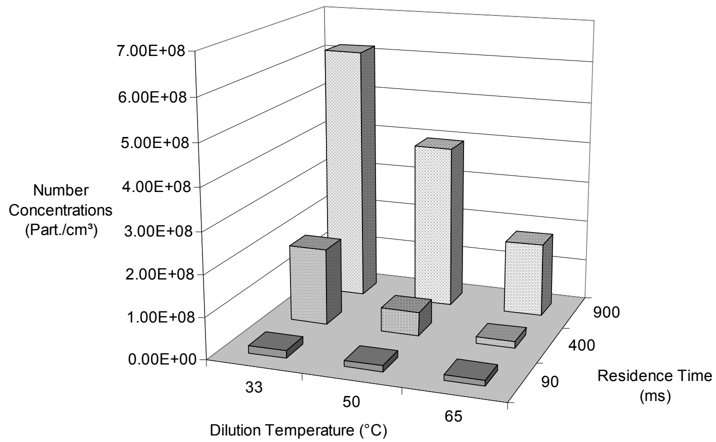
- Work done at University of California, Riverside, CE-CERT
  - Johnson, Kent C., Thomas D. Durbin, Heejung Jung, Ajay Chaudhary, David R. Cocker III, Jorn D. Herner, William H. Robertson, Tao Huai, Alberto Ayala, and David Kittelson, 2009. Evaluation of the European PMP Methodologies during On-Road 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 Liu, Thomas D. Durbin, Shaohua Hu, Tao Huai, David B. Kittelson, and Heejung Jung, 2011. Investigation of solid particle number measurement: Existence and nature of sub-23nm particles under PMP methodology, Journal of Aerosol Science 42 (2011) 883–897.
- 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.
  - Swanson, Jacob and David Kittelson, 2012. Evaluation of PMP APC and catalytic stripper methods for solid particle measurements, in preparation

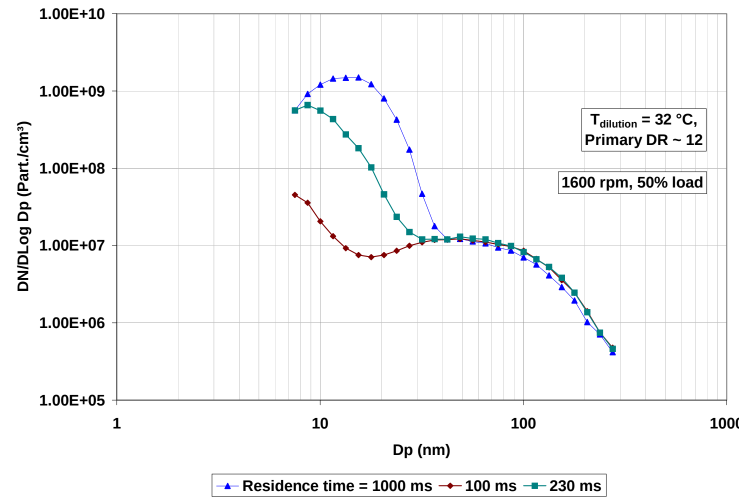
PMP number measurement system

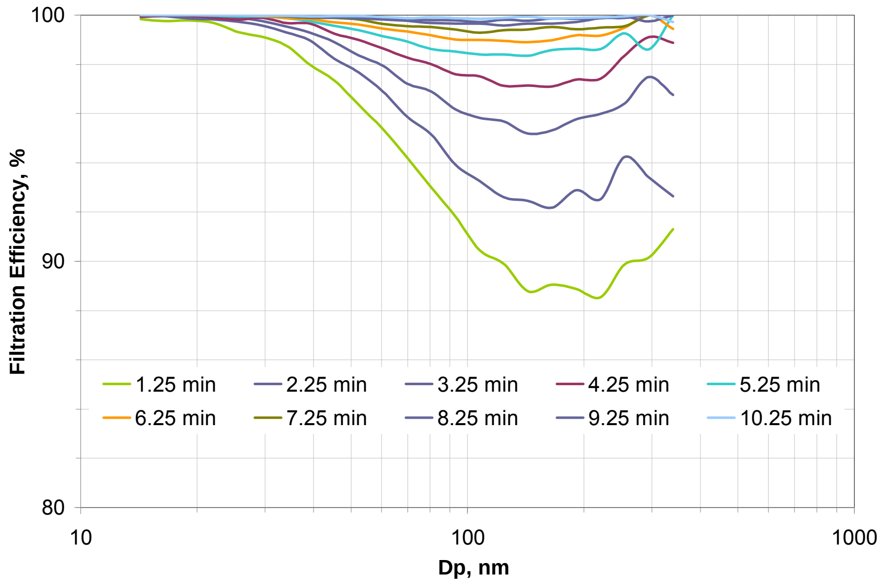


A specially designed CPC with a lower size cutoff of 23 nm is used

Why solid, why only larger than 23 nm?

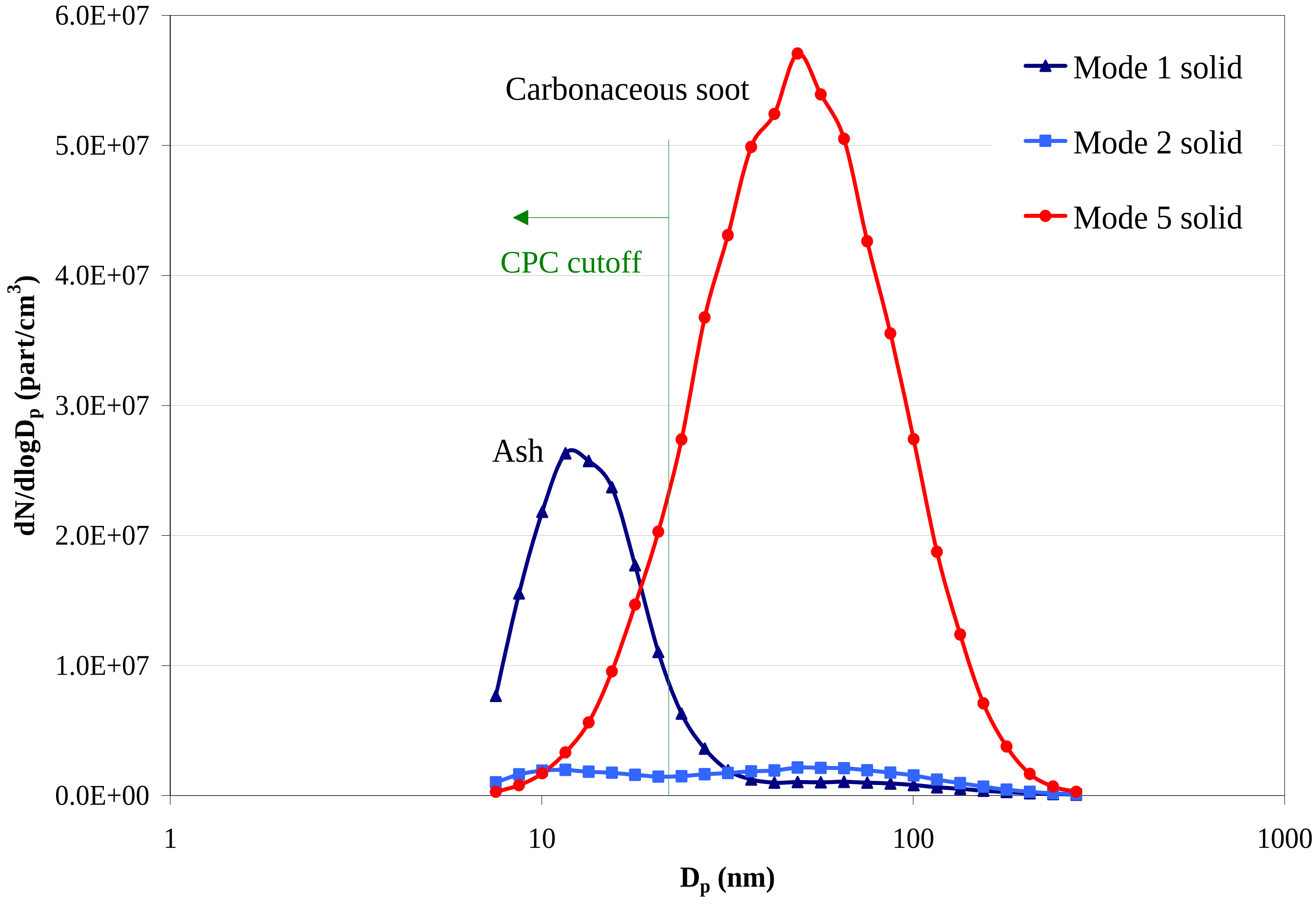






- The concentration of volatile nucleation mode particles is very dependent on sampling conditions
- Most of these particles are smaller than 23 nm
- If the engine is fitted with a particle filter particles below 50 nm or so are very effectively removed
- Thus regulating solid particles above 23 nm is 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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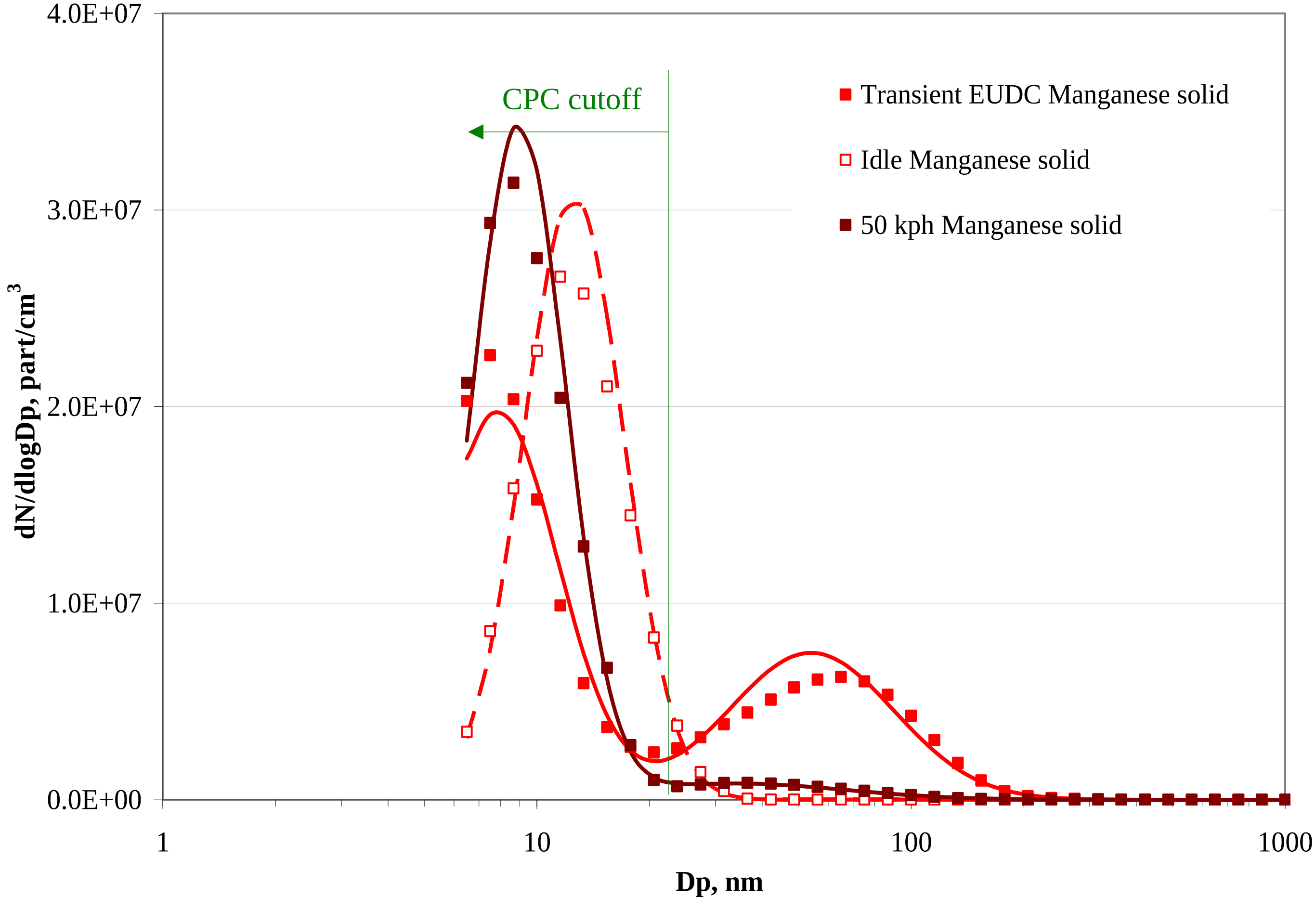
Spark ignition engines can also produce tiny solid nanoparticles, especially with metal additives



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.

Recently published results from SWRI show solid particles between 10 and 23 nm for a modern GDI car

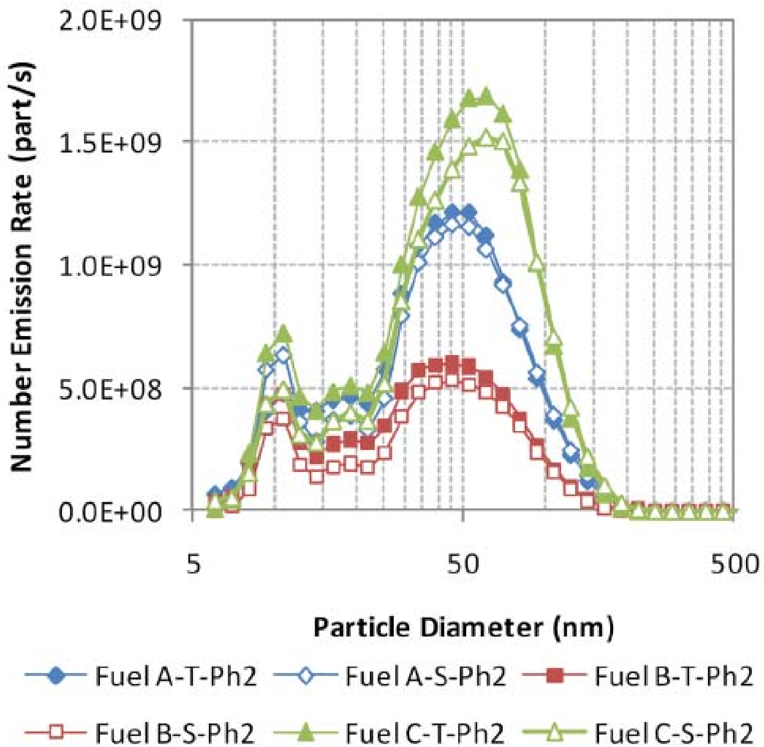


Figure 13. Phase 2 Total and Solid Particle Number-Weighted Size Distribution for Fuels A, B, and C

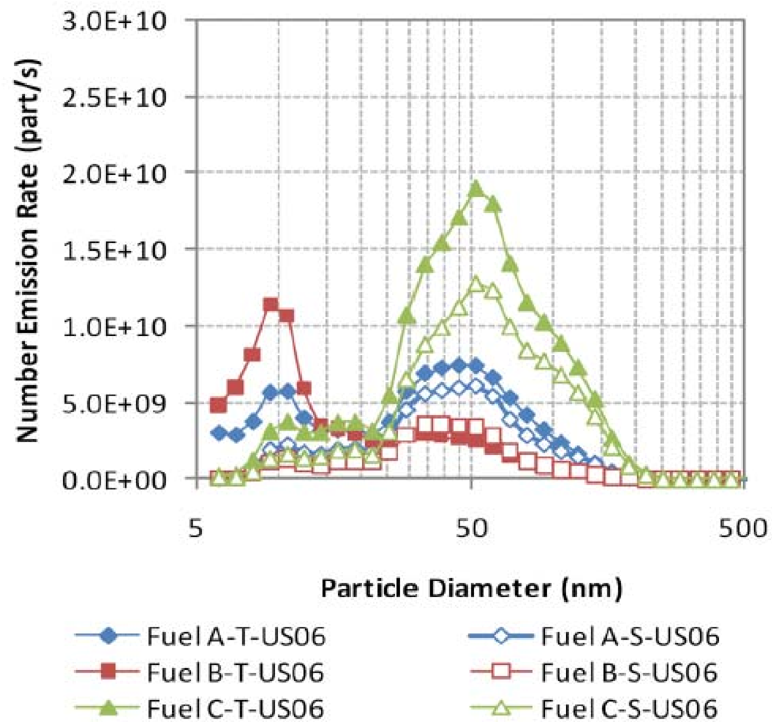
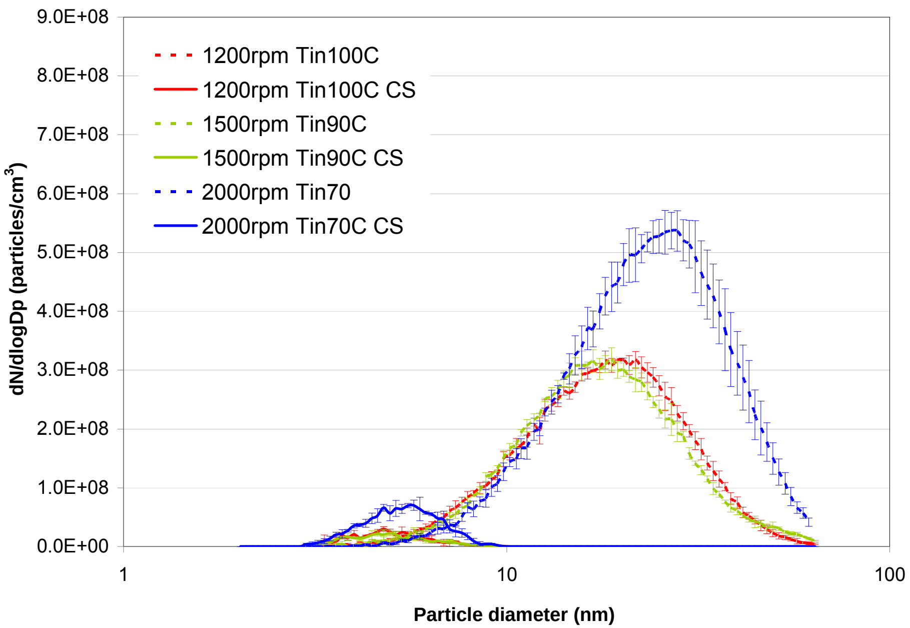
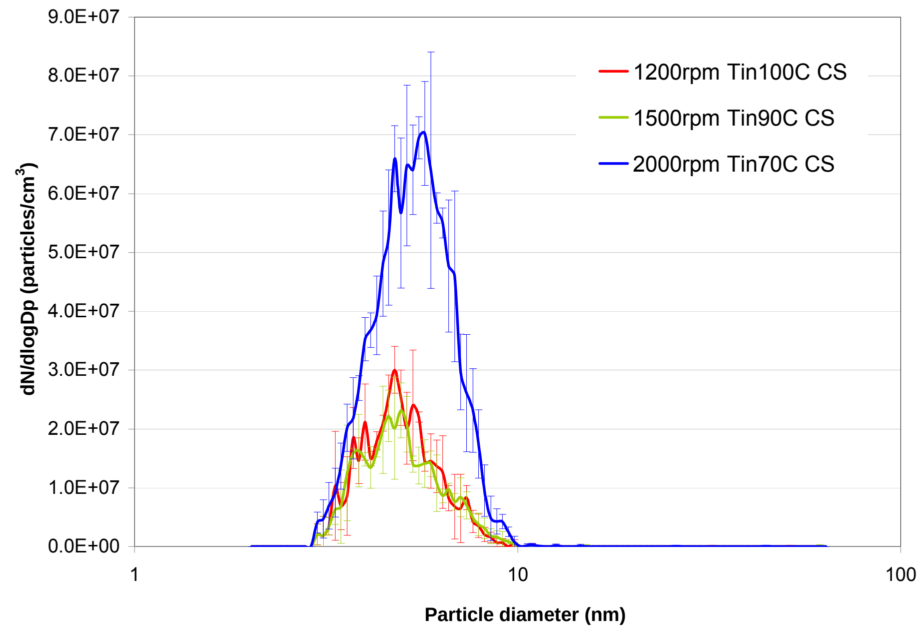


Figure 15. US06 Total and Solid Particle Number-Weighted Size Distribution for Fuels A, B, and C

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 running in pure HCCI mode shows no solid particles above 10 nm



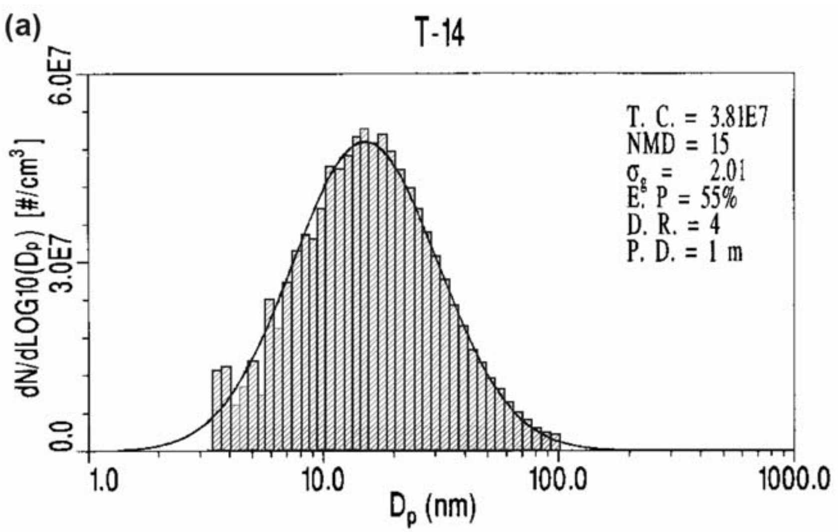


- Emissions depend upon speed, load, temperature – in-cylinder thermal processing
- Solid PN measured with catalytic stripper (CS) total PN without
- Right plot shows solid fraction on 10x expanded scale
- Most of the particles emitted are volatile but the solid ones are very small

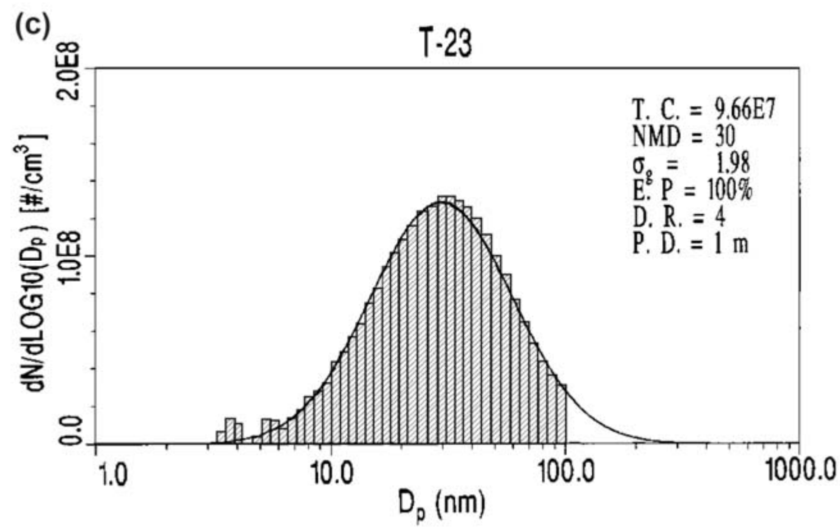
From: Bika, Anil, Wei Fang, Luke Franklin, Bin Huang, and David Kittelson, 2011. Particle Emissions from a Soot Free Engine, 15th ETH-Conference on Combustion Generated Nanoparticles, June 2011.

Using a 23 nm cut with aircraft plumes will lead to undercounting a significant fraction of the particles

78% below 23 nm



41% below 23 nm



Typical fast-scan size distributions measured from a J85-GE turbo-jet engine at various engine power settings:

Han, H.-S.; Chen, D.-R.; Pui, D.Y.H.; and Anderson, B.E. A nanometer aerosol size analyzer (nASA) for rapid measurement of high-concentration size distributions, Journal of Nanoparticle Research, v 2, n 1, p 43-52, March 2000

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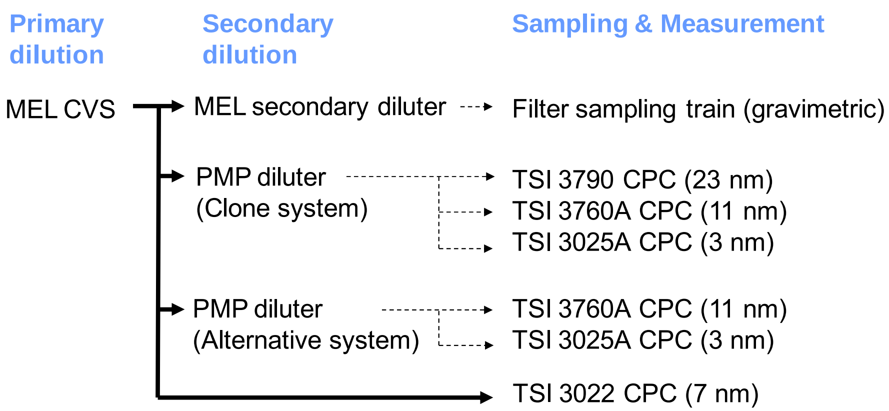
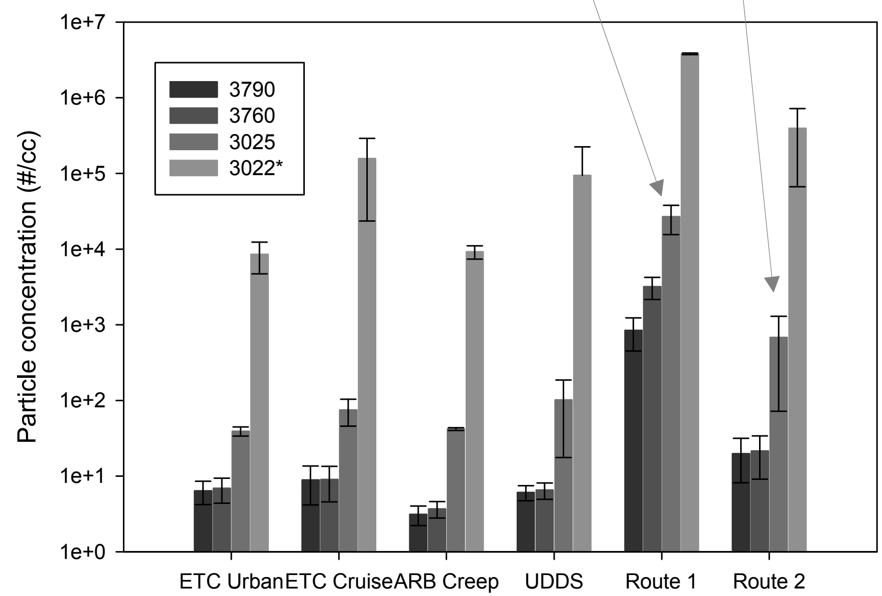
UCR on road tests using PMP protocol show unexpected "solid" particles and many particles below 23 nm

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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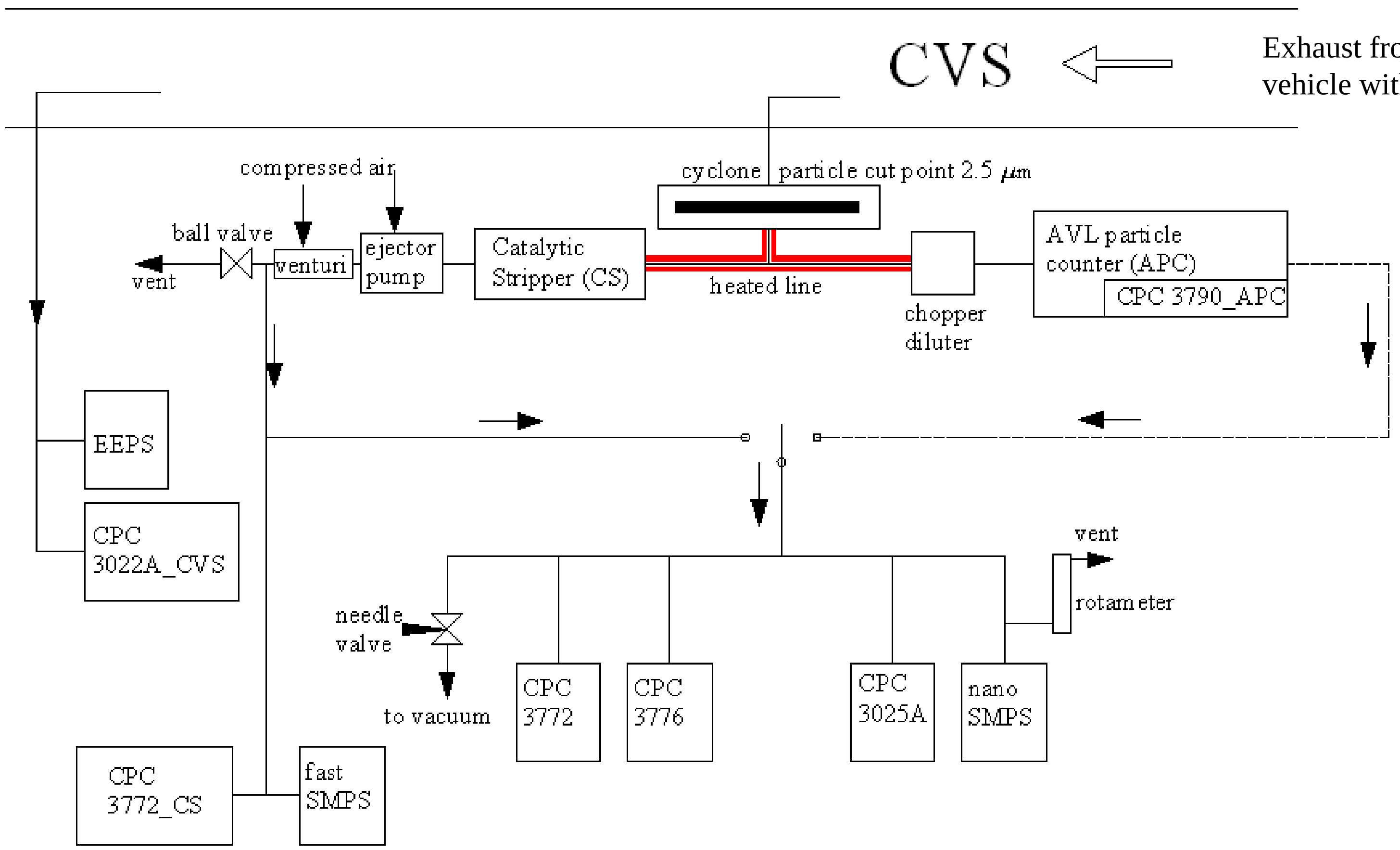
UCR chassis dynamometer tests comparing APC and catalytic stripper (CS)

- 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^{TM})
    - Two steady state cruise conditions, constant speed 56 mph at 26% and 74% of full load
  - Tests with laboratory challenge aerosols

Zhongqing Zheng, Kent C. Johnson, Zhihua Liu, Thomas D. Durbin, Shaohua Hu, Tao Huai, David B. Kittelson, Heejung S. Jung, Investigation of solid particle number measurement: existence and nature of sub 23 nm particles under PMP methodology, Journal of Aerosol Science 42 (2011) 883–897.

Comparisons of a Catalytic Stripper and APC Volatile Particle Remover with exhaust aerosols



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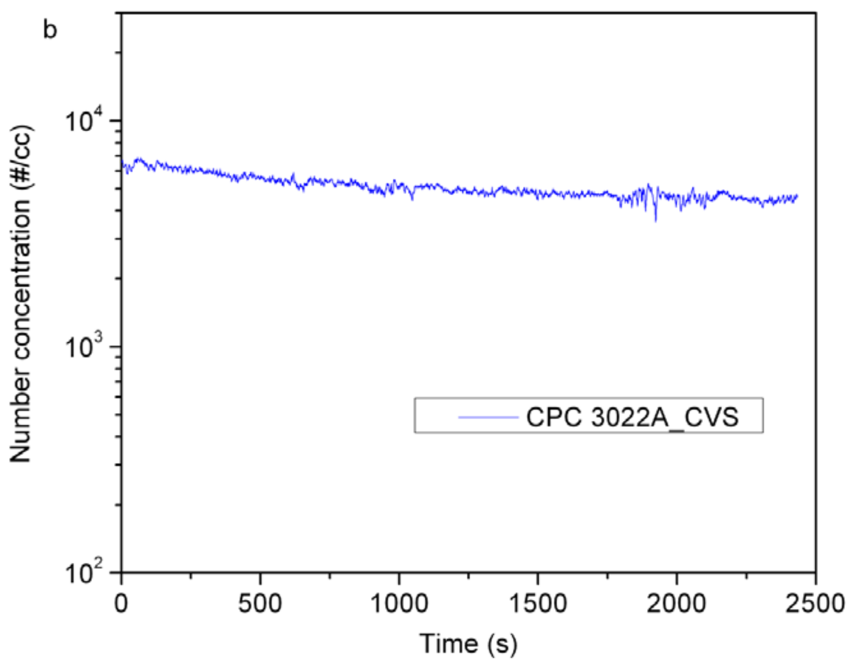
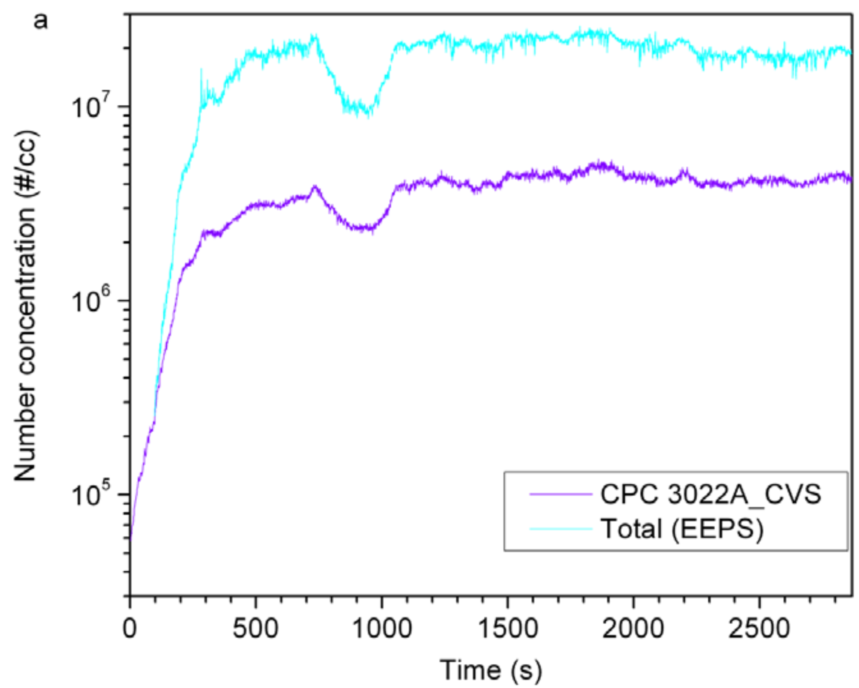
Steady state total particle number measurements

26% load



74% load



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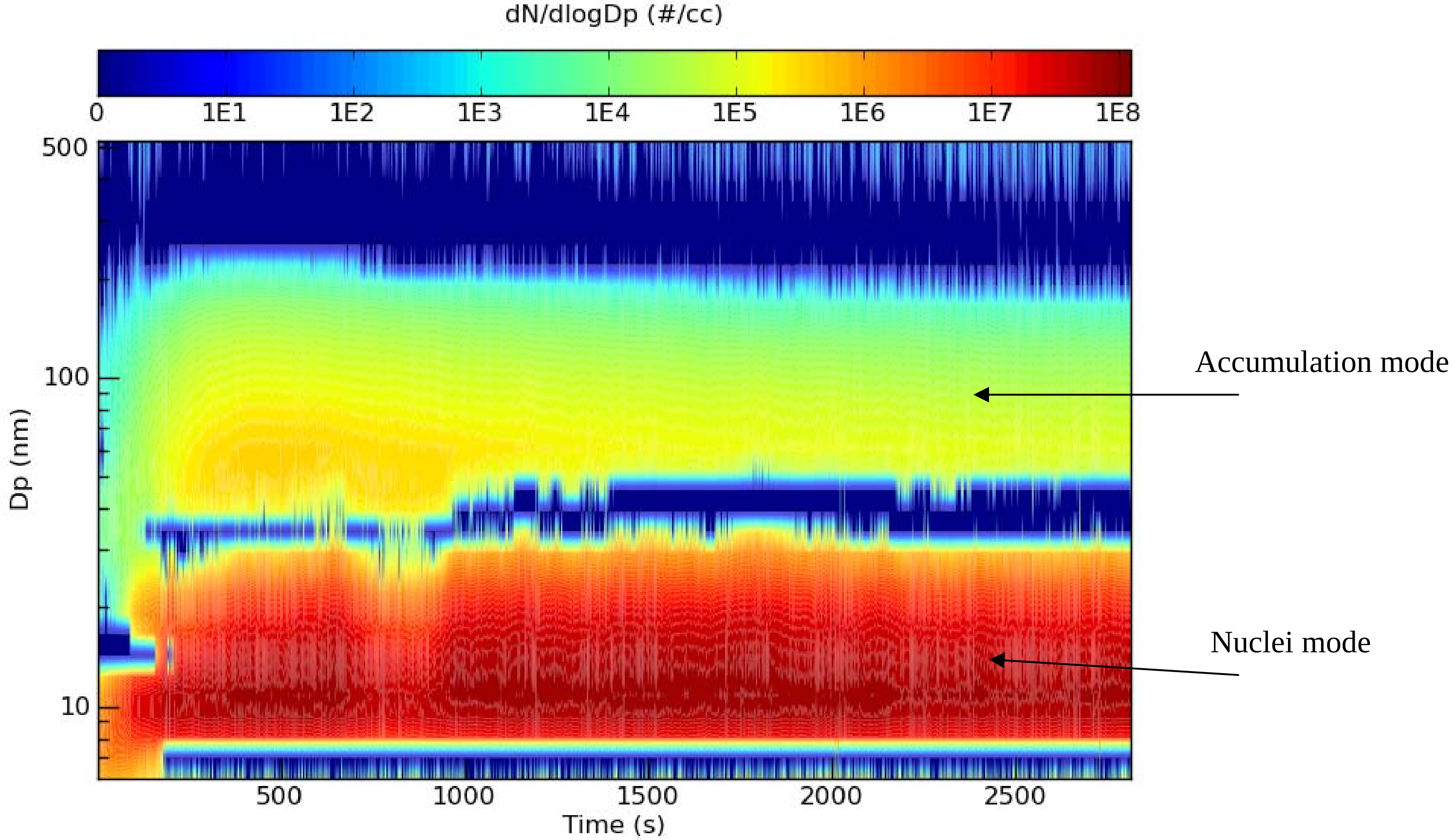
Steady state 74% load strongly bimodal



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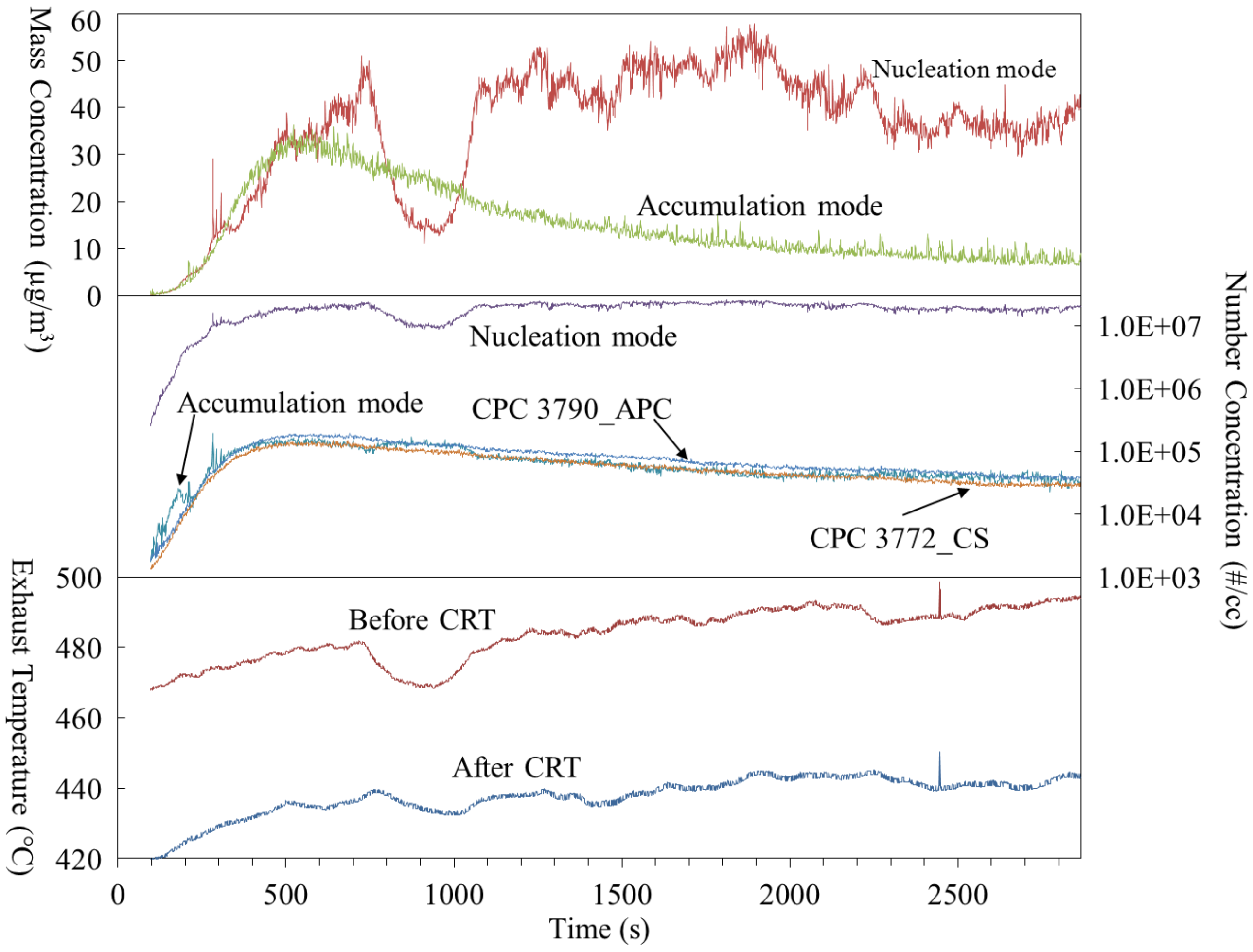
At 74% load PMP compliant system closely tracks the accumulation mode



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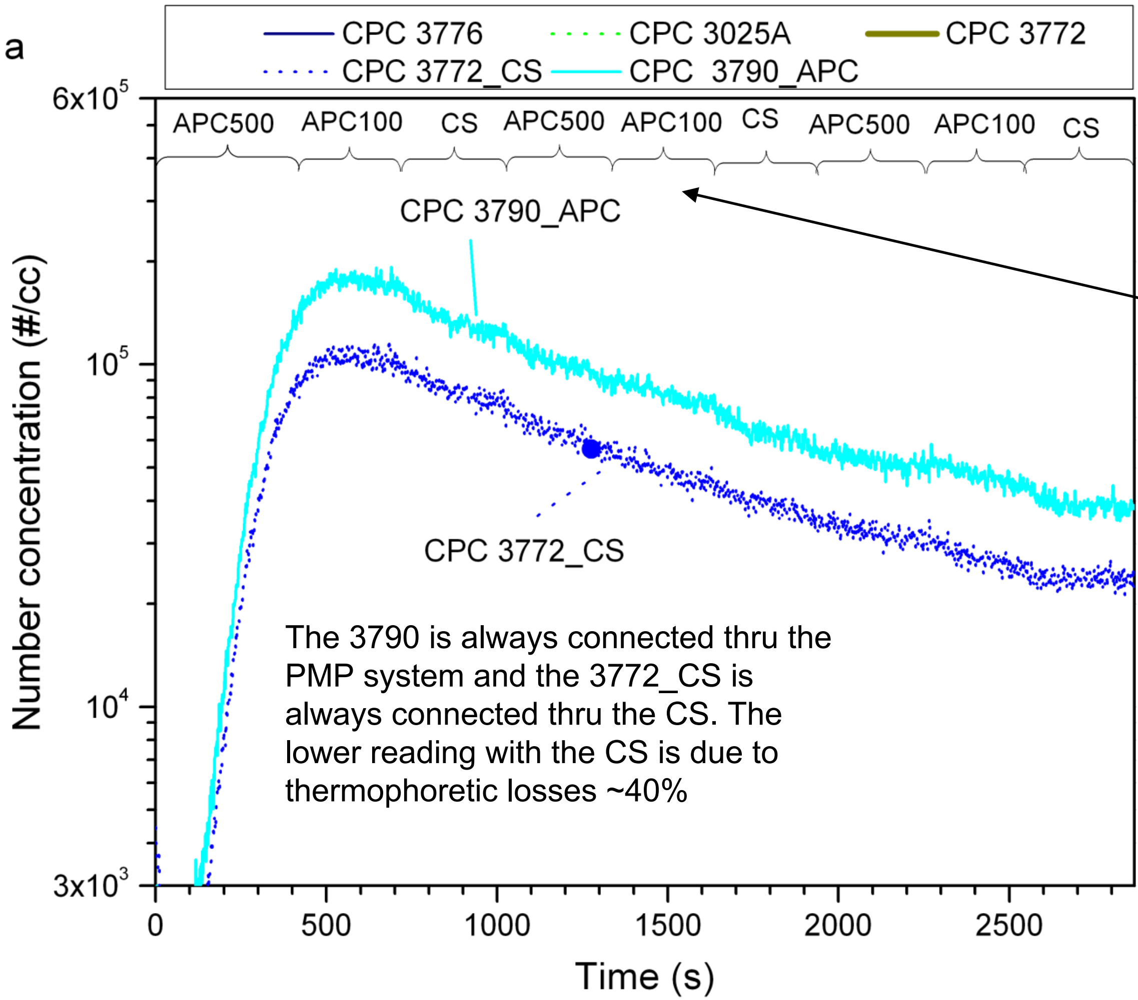
74% load
3790_APC (23 nm) and 3772_CS (10nm)



APC500 – PMP system, 500 dilution ratio

APC100 – PMP system, 100 dilution ratio

CS – Catalytic Stripper

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

Changing APC dilution ratio doesn't change results – it shouldn't

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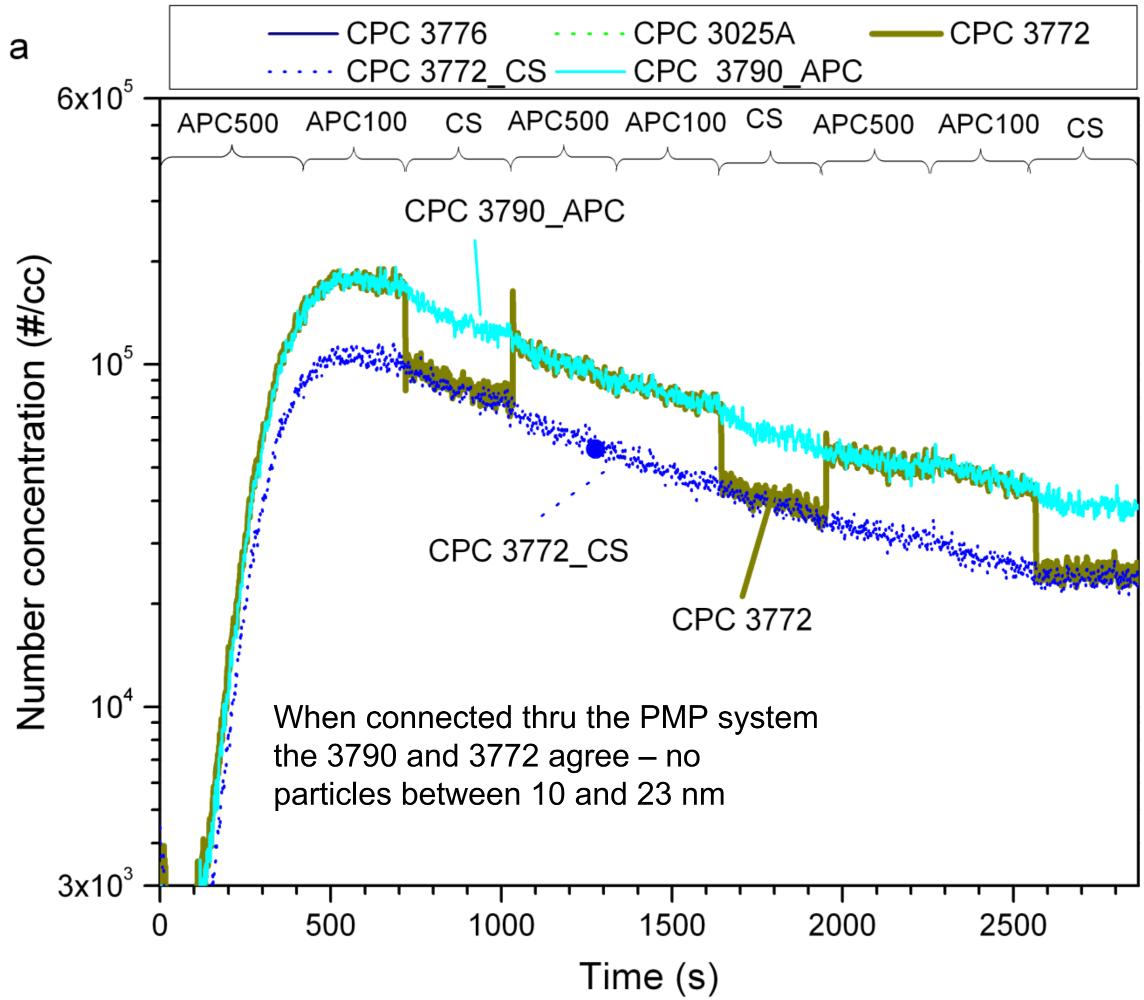
74% load

3790_APC (23 nm) on APC, 3772_CS (10 nm) on CS
3772 (10 nm) switched between APC and CS

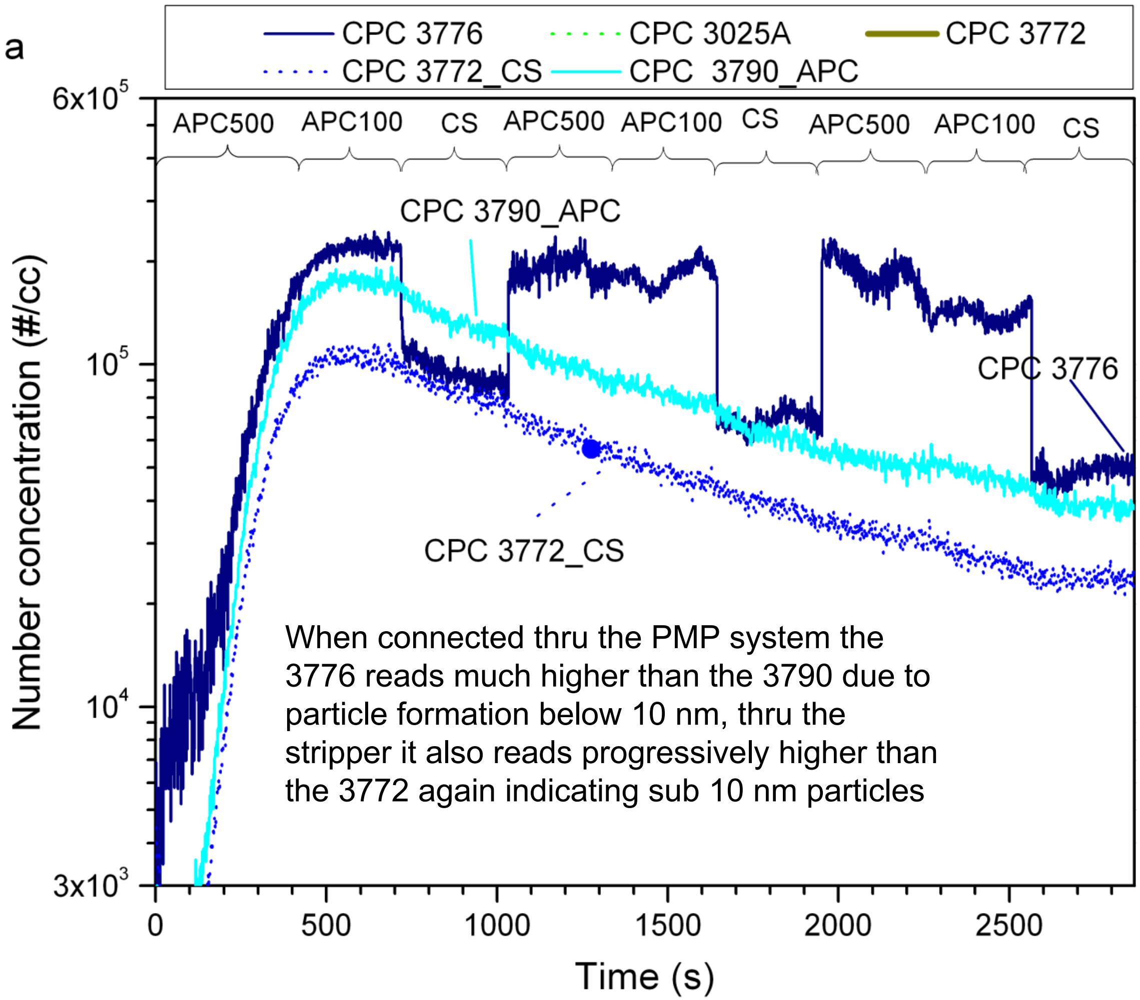


Switching from 100 to 500 overall dilution ratio has no impact on the APC results – the desired result

Zhongqing Zheng, Kent C. Johnson, Zhihua Liu, Thomas D. Durbin, Shaohua Hu, Tao Huai, David B. Kittelson, Heejung S. Jung, Investigation of solid particle number measurement: existence and nature of sub 23 nm particles under PMP methodology, Journal of Aerosol Science 42 (2011) 883–897.

74% load

3790_APC (23 nm) on APC, 3772_CS (10 nm) on CS
3776 (2.5 nm) switched between APC and CS



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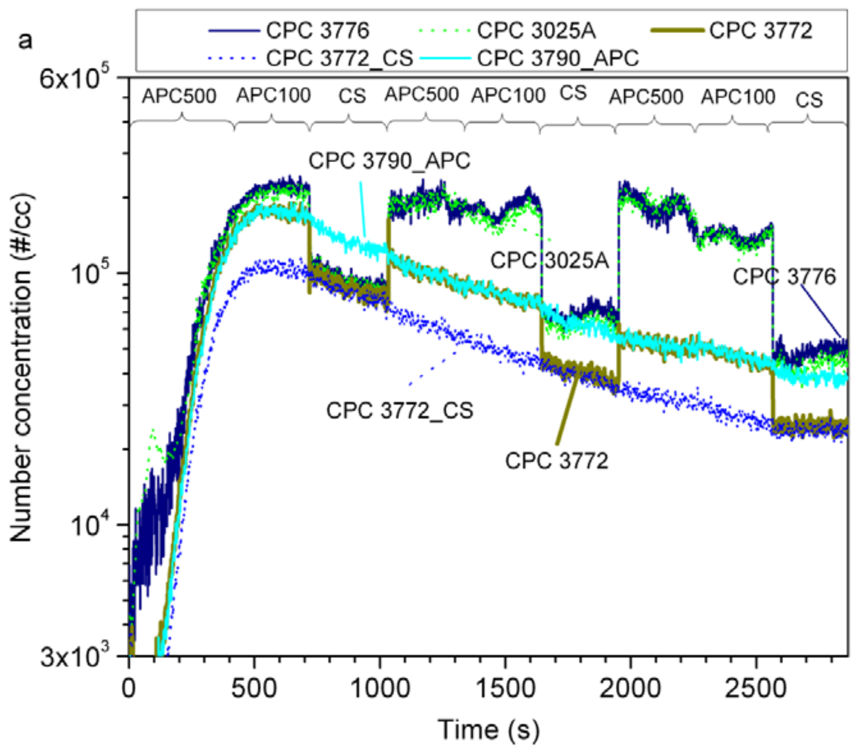
Summary of results at 74% load cruise



- Downstream of PMP system
  - 3790 and 3772 agree – no particles between 10 and 23 nn
  - 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

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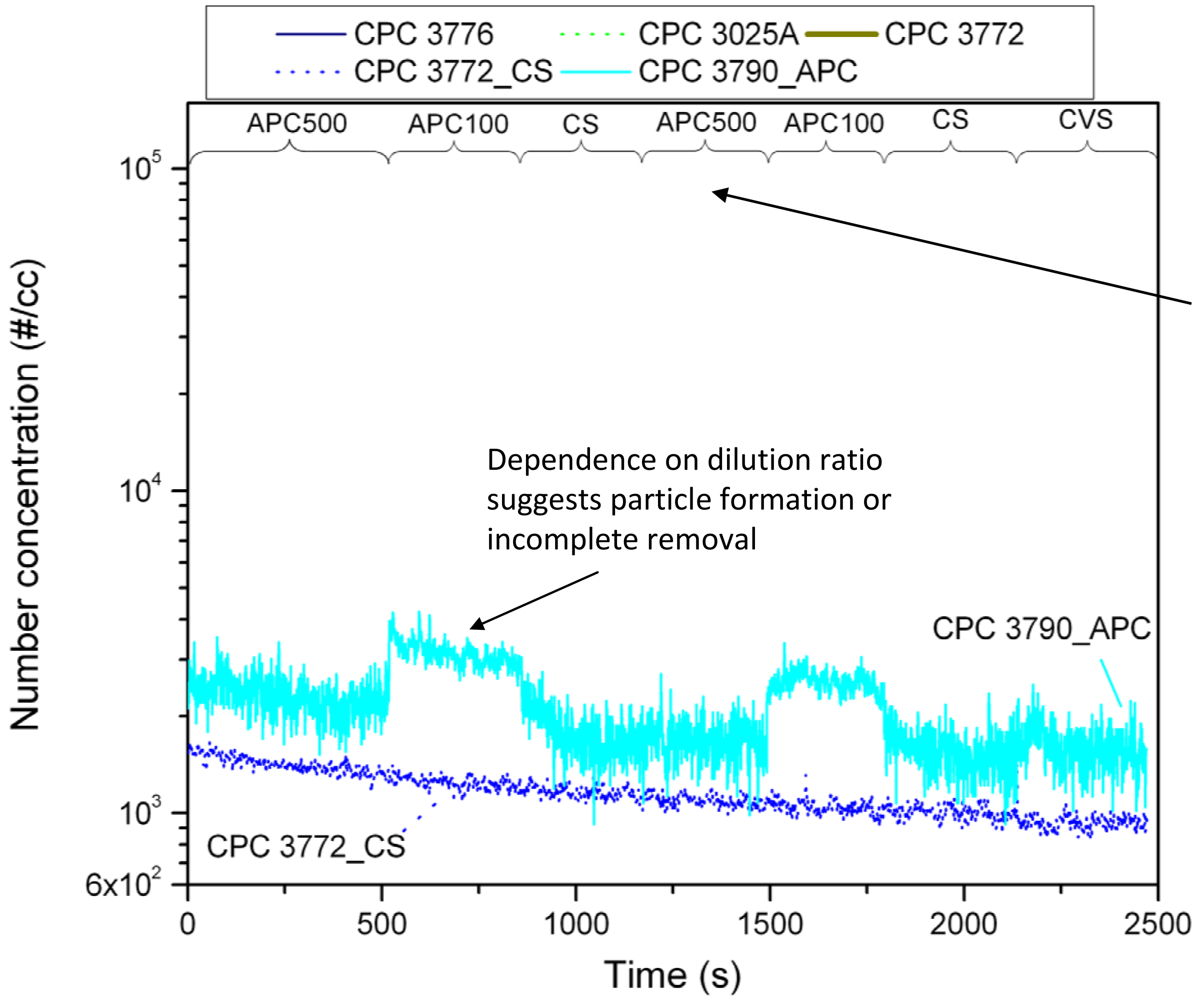
26% load
3790_APC (23 nm) and 3772_CS (10 nm)



APC500 – PMP system, 500 dilution ratio

APC100 – PMP system, 100 dilution ratio

CS – Catalytic Stripper

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

Changing APC dilution ratio changes results – it shouldn't

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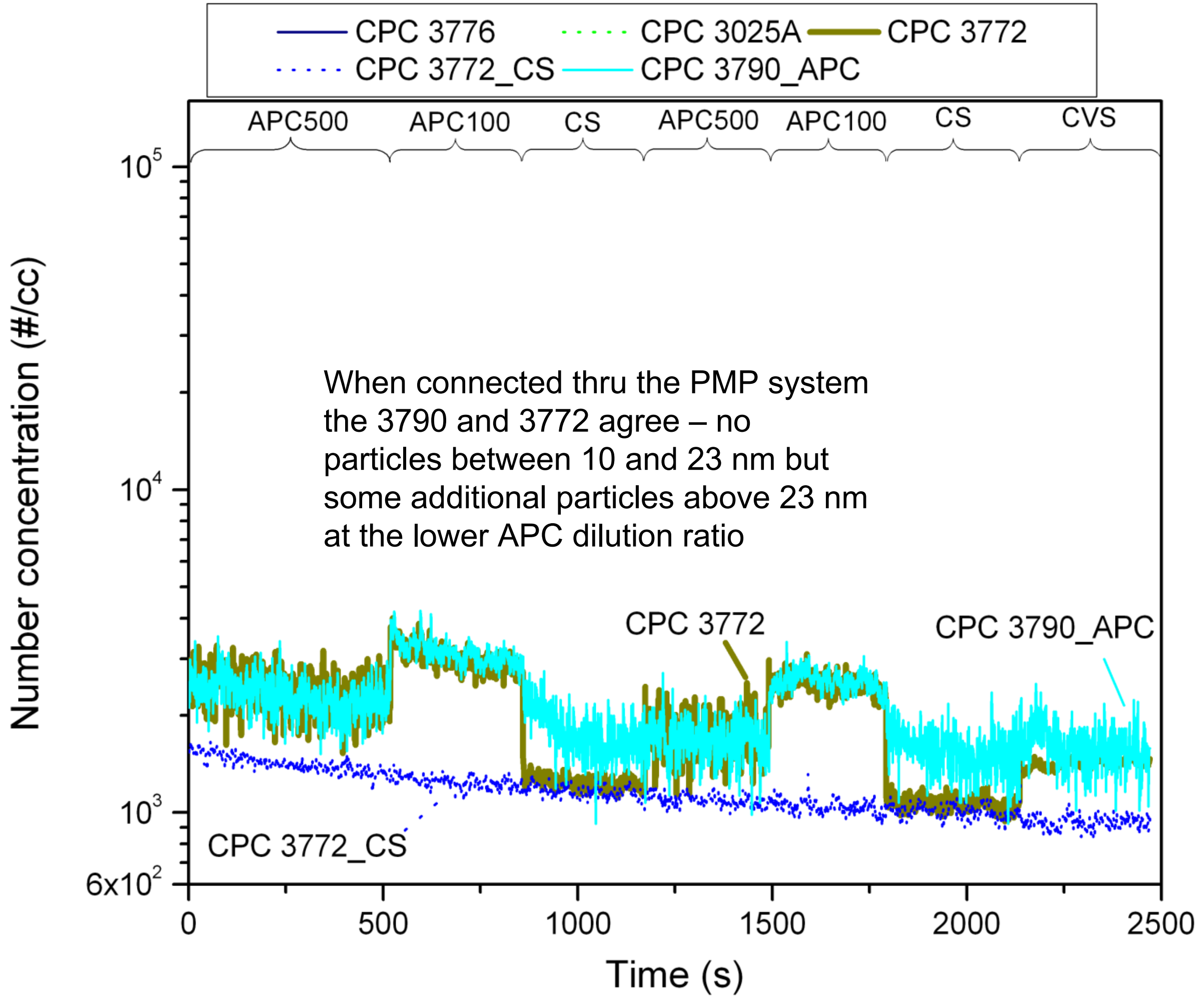

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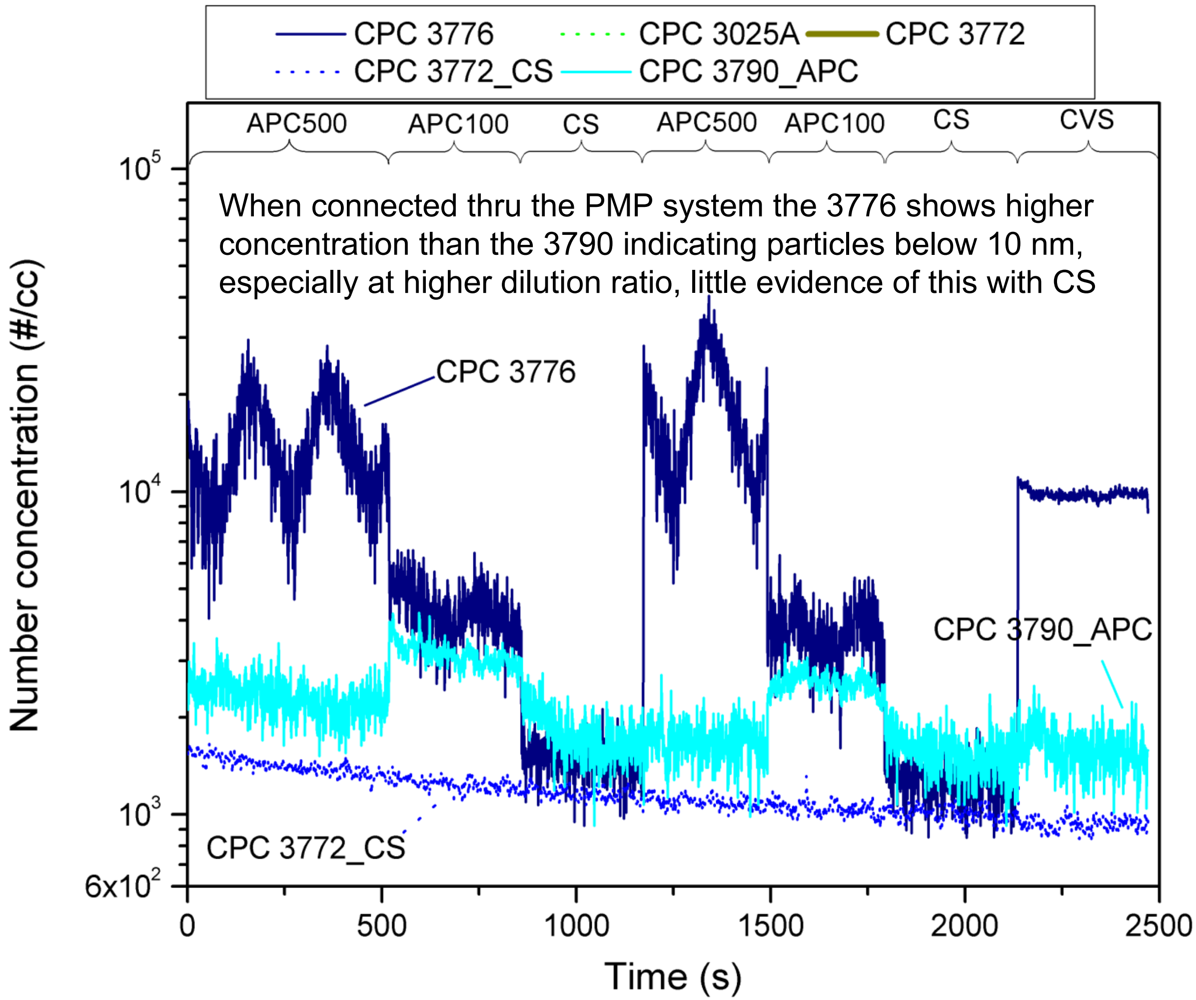
26% load

3790_APC (23 nm) on APC, 3772_CS (10 nm) on CS
3776 (2.5 nm) switched between APC and CS



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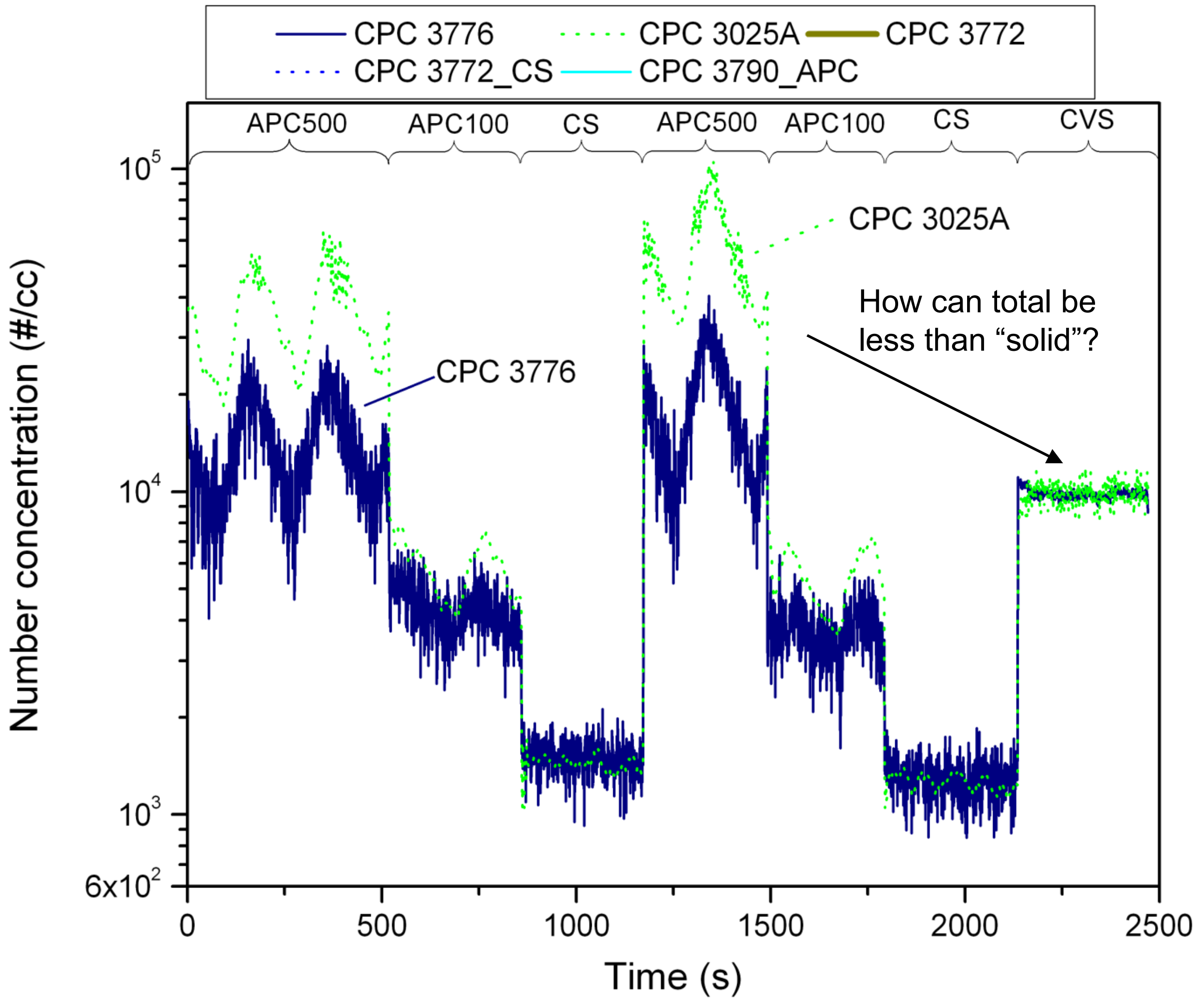
26% load

3025A (3 nm) and 3776 (2.5 nm)

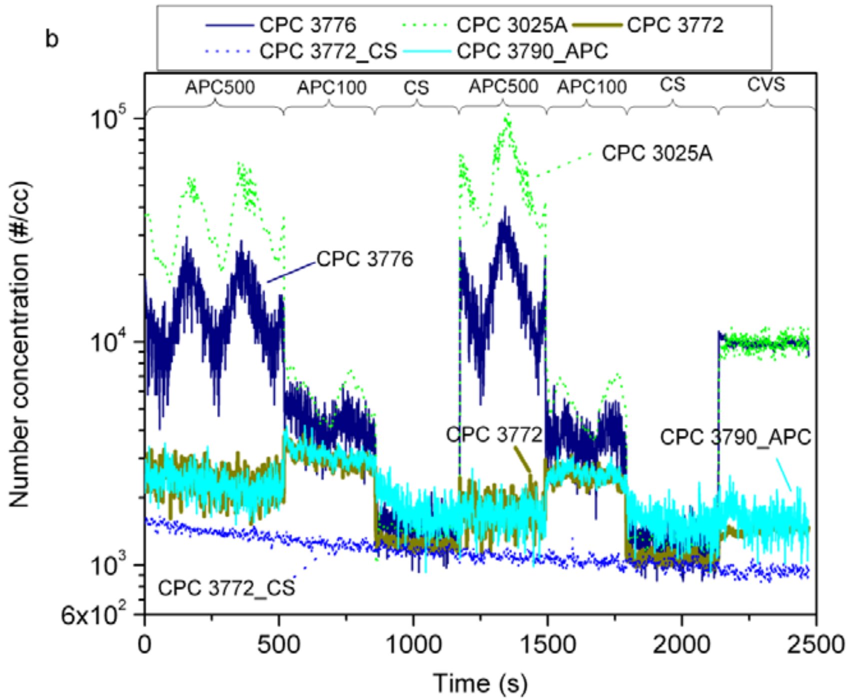


The 3025A and 3776 disagree at the higher dilution ratio downstream of the PMP system but agree for 50 nm calibration aerosols suggesting that the particles are near the lower detection sizes of the instruments, < 3 nm..

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

Zhongqing Zheng, Kent C. Johnson, Zhihua Liu, Thomas D. Durbin, Shaohua Hu, Tao Huai, David B. Kittelson, Heejung S. Jung, Investigation of solid particle number measurement: existence and nature of sub 23 nm particles under PMP methodology, Journal of Aerosol Science 42 (2011) 883–897.

Summary of results at 26% load cruise

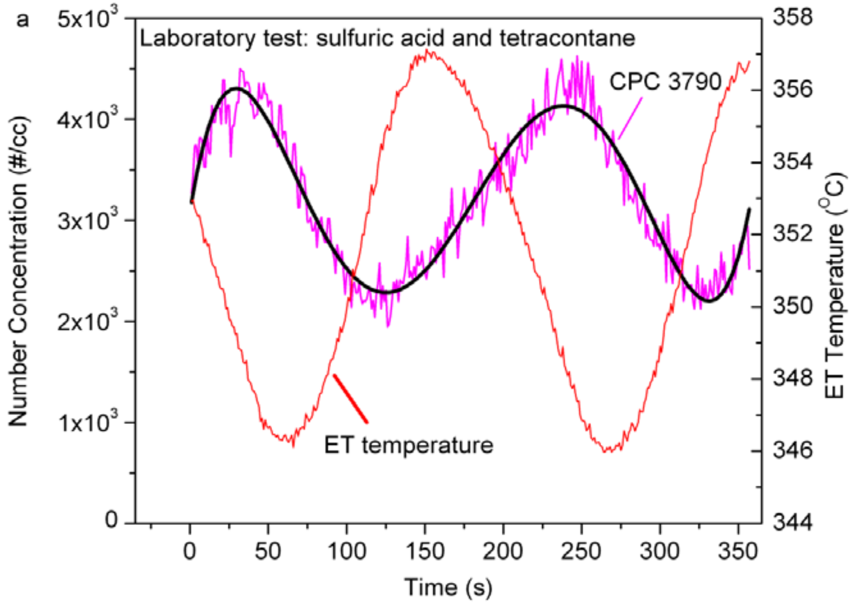


- Much lower concentrations than at 74%
  - Downstream of PMP system
    - In first time window, DR = 500
      - 3790 and 3772 agree – no particles between 10 and 23 nm
      - 3776 and 3025A read much higher and disagree – many particles below lower cutoff size of these instruments, 2.5 to 3 nm
  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

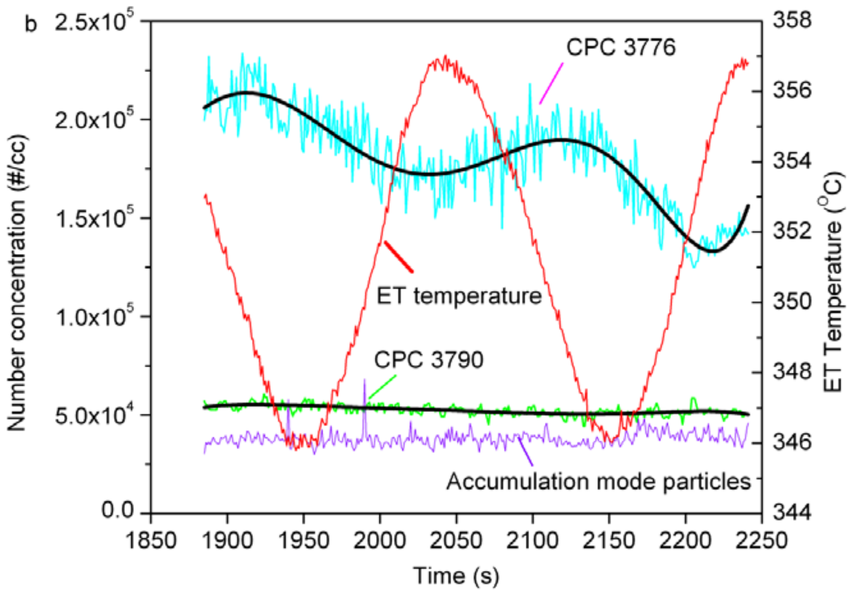
Zhongqing Zheng, Kent C. Johnson, Zhihua Liu, Thomas D. Durbin, Shaohua Hu, Tao Huai, David B. Kittelson, Heejung S. Jung, Investigation of solid particle number measurement: existence and nature of sub 23 nm particles under PMP methodology, Journal of Aerosol Science 42 (2011) 883–897.

Laboratory and engine tests both show concentration swings tracking VPR temperature

Laboratory test aerosol



Chassis dyno 74% load



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Summary – UCR tests

- High load on-road tests of CRT equipped heavy-duty truck shows evidence of overloading PMP system
  - Large increase in particle counts with all CPCs – even PMP 3790
  - May be associated with storage and release of sulfate
- Chassis dynamometer tests at 74% and 26% load highway cruise
  - At 74% load
    - APC and CS agree above 10 nm and track accumulation mode
    - APC and to a lesser extent CS show significant particle formation below 10 nm
    - APC sub 10 nm concentration swings associated with evaporation tube temperature
  - At 26% load
    - APC shows dilution ratio dependence – evidence of particle formation above 23 nm
    - APC leads to formation of extremely small particles ~ 3 nm
- Laboratory generated aerosols show formation or incomplete removal of particles larger than 23 nm with evaporation tube temperature dependence.

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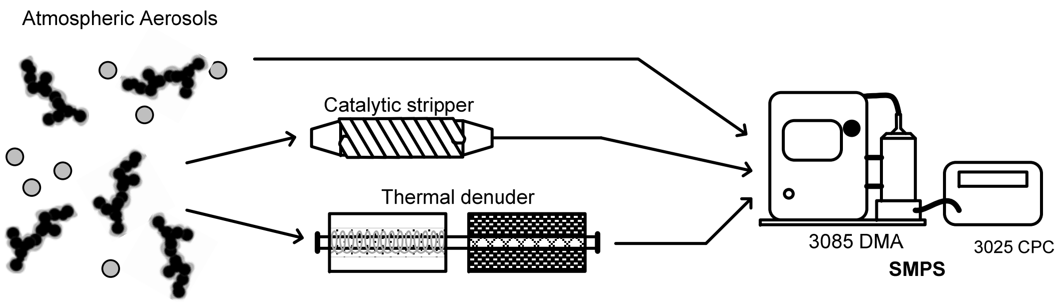
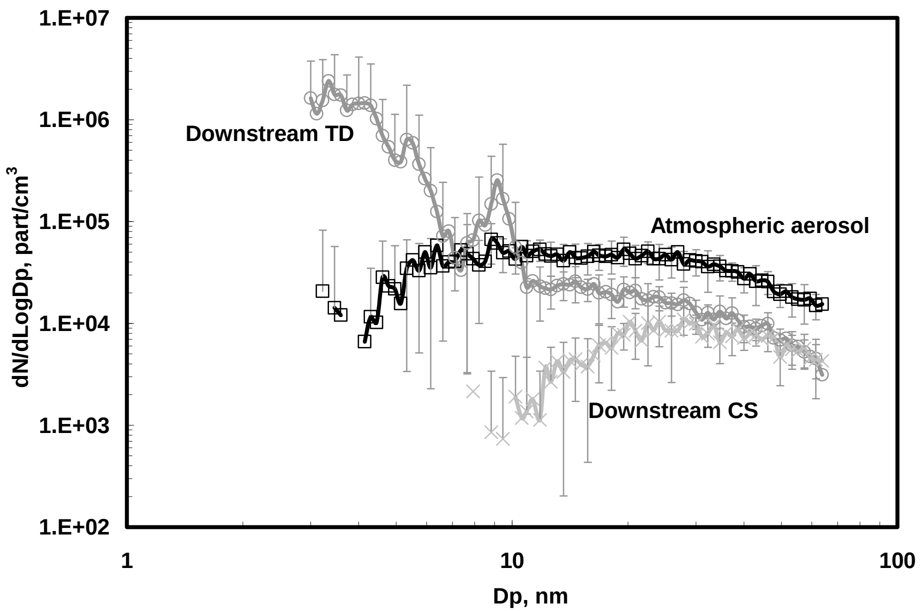
Performance of thermal denuder and catalytic stripper with ambient aerosol



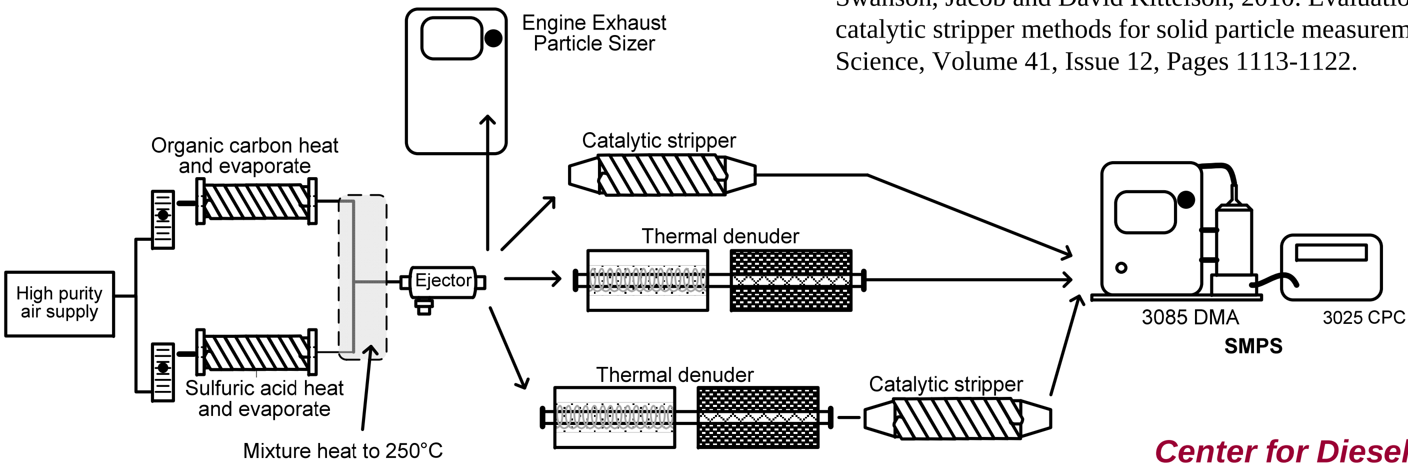


Swanson, Jacob and David Kittelson, 2010. Evaluation of thermal denuder and catalytic stripper methods for solid particle measurements, Journal of Aerosol Science, Volume 41, Issue 12, Pages 1113-1122.

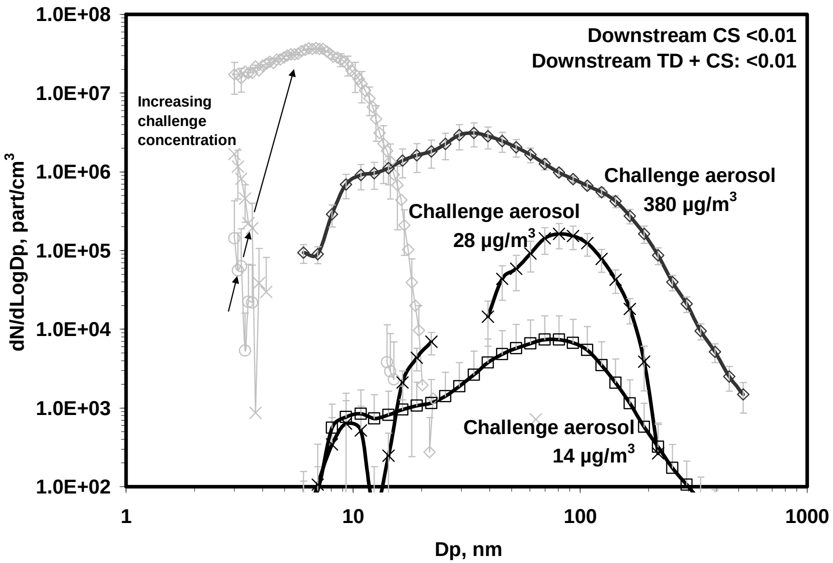
Evaluating thermal denuder and catalytic stripper with pure semi-volatile challenge aerosols

- 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.

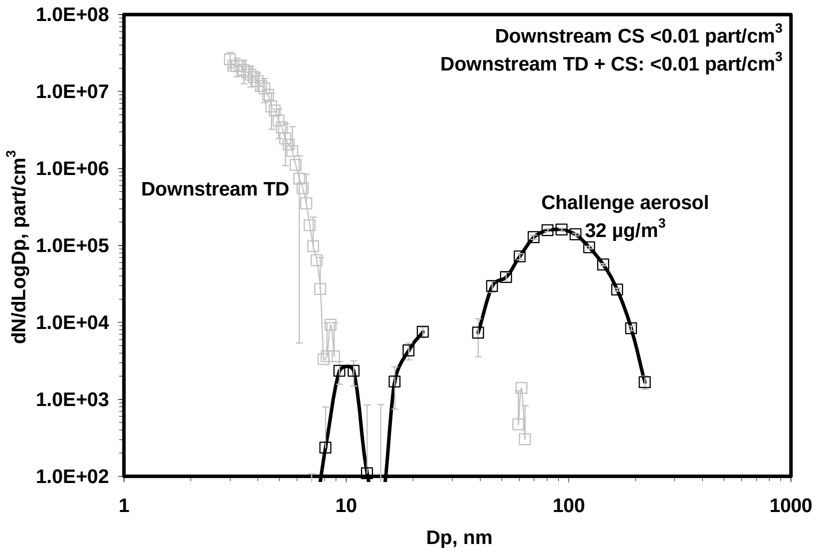
Swanson, Jacob and David Kittelson, 2010. Evaluation of thermal denuder and catalytic stripper methods for solid particle measurements, Journal of Aerosol Science, Volume 41, Issue 12, Pages 1113-1122.



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



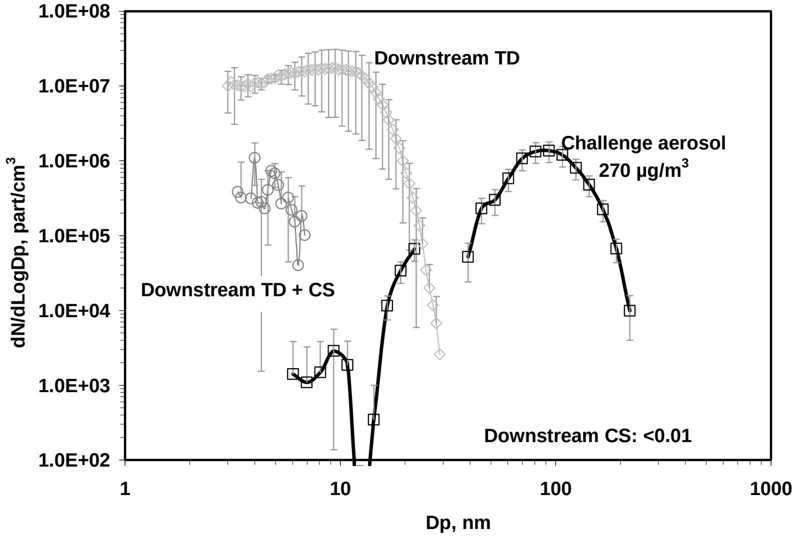
- Pure tetracosane challenge aerosol
  - Wide range of concentrations
  - Particles form downstream of TD
  - No particle downstream of CS
  - No particles downstream of TD + CS – particles formed by TD volatile

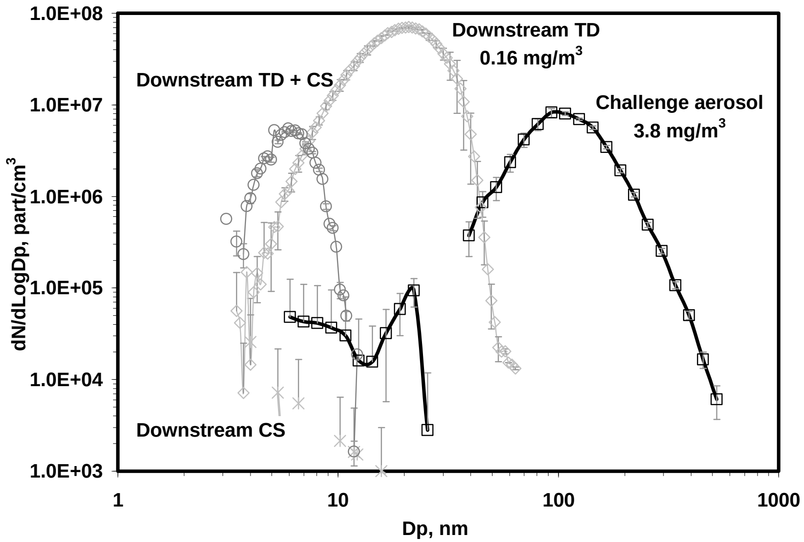


- Tetracosane plus sulfuric acid challenge aerosol
  - Significant particle formation downstream of TD
  - No particle downstream of CS
  - No particles downstream of TD + CS – particles formed by TD volatile

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



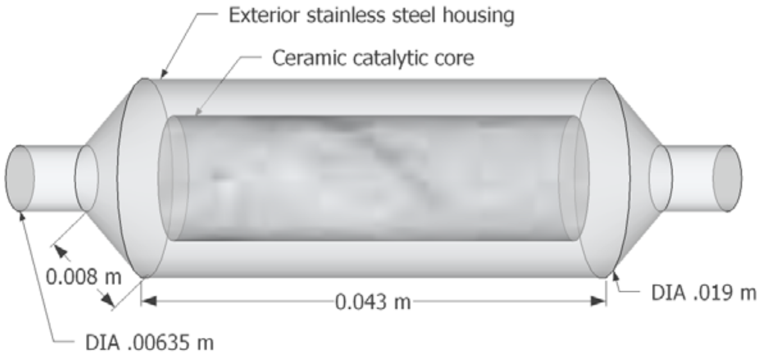


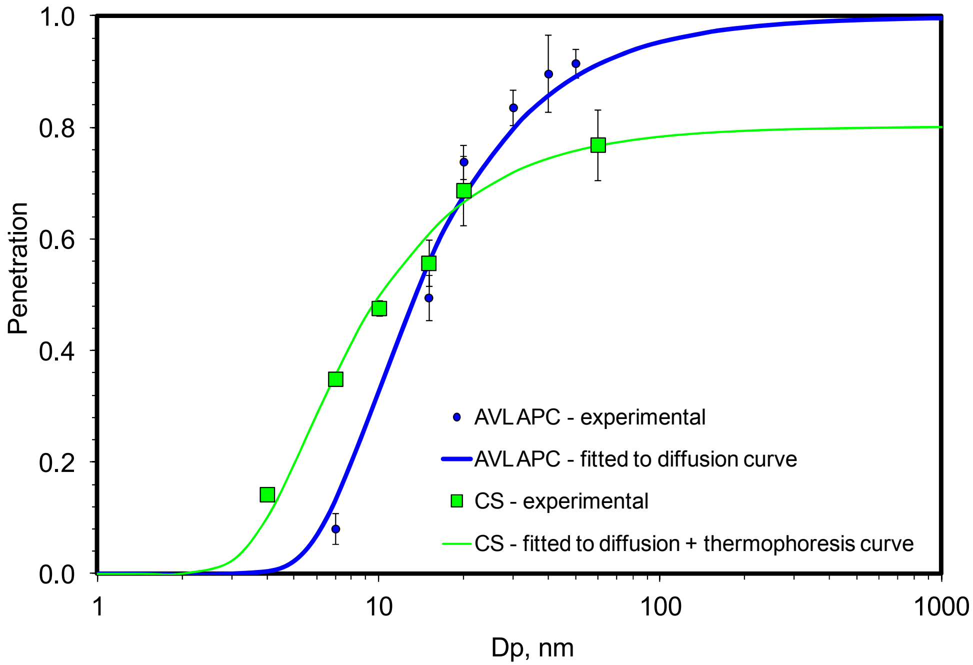
- Tetracosane plus sulfuric acid challenge aerosols
  - Higher challenge aerosol concentrations
  - Significant particle formation downstream of TD
  - A few particles downstream of CS at highest challenge aerosol concentrations
  - Particles downstream of TD + CS – particles suggesting solid particle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

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.

New miniature CS for use in APC

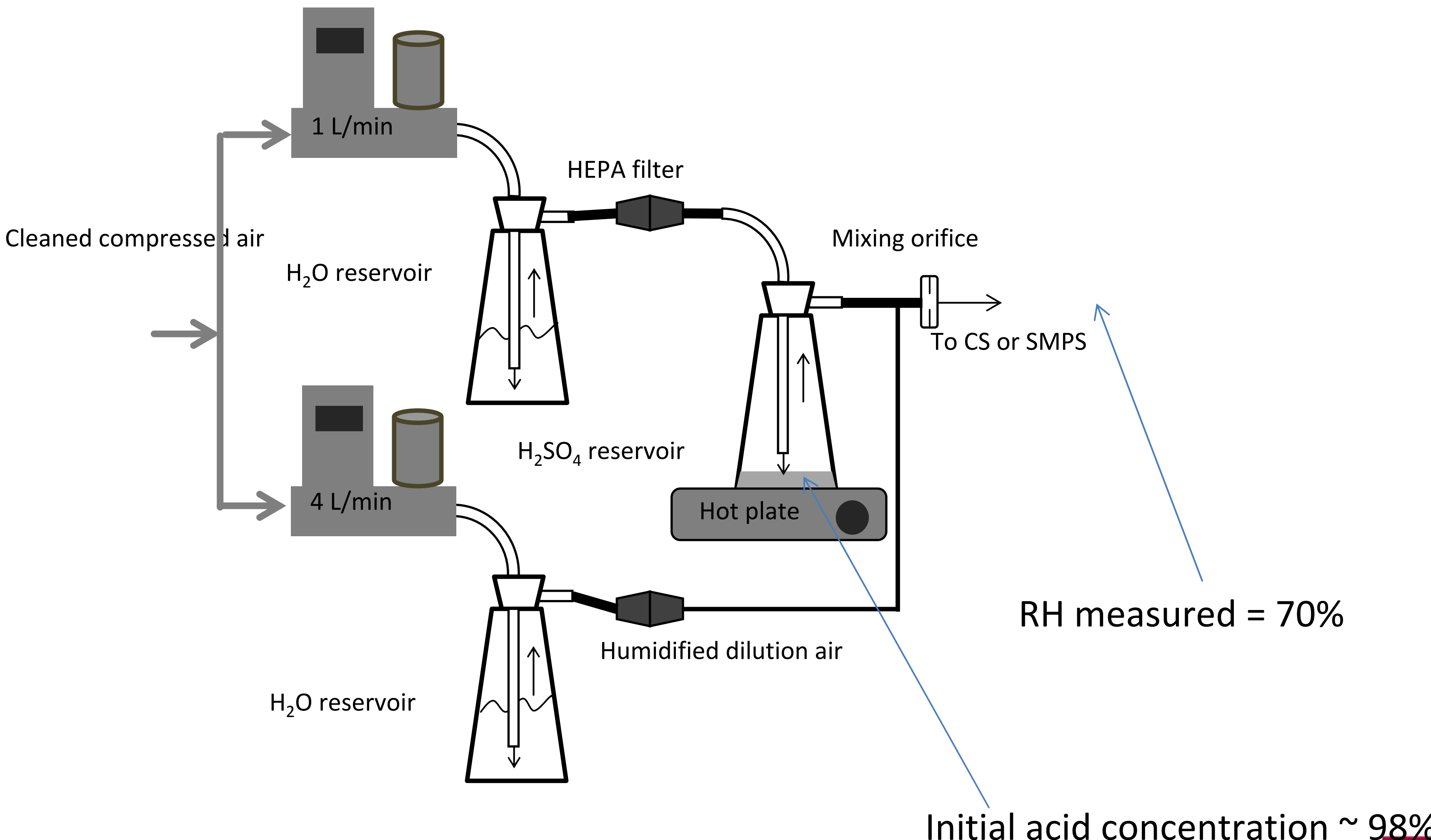
Core length	0.038	m
Core width	0.015	m
Cell density	600	cells/in
Wall thickness	2.5	mil
Flowrate	1.5	L/min
$C_{40}H_{82}$ penetration	0.2	%
SO_4^{2-} penetration	0.0014	%
50% cut off size	7	nm



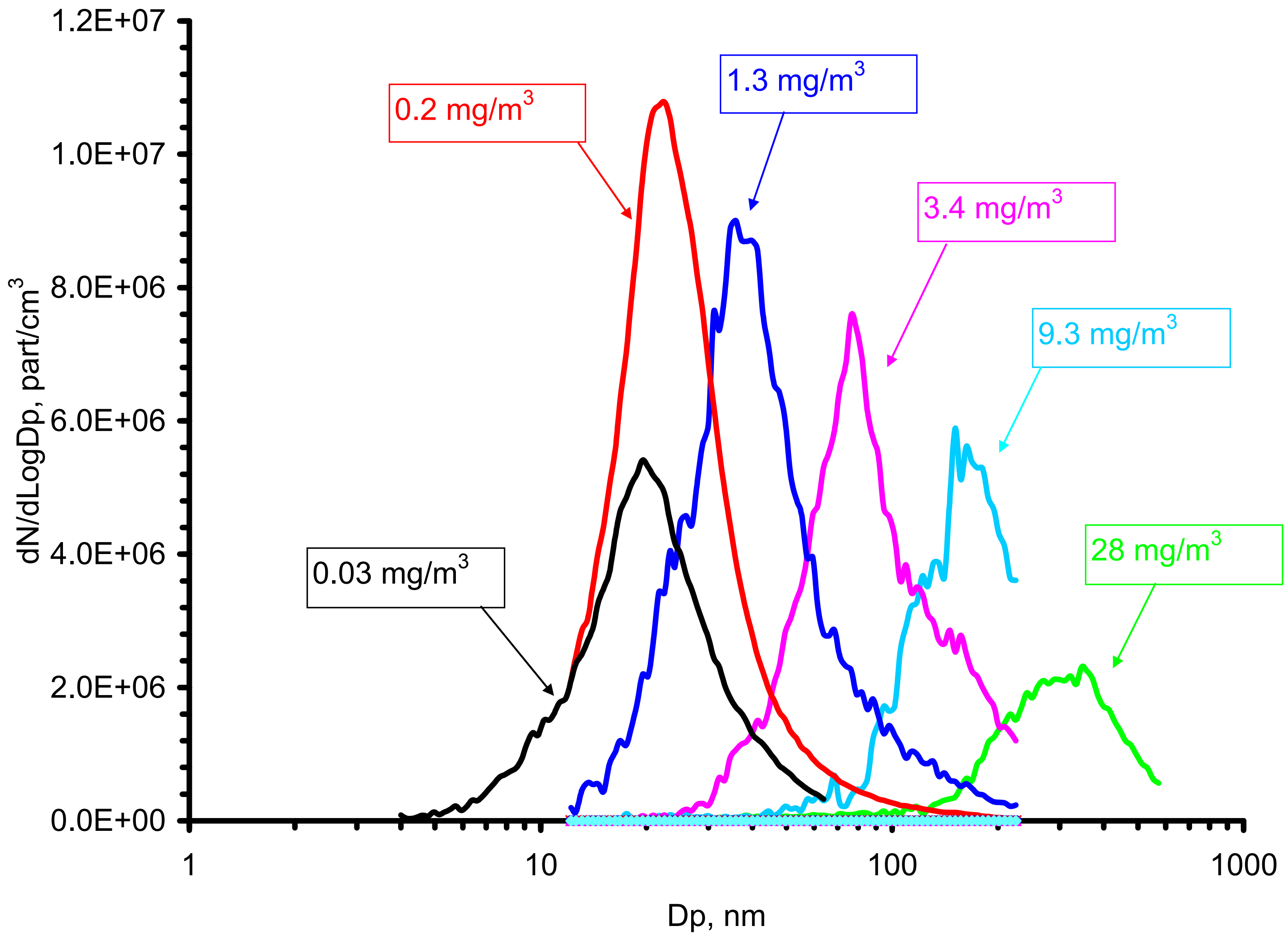


Penetration curves for the CS and AVL APC. For the CS, the data are fitted to diffusion and thermophoresis loss model. For the APC, the data are fitted to a diffusion model only.

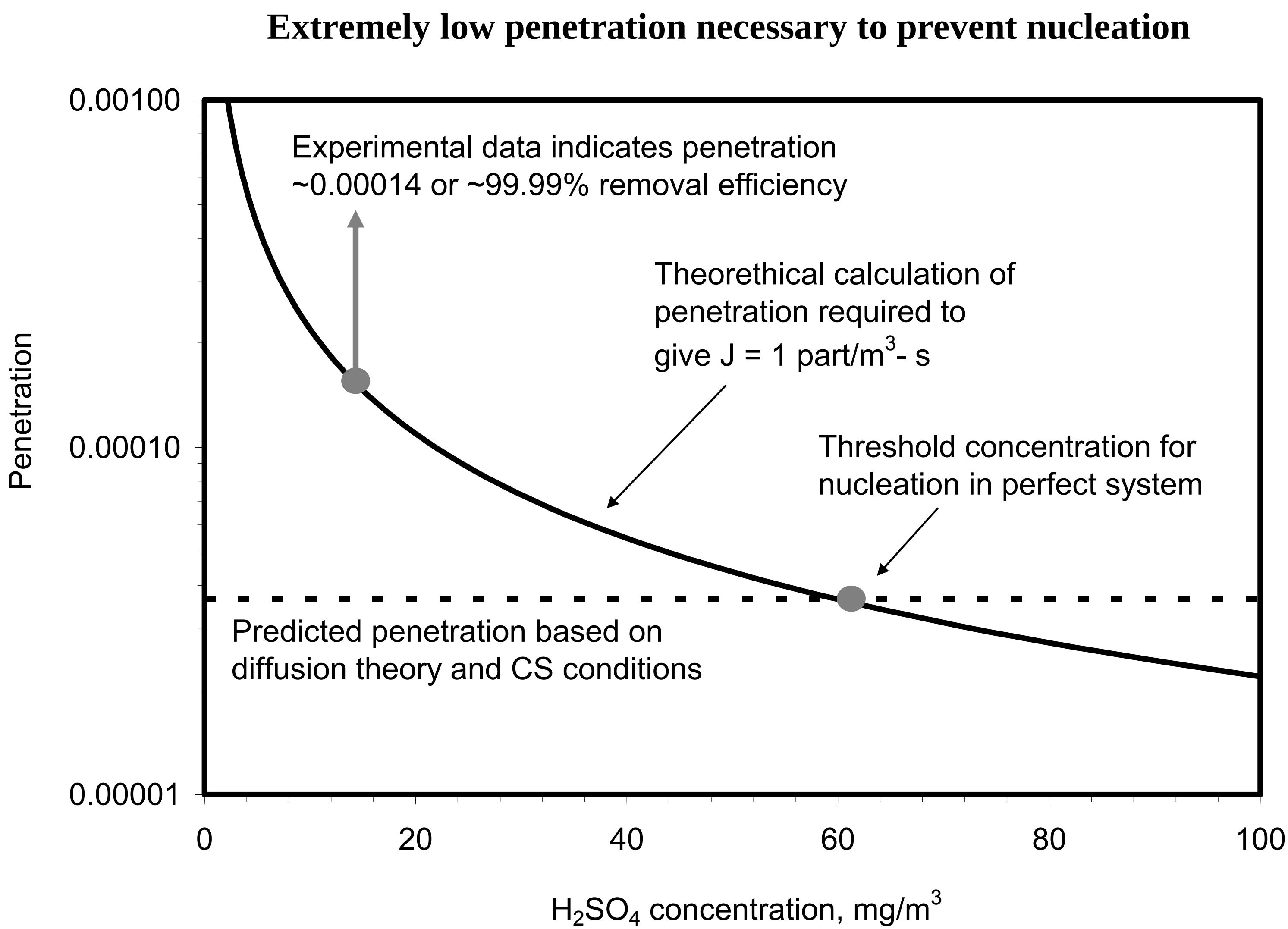
H_2SO_4 particle generation method



H_2SO_4 particle distributions



Some calculations of theoretical threshold for sulfuric acid nucleation and experimentally observed ~ 14 mg/m^3



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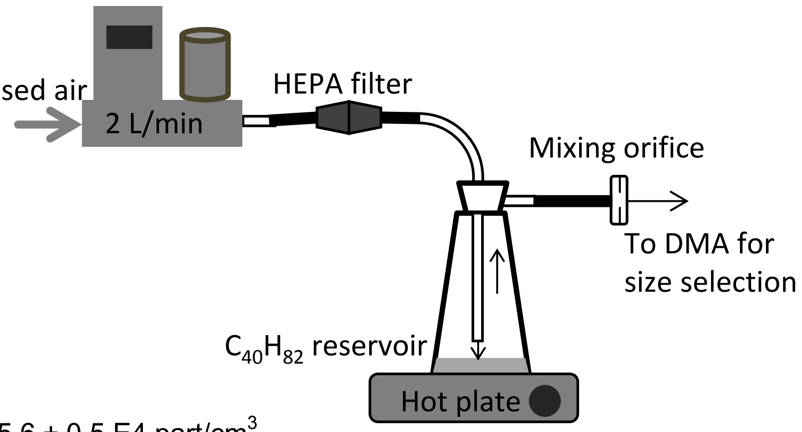
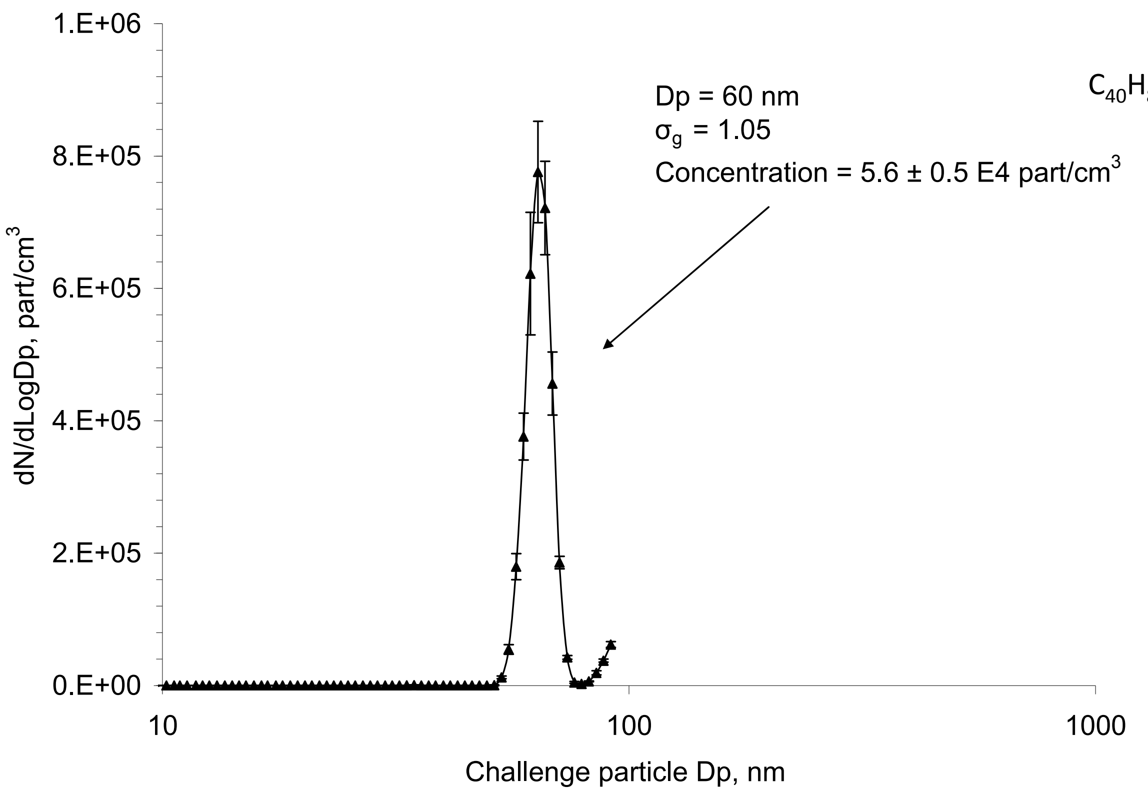
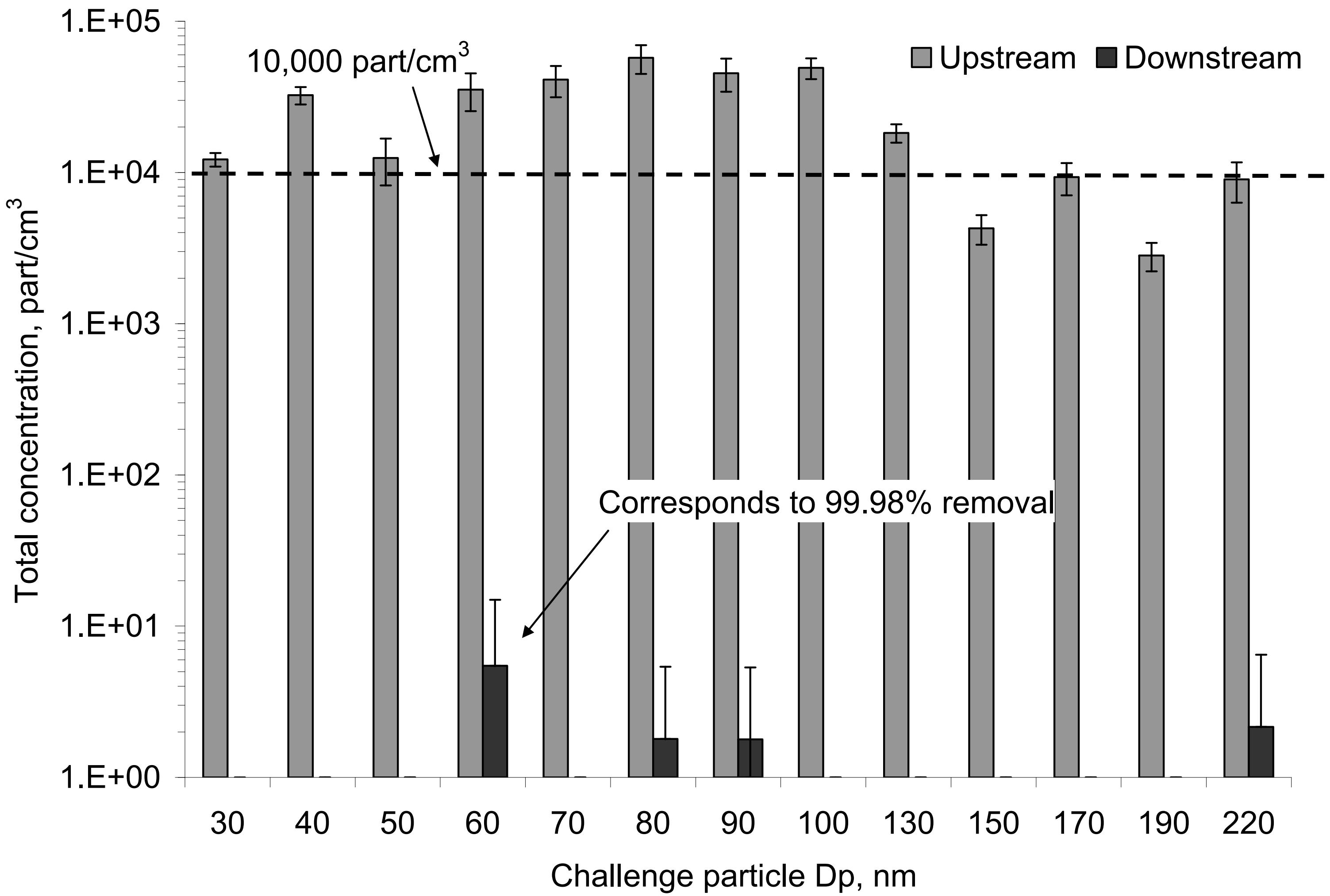
Generation of hydrocarbon particles





Hydrocarbon particle removal



Conclusions – UMN lab tests

- Thermal denuders and related devices have significant potential for downstream nucleation and at high concentrations may create solid residue from pure volatile materials
- CS system only shows downstream nucleation of sulfuric acid at very high upstream concentrations ~ 14 mg/m^3
- APC VPR system shows downstream sulfuric acid nucleation at ~ 100$\mu g/m^3$
- Renucleation of sulfuric acid or other low vapor pressure species critical – need performance standard?

Outline

- Background
- UCR on-road and laboratory tests
- UMN laboratory tests
- Conclusions

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
  - The next generation of high efficiency direct injection gasoline engines are challenged by the current standard even with the 23 nm limit
- An international solid number standard for aircraft emissions is being considered and is likely use a lower counting limit to 10 nm
- 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
  - Downstream nucleation and solid particle losses greatly reduced in new mini CS
  - Removal of sulfate or other low vapor pressure species critical

Acknowledgements

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

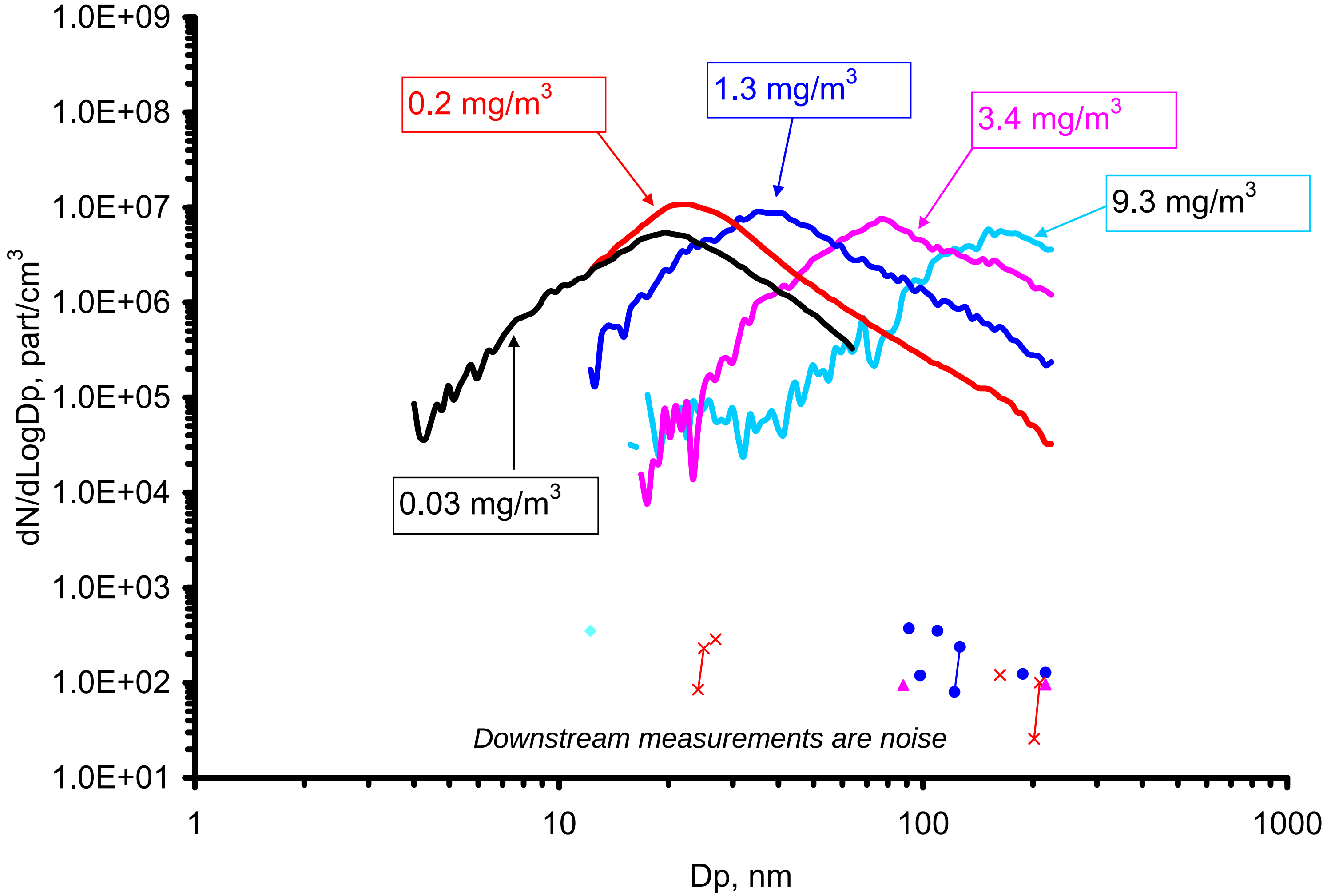
Questions?

Backup slides

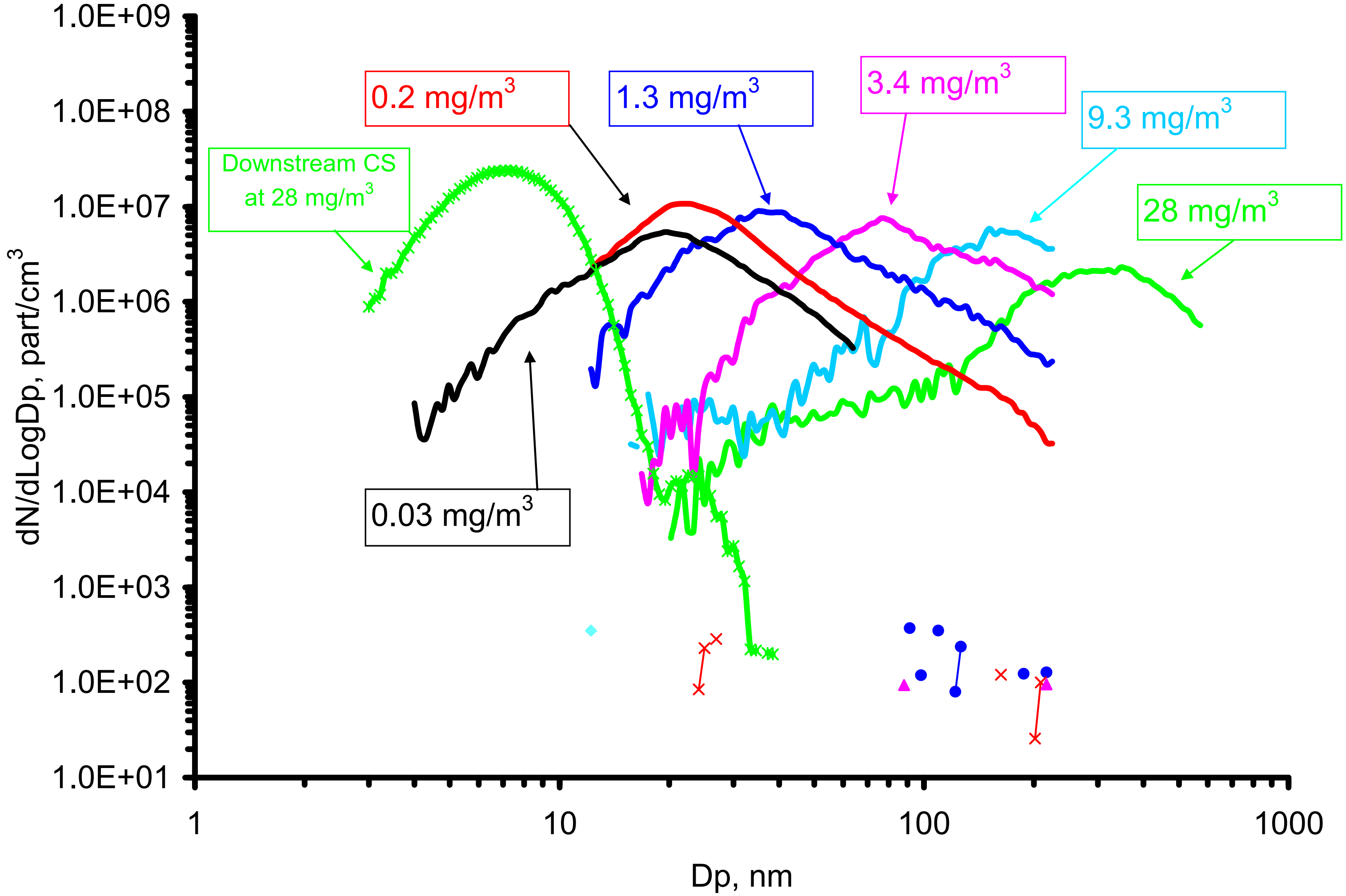
Outline

- H_2SO_4 particle generation method
- Results for challenge concentrations 0.03 to 28 mg/m^3
- Brief conclusion
- Previous test schematic and experimental results
- Calculations
- Hydrocarbon removal

H_2SO_4 particle distributions for challenge concentrations <10 mg/m³



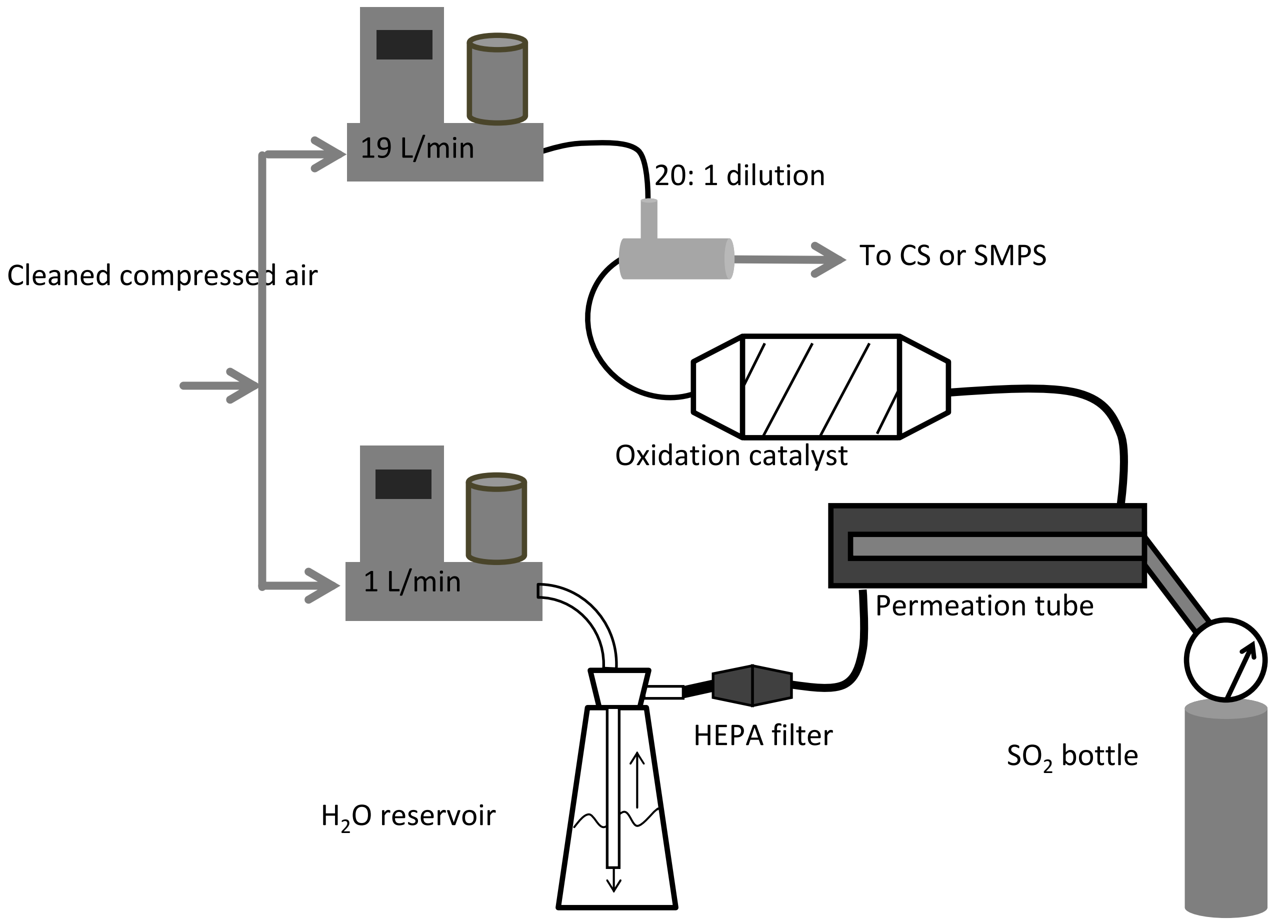
Results show renucleation of H_2SO_4 vapor for particle challenge concentrations ~28 mg/m³



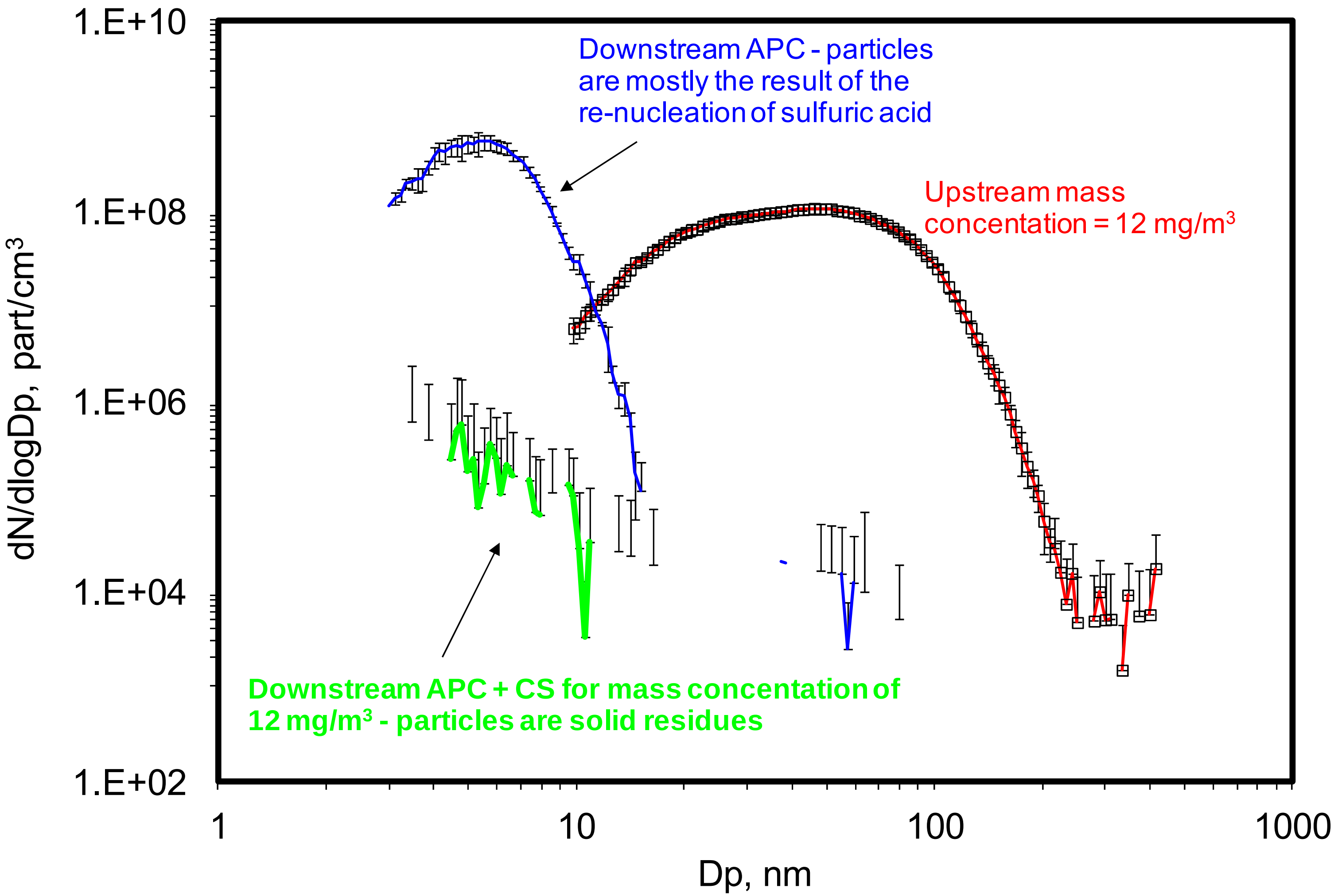
Quick summary

- Current results suggest re-nucleation occurs between 10 and 28 mg/m^3 upstream

Past results - H_2SO_4 particle generation method

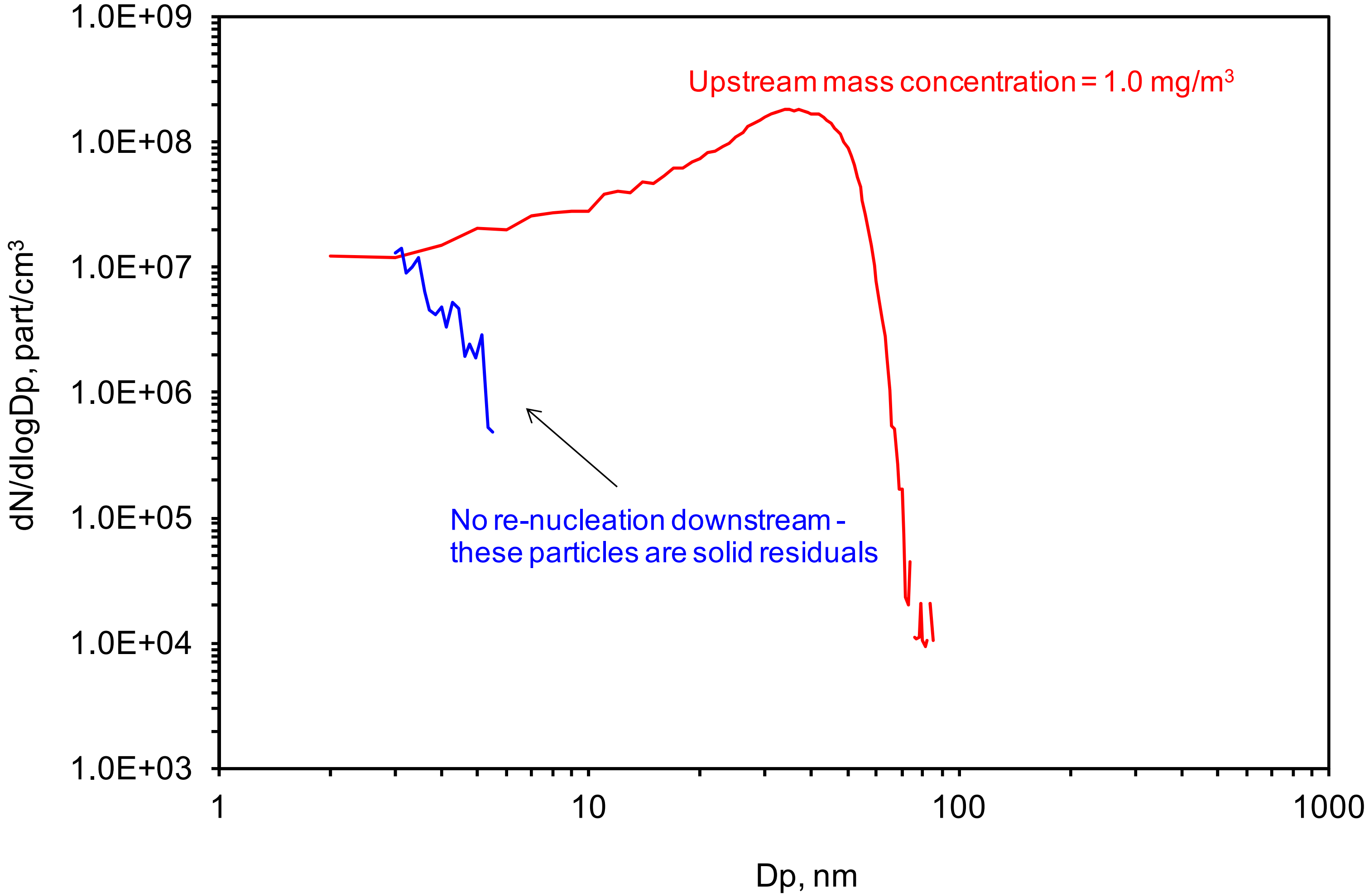


APC challenge with 12 mg/m³



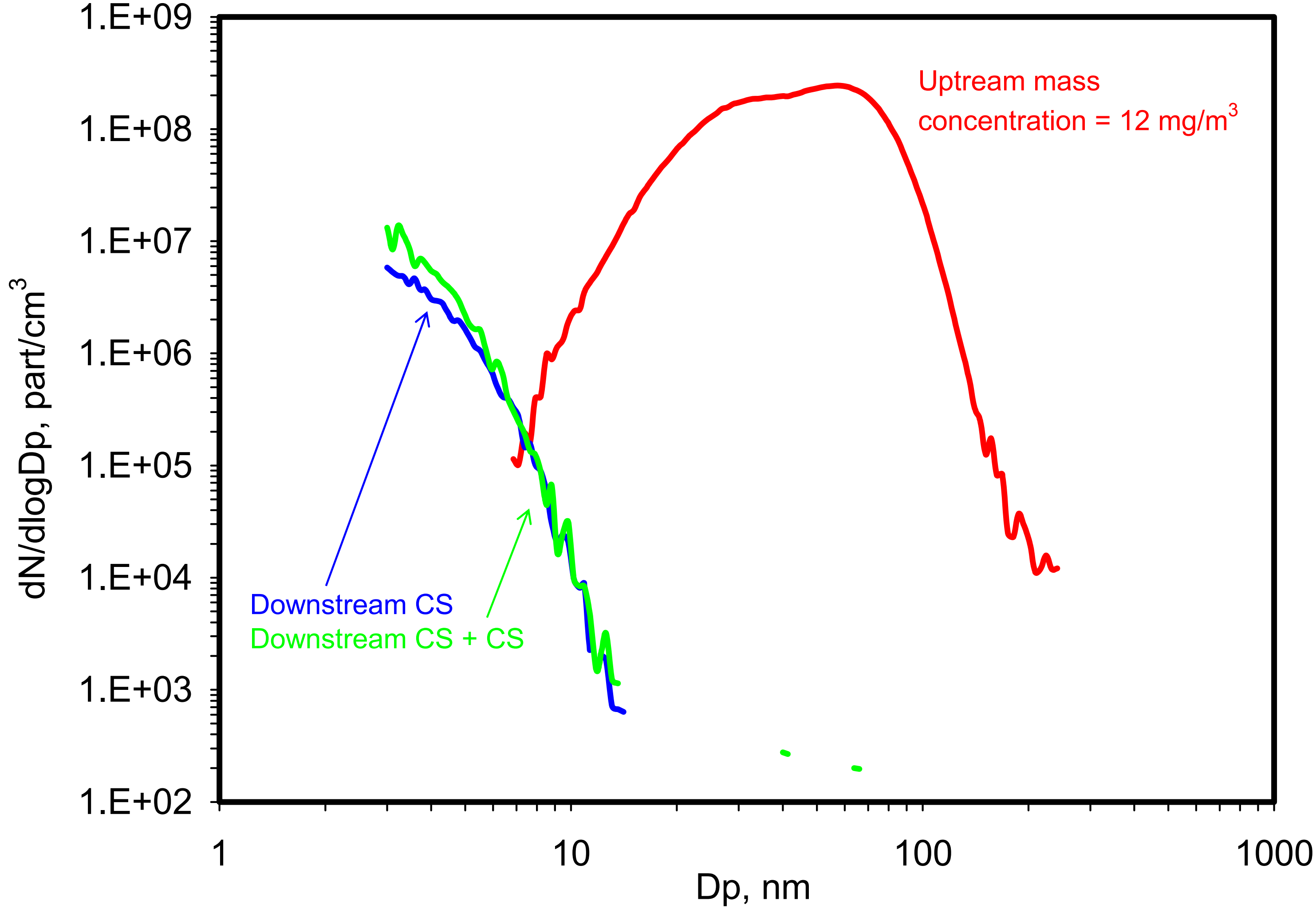
APC challenge with 1.0 mg/m³

Highest inlet concentration possible without re-nucleation downstream. Inlet concentration is really 100 µg/m³ because aerosol is first diluted 10x.



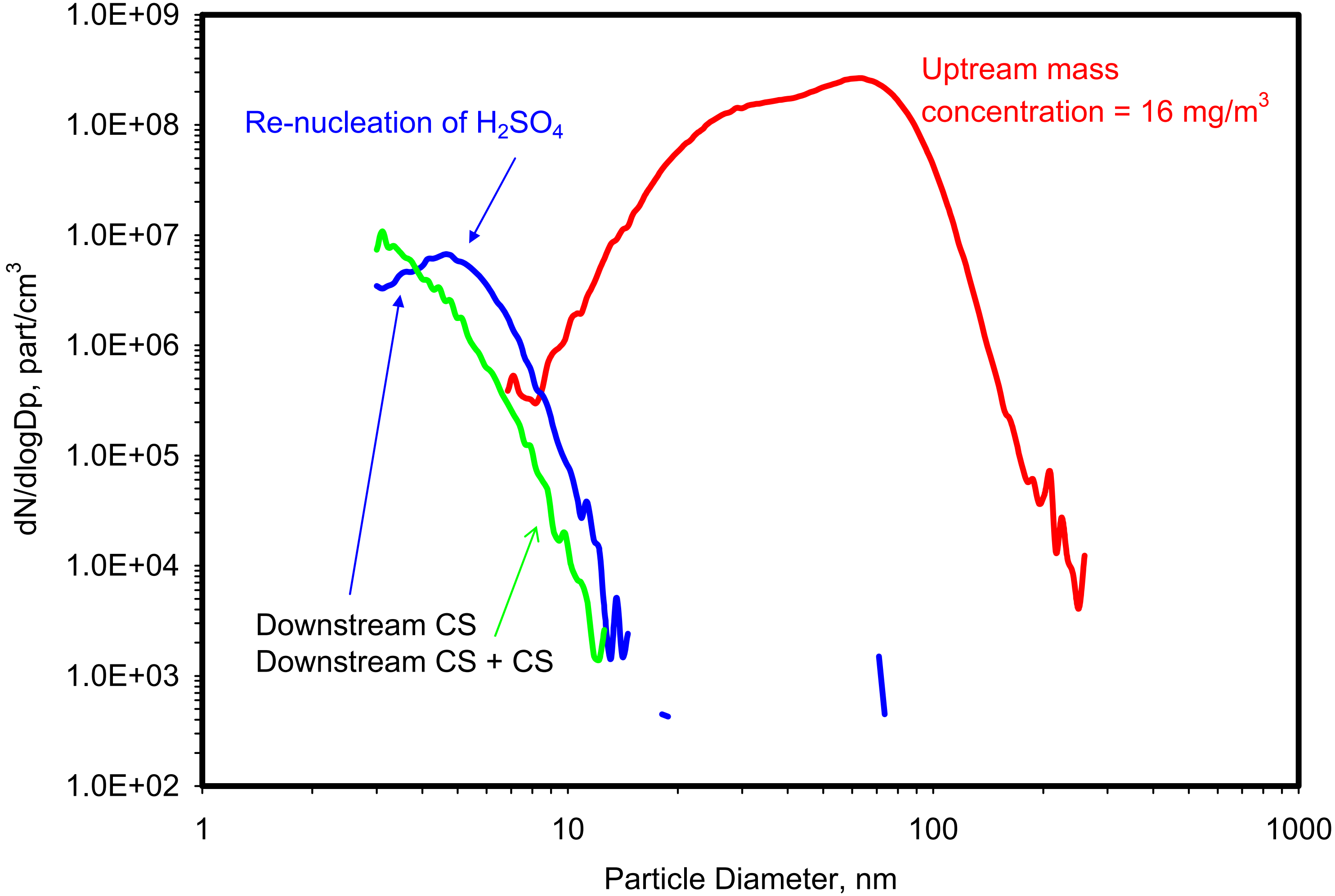
CS challenge – 12 mg/m³

No difference between 1 or 2 CS units, corrected for size dependant penetration



CS challenge – 16 mg/m^3

Use of 2 CS units shows sulfuric acid re-nucleation



Conclusions

- New particle generation method using glass beakers eliminates solid particle residues
- Method is not completely stable due to constant uptake of water by the acid – but it works
- Current results suggest renucleation occurs between 10 and 28 mg/m^3 upstream
  - Consistent with past result where renucleation was observed at 12 mg/m^3
  - Compared to renucleation in APC at ~ 100$\mu g/m^3$