Ultrafine Particle Emission & Control Strategies

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South Coast Air Quality Management District
Conference on Ultrafine Particles: The Science, Technology, and Policy Issues

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Some slides have been added and modified. If you wish an updated copy contact me at kitte001@umn.edu

Outline

- Introduction
  - Emission standard
  - Typical engine and atmospheric size distributions
  - Why do we care about particle size
- Particle Formation by Diesel Engines
  - Structure and composition of ultrafine and nanoparticles
  - Particle formation during dilution
- Dilution and Sampling issues
  - Laboratory measurements
  - On-road measurement
- Diesel particle removal systems
  - Description
  - On-road evaluation
- Particles from gasoline spark ignition engines
- Future issues and conclusions

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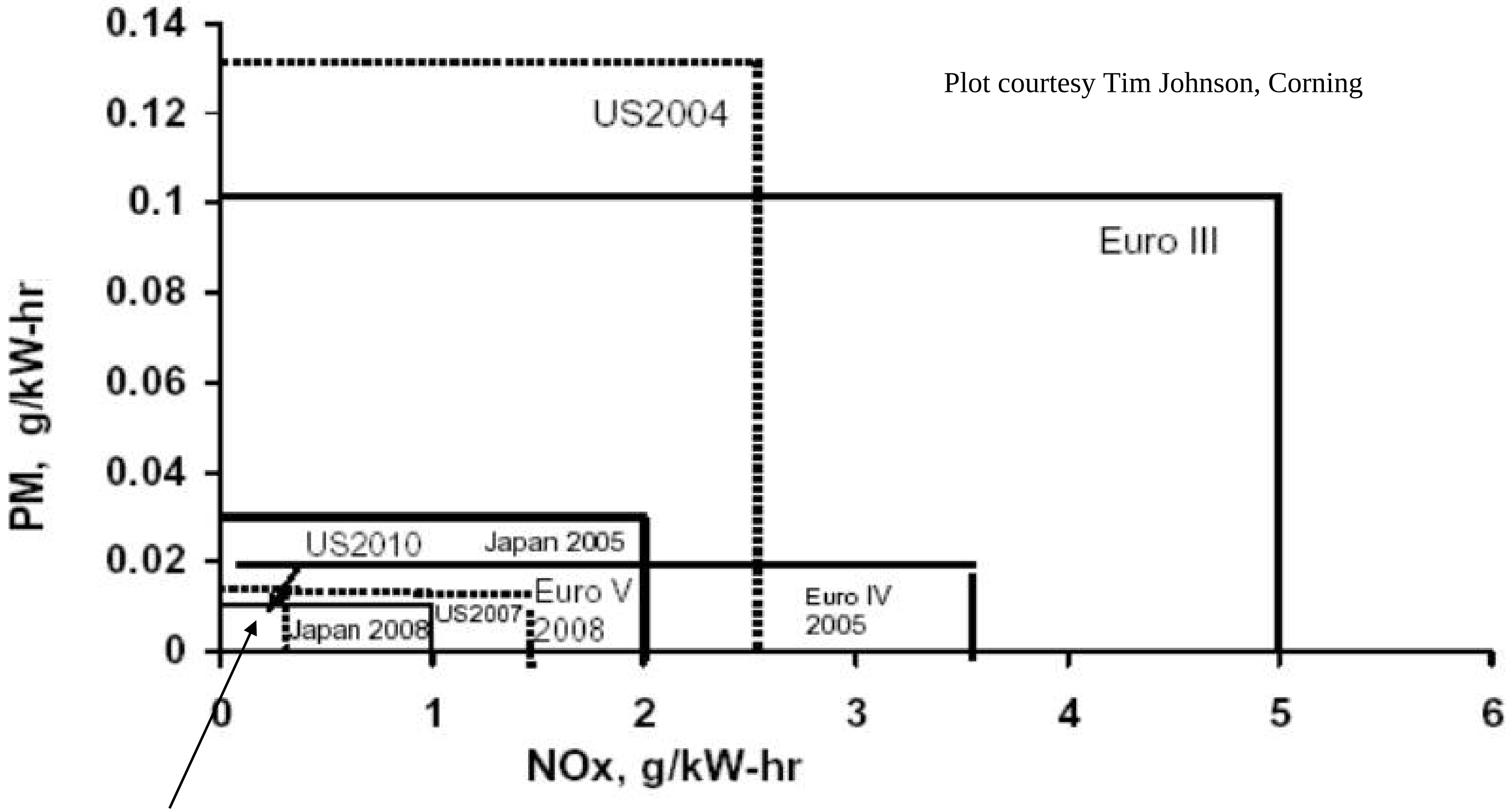
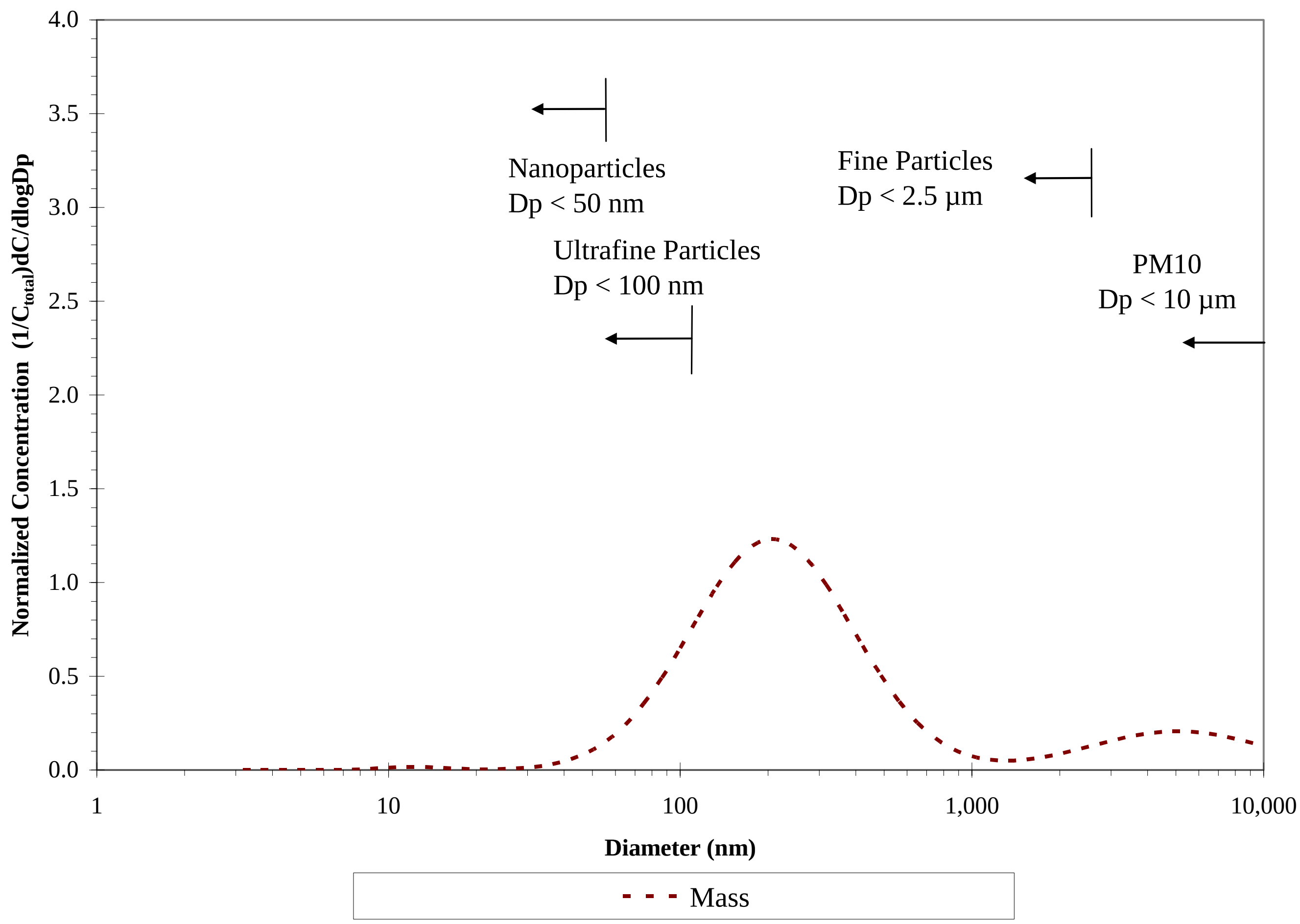
Emissions standards are becoming much tighter worldwide making exhaust aftertreatment essential



•US 2010 levels correspond to about 99% reduction in PM and 98% reduction in NOx

•2007 prototypes are better than the PM standard by factors of 5 to 20

Typical engine exhaust particle size distribution by mass, it consists of 3 size modes formed by different processes



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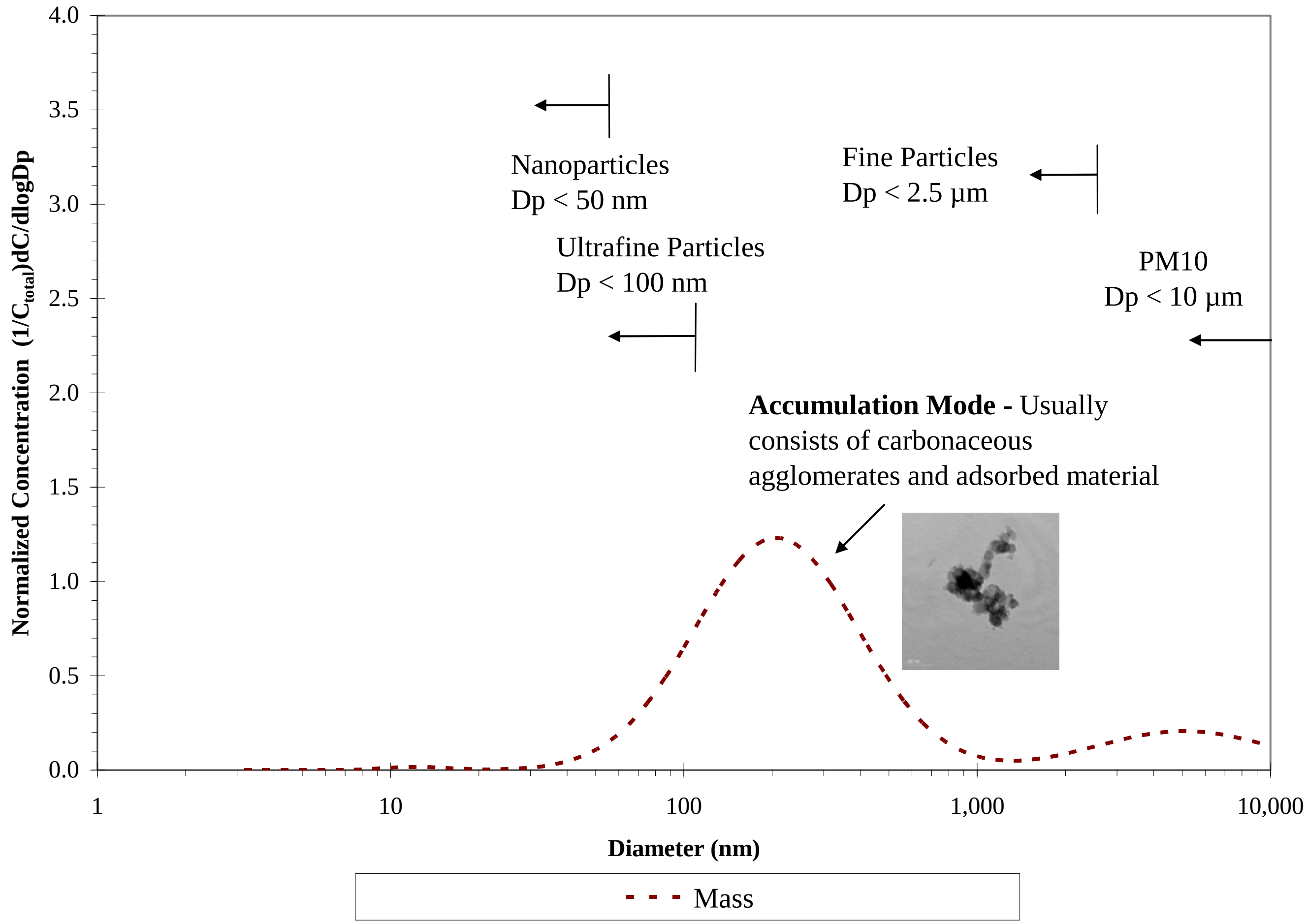

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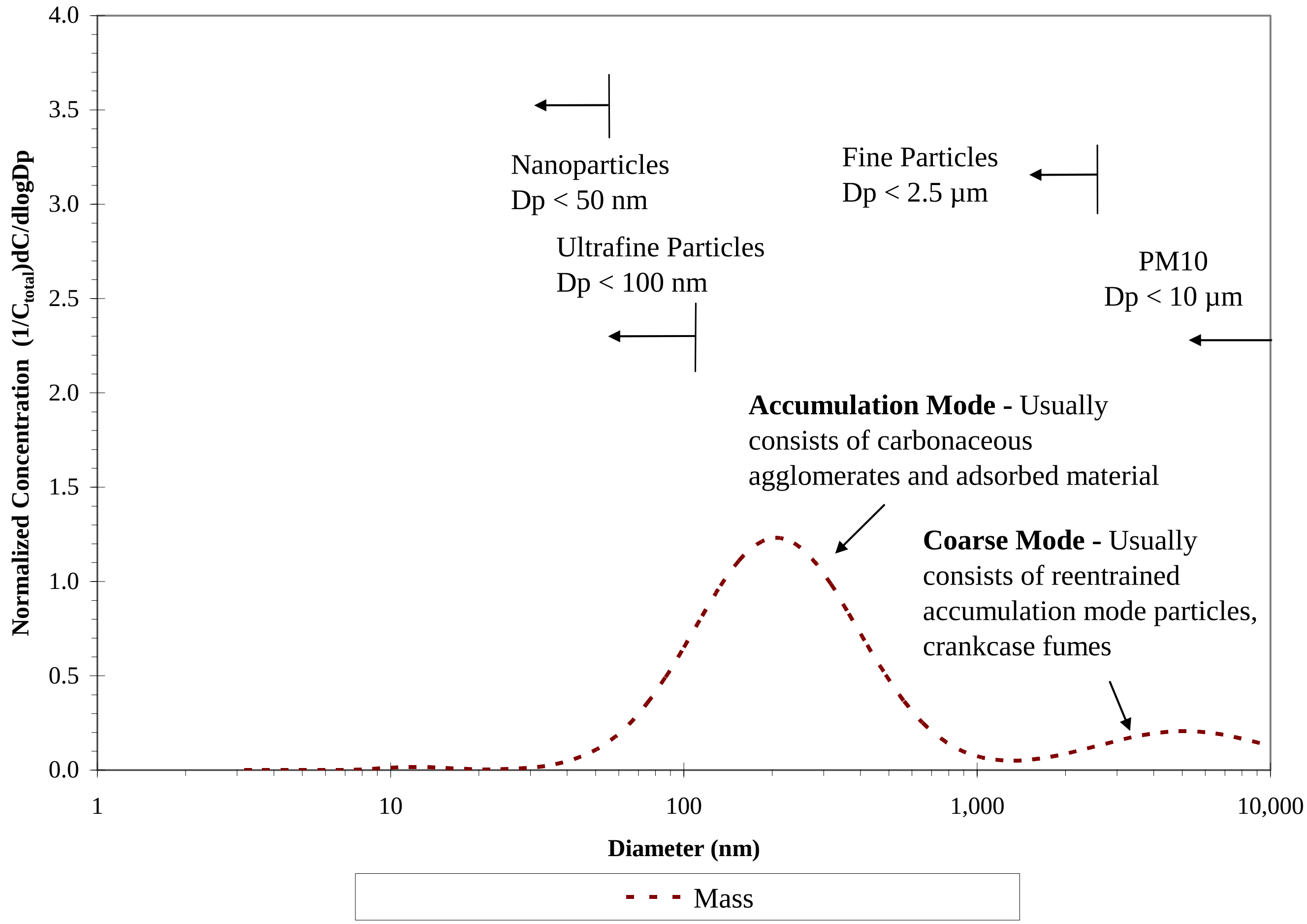

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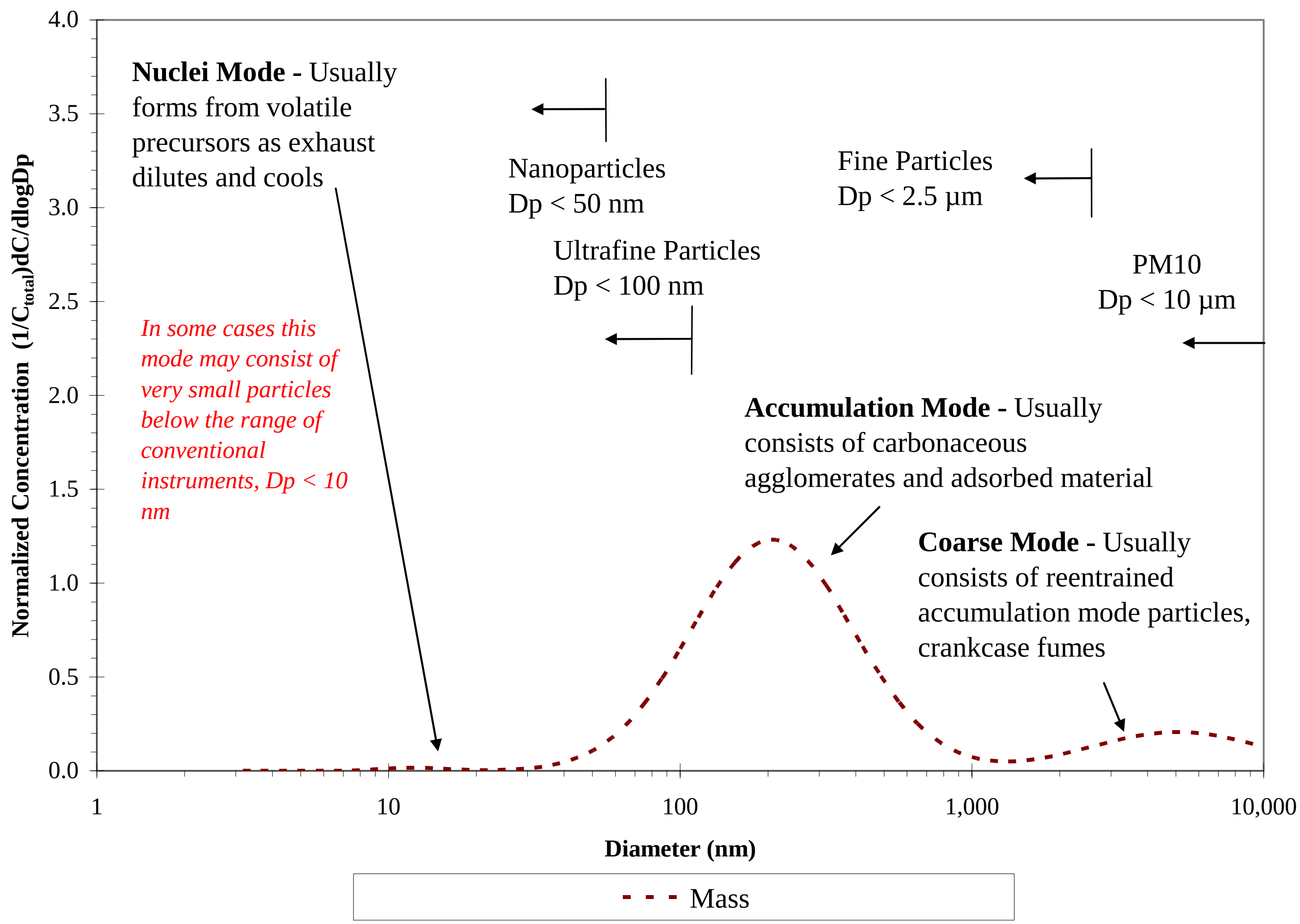
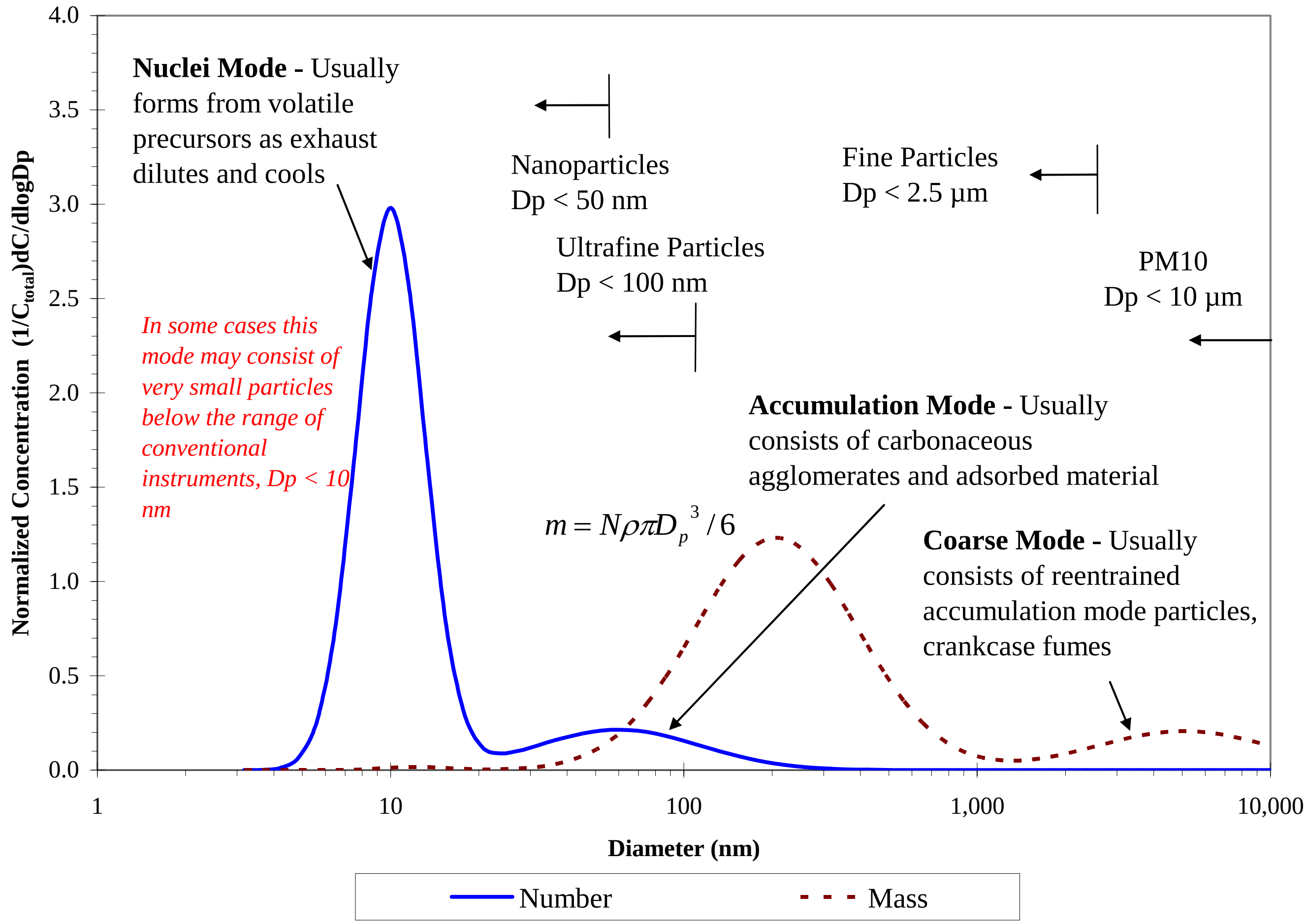
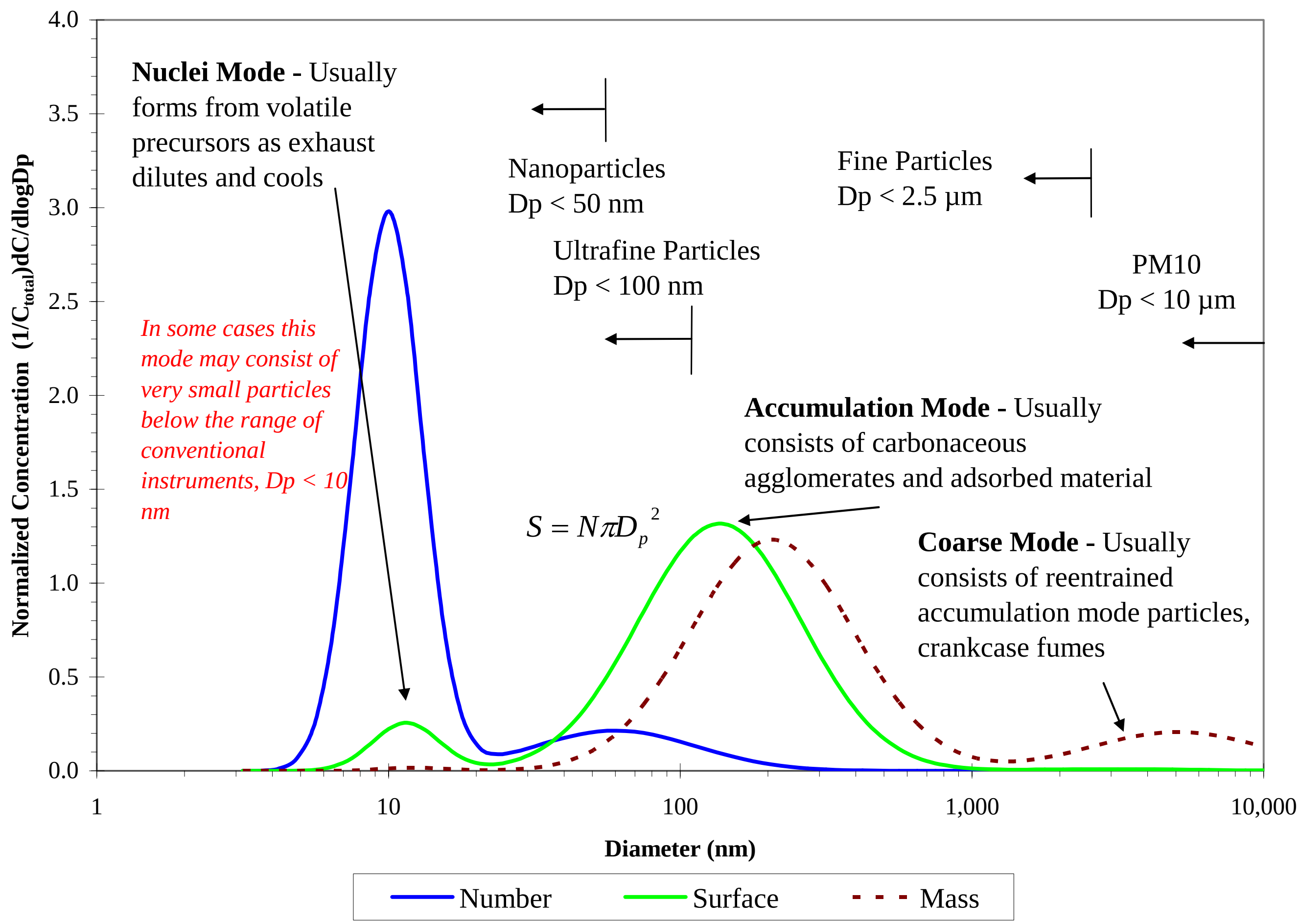


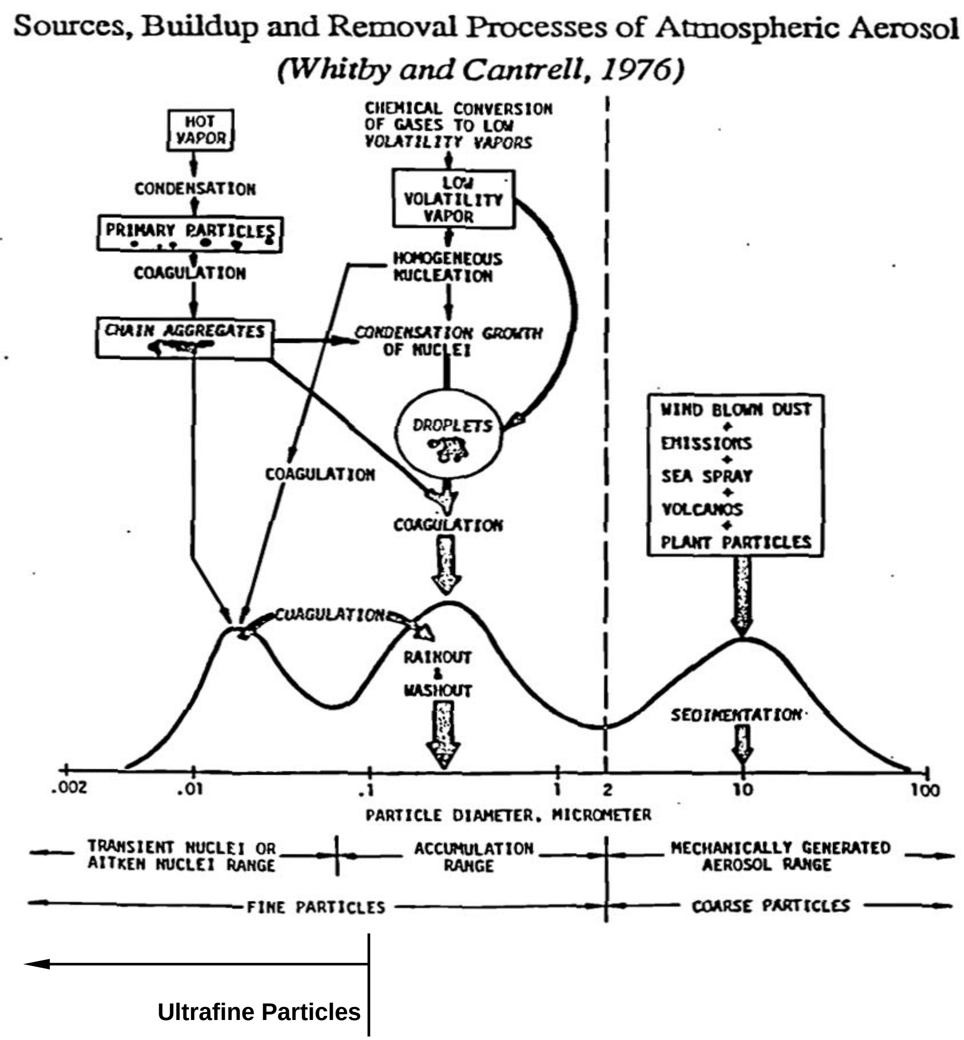
Typical engine exhaust particle size distribution by mass and number, most of number in nucleation mode



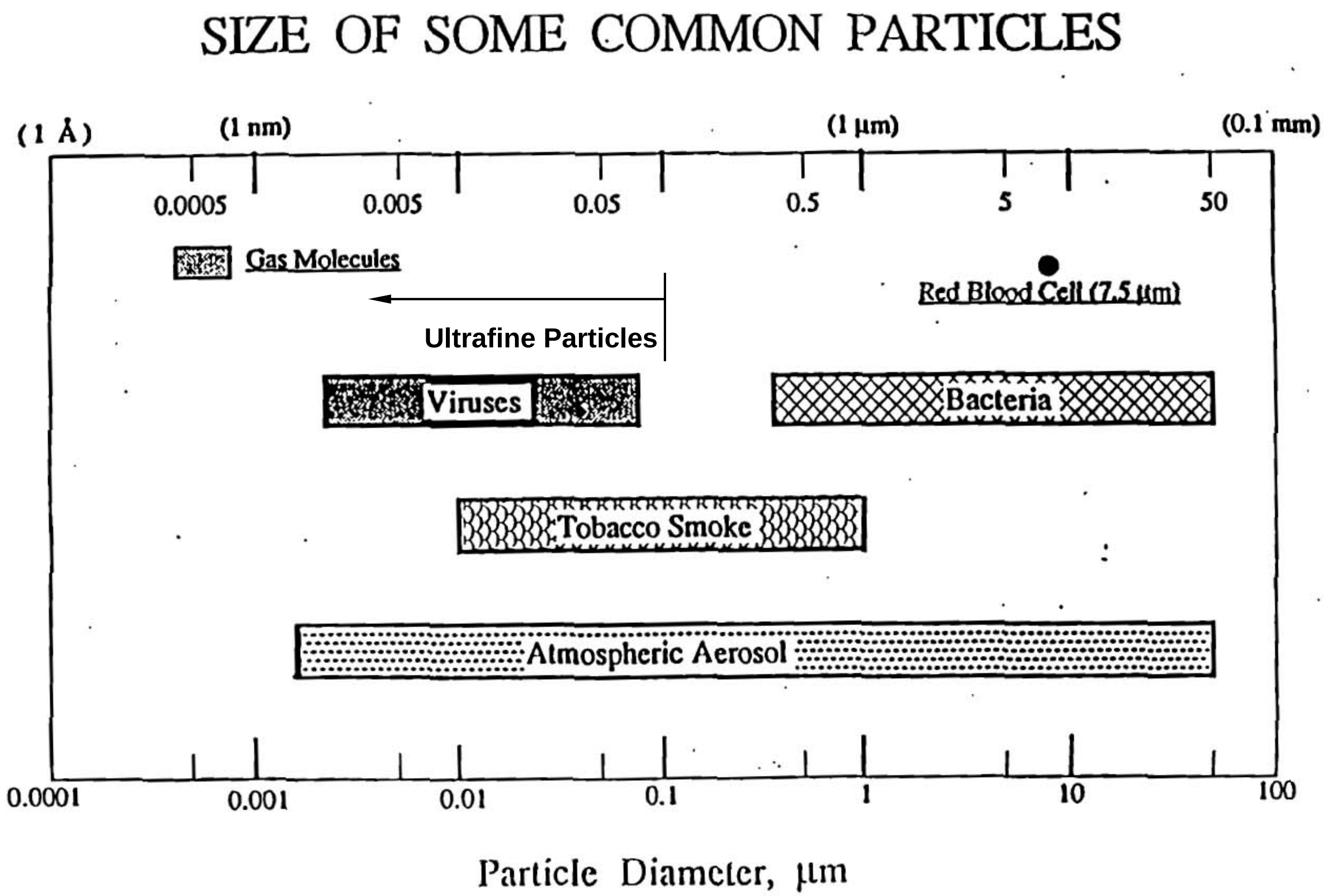
Typical engine exhaust particle size distribution by mass, number and surface area



Atmospheric Aerosols Generally Have a Trimodal Size Distribution



Particles Sizes Span a Very Wide Range



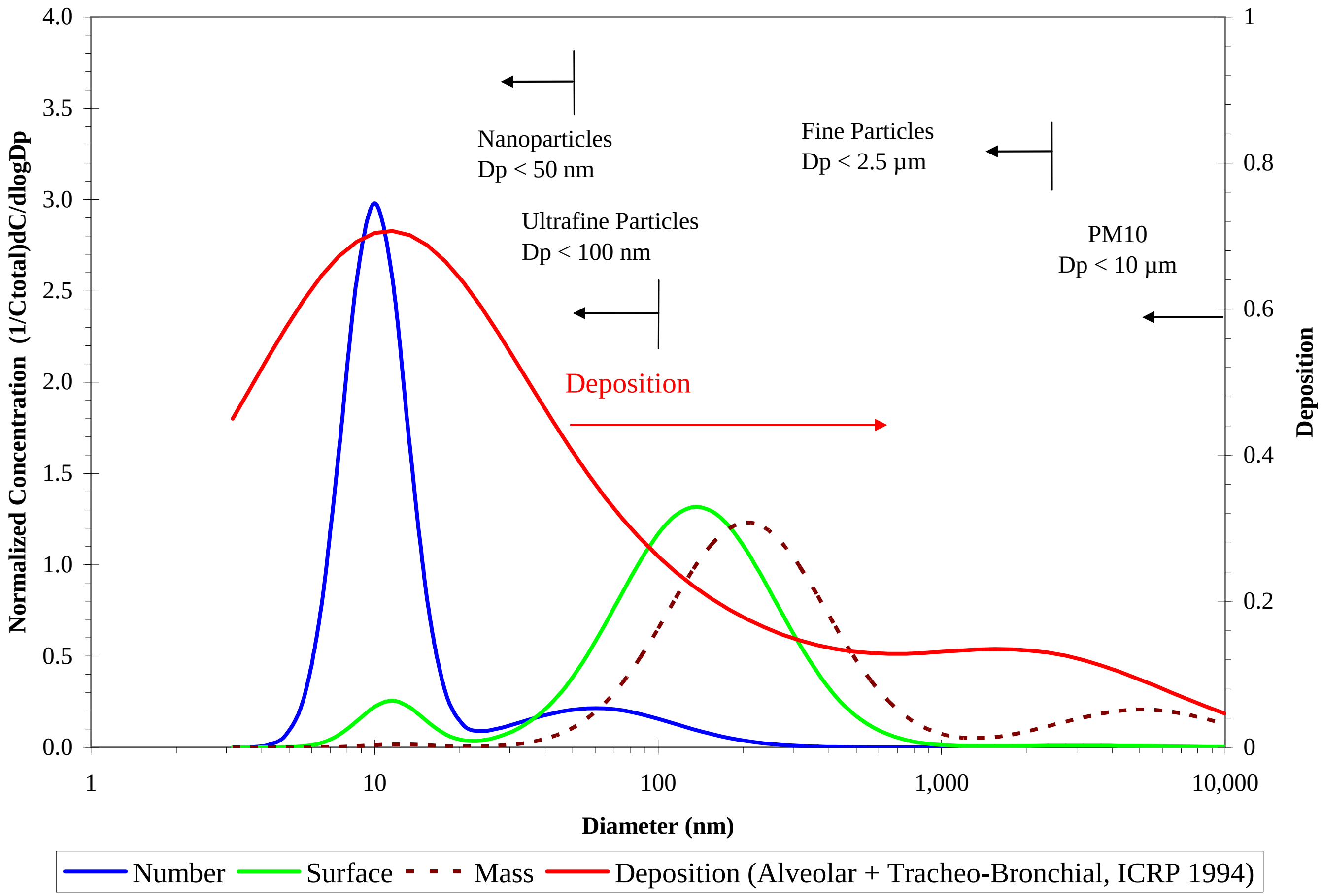
Why Are We Concerned about Particle Size?

- Health effects
- Behavior in atmospheric
  - Visibility
  - Residence time
  - Surface reactions
- Performance of aftertreatment devices
- Concerns that low (mass) emission engines may emit much smaller particles and higher number concentrations

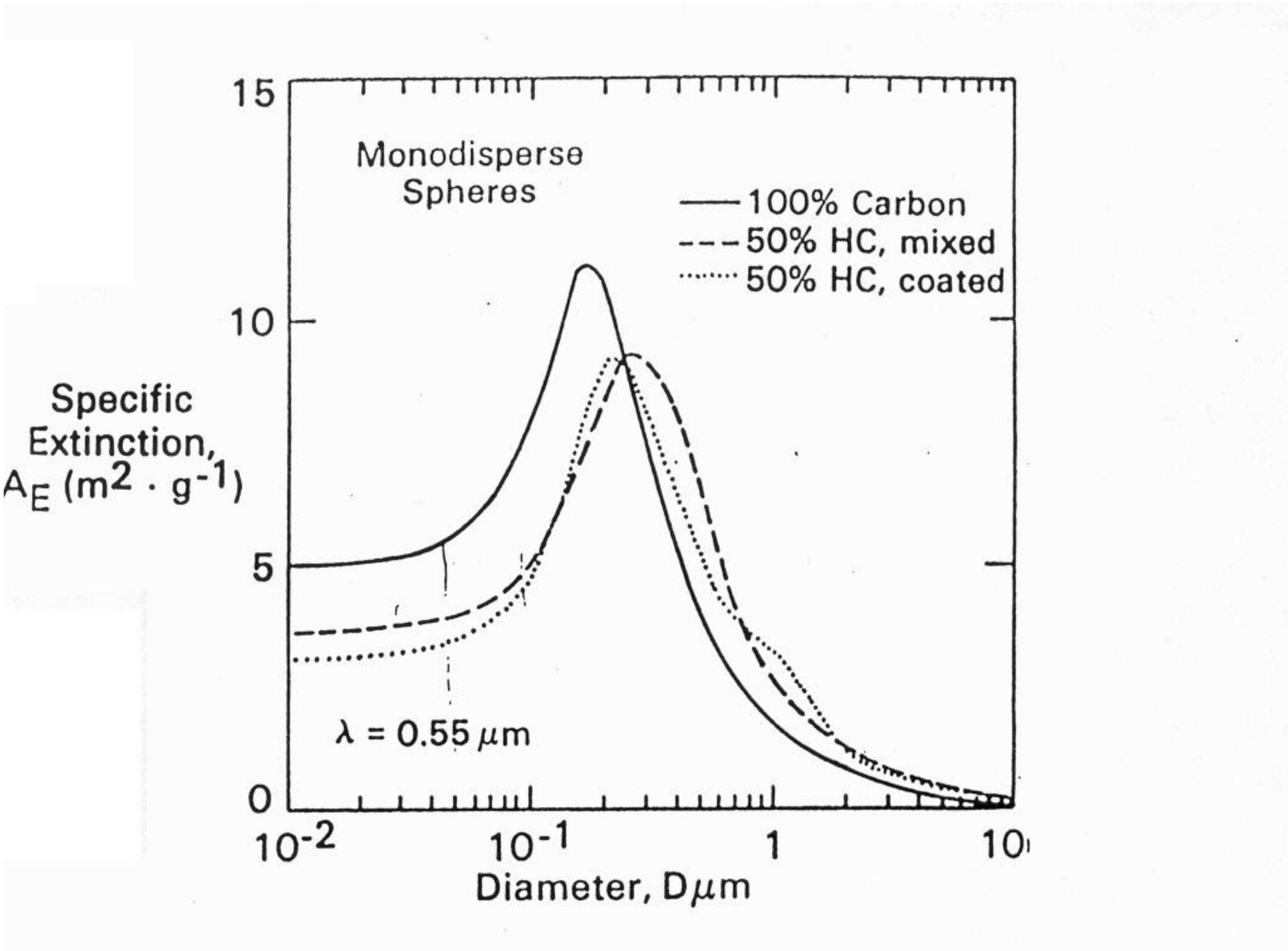
Health

- Correlations between fine particles and excess deaths
- Increased asthma and respiratory problems in children living near roadways
- Special concerns about ultrafine and nanoparticles
  - More surface area and number per unit mass
  - Increased deep lung deposition efficiency
  - Very small particles may pass through cell membranes and along neurons
  - Effects of solid particles clear, volatile particles uncertain

Health – Ultrafine particles are deposited on the deep lung regions more efficiently than fine particles

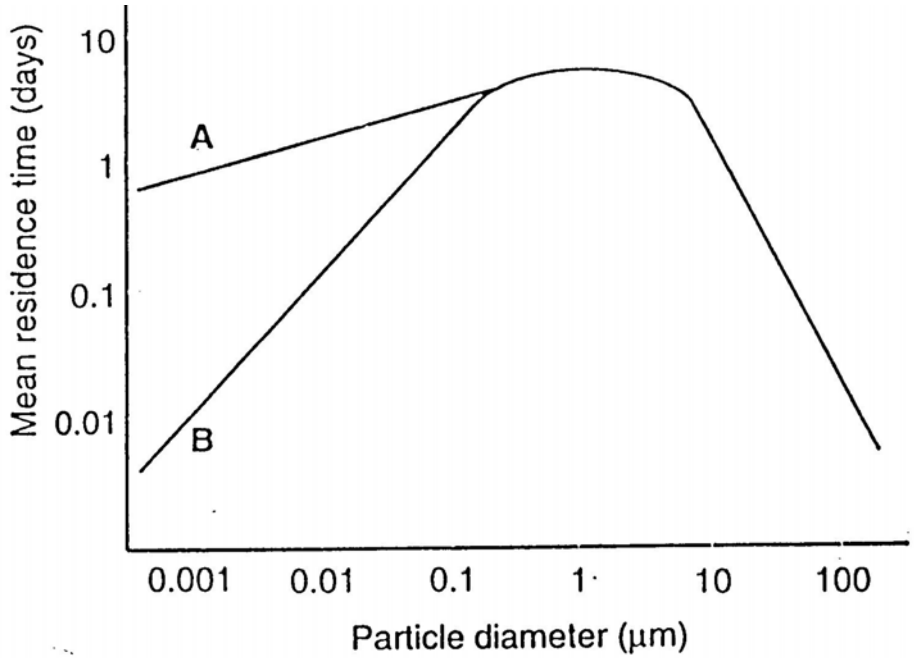


Optical Extinction by an Aerosol is also a Strong Function of Particle Size



Roessler, et al, 1981

Size Also Determines Residence Times in the Atmospheric Boundary Layer



Source: Adapted from Jaenicke, 1993.
Note: Curve A represents the deposition of aerosol particles to the ground, while curve B also includes the effect of coagulation, which reduces the number of small particles without removing their substance from the air.

"Airborne Particulate Matter in the United Kingdom," Third Report of the Quality of Urban Air Review Group, The University of Birmingham, Edgbaston, England, prepared at the request of the Department of the Environment, UK (May 1996).

Size and Filtration (Trap Performance)

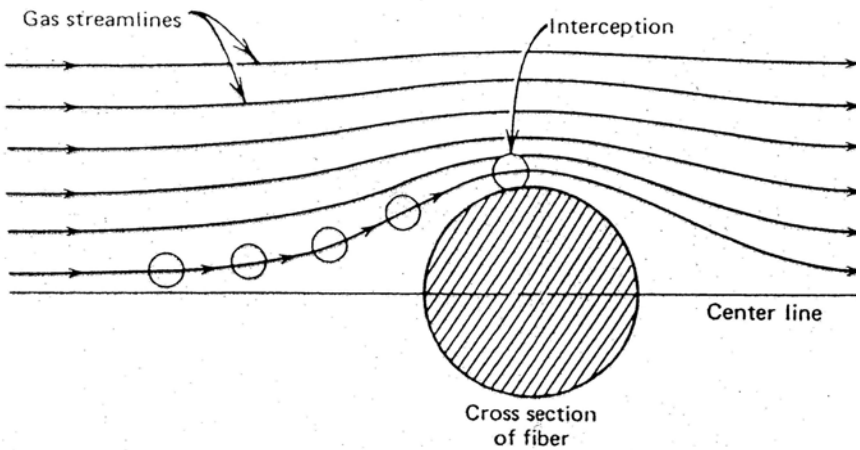


FIGURE 9.5 Single-fiber collection by interception.

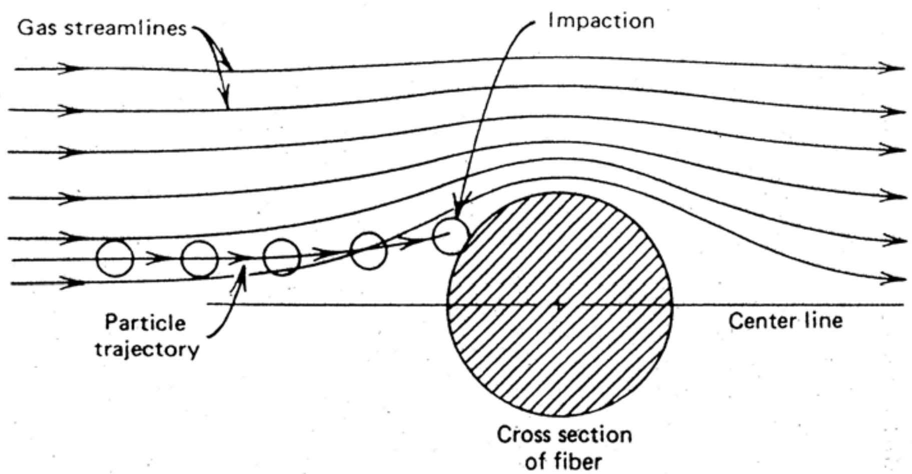


FIGURE 9.6 Single-fiber collection by impaction.

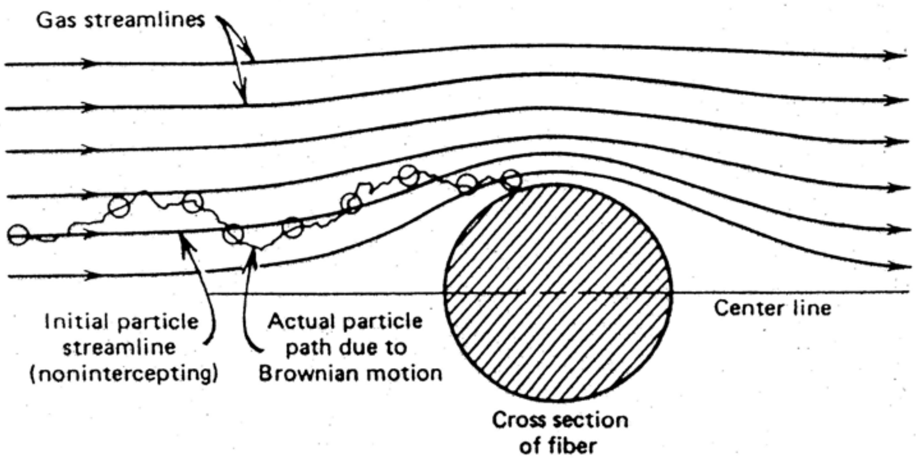


FIGURE 9.7 Single-fiber collection by diffusion.

Adapted from: Hinds, W.C., (1982) Aerosol Technology: Properties, Behavior and Measurement of Airborne Particles, John Wiley & Sons

Size and Filtration (Trap Performance)

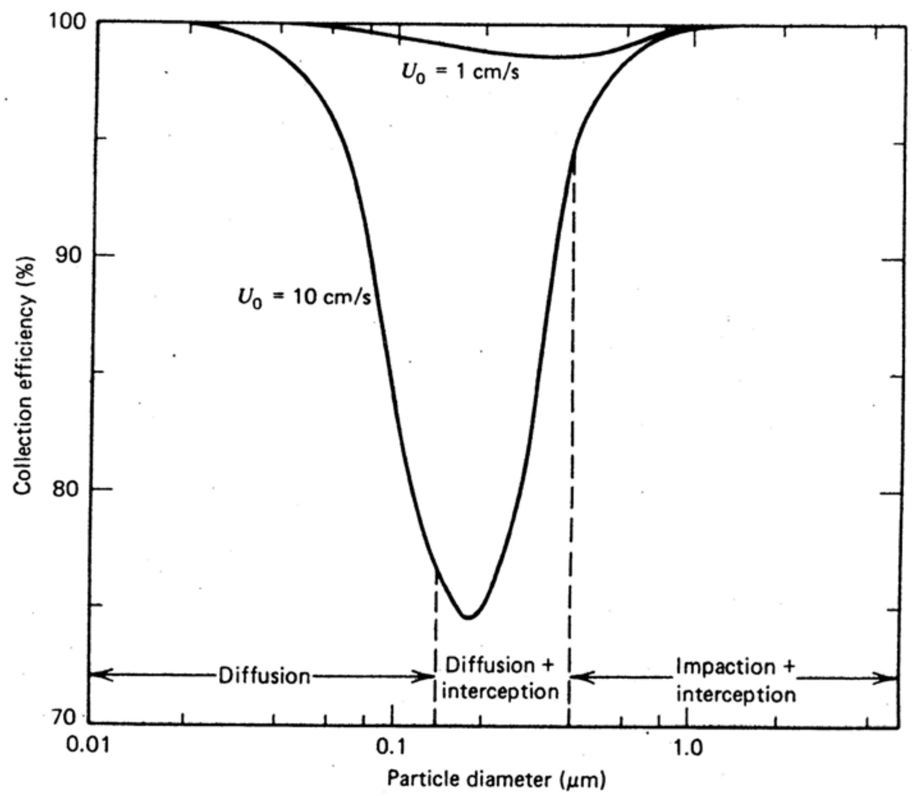


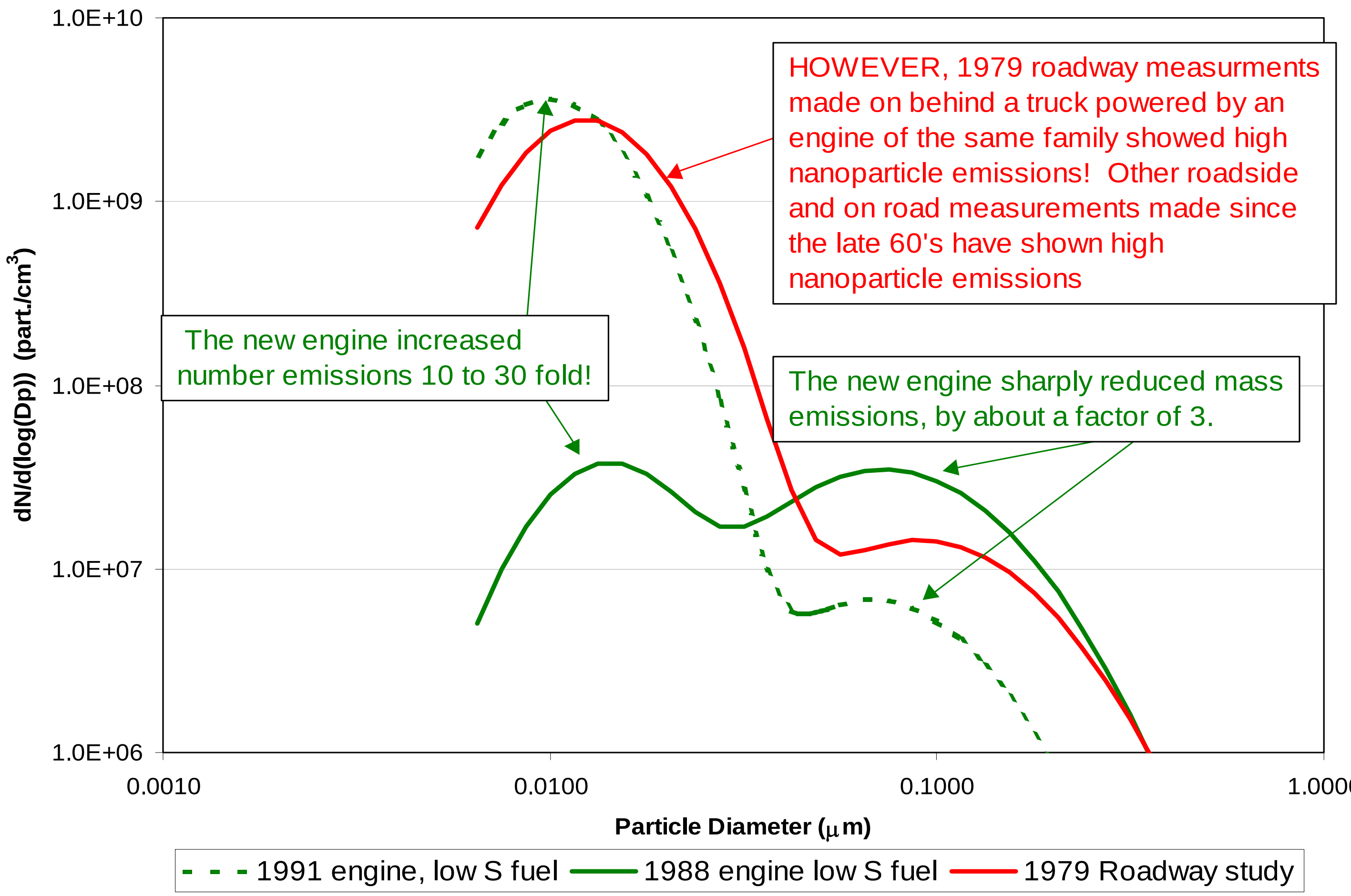
FIGURE 9.9 Filter efficiency versus particle size for face velocities of 0.01 and 0.1 m/s [1 and 10 cm/s]; t = 1 mm, α = 0.05, and d_f = 2 μm.

Adapted from: Hinds, W.C., (1982) Aerosol Technology: Properties, Behavior and Measurement of Airborne Particles, John Wiley & Sons

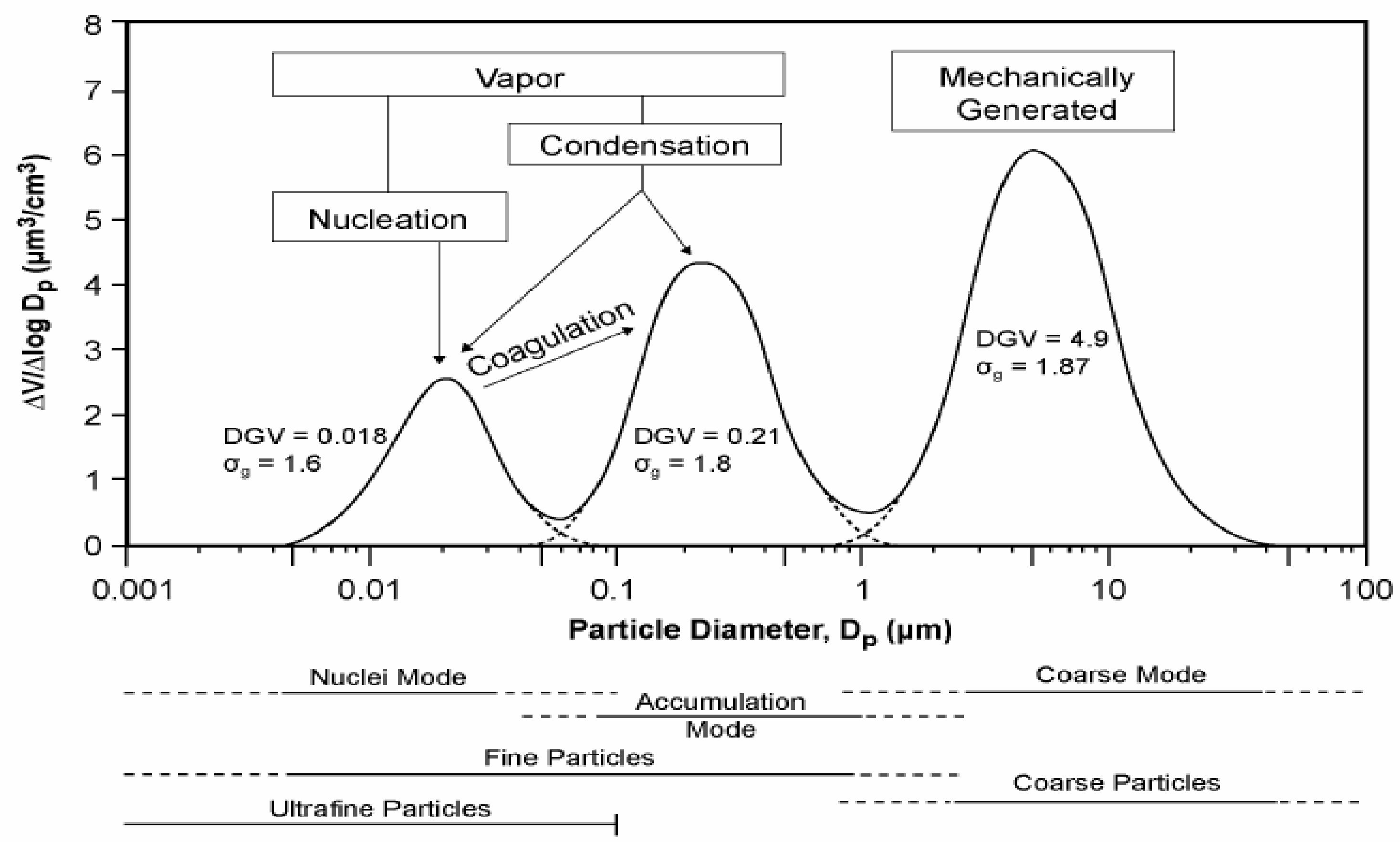
Background - Historical Perspective

- Often cited 1996 HEI study showed dramatic increase in nanoparticle emissions
  - For a 1991 engine compared to 1988 engine, running on very low sulfur fuel
  - But 1988 engine also produced high nanoparticle emissions with 0.3% fuel
- Measurements made during 70’s and 80’s often showed high nanoparticle emissions
  - Roadway measurements nearly always associated with large nuclei (nanoparticle) mode
  - Both diesel and spark ignition sources
  - Nanoparticles mostly volatile, except with metallic additives
- **High nanoparticle emissions are not a new development!**

Number Size Distribution Data from HEI Report and 1979 CRC Roadway Study



Volume size distribution, measured in traffic in the 1970s, note large concentration of ultrafine particles



DGV (geometric mean diameter by volume, equivalent to volume median diameter) and σ_g (geometric standard deviation) are shown for each mode.

Source: Air Quality Criteria for Particulate Matter: Volume I, EPA/600/P-99/002aF, October 2004.

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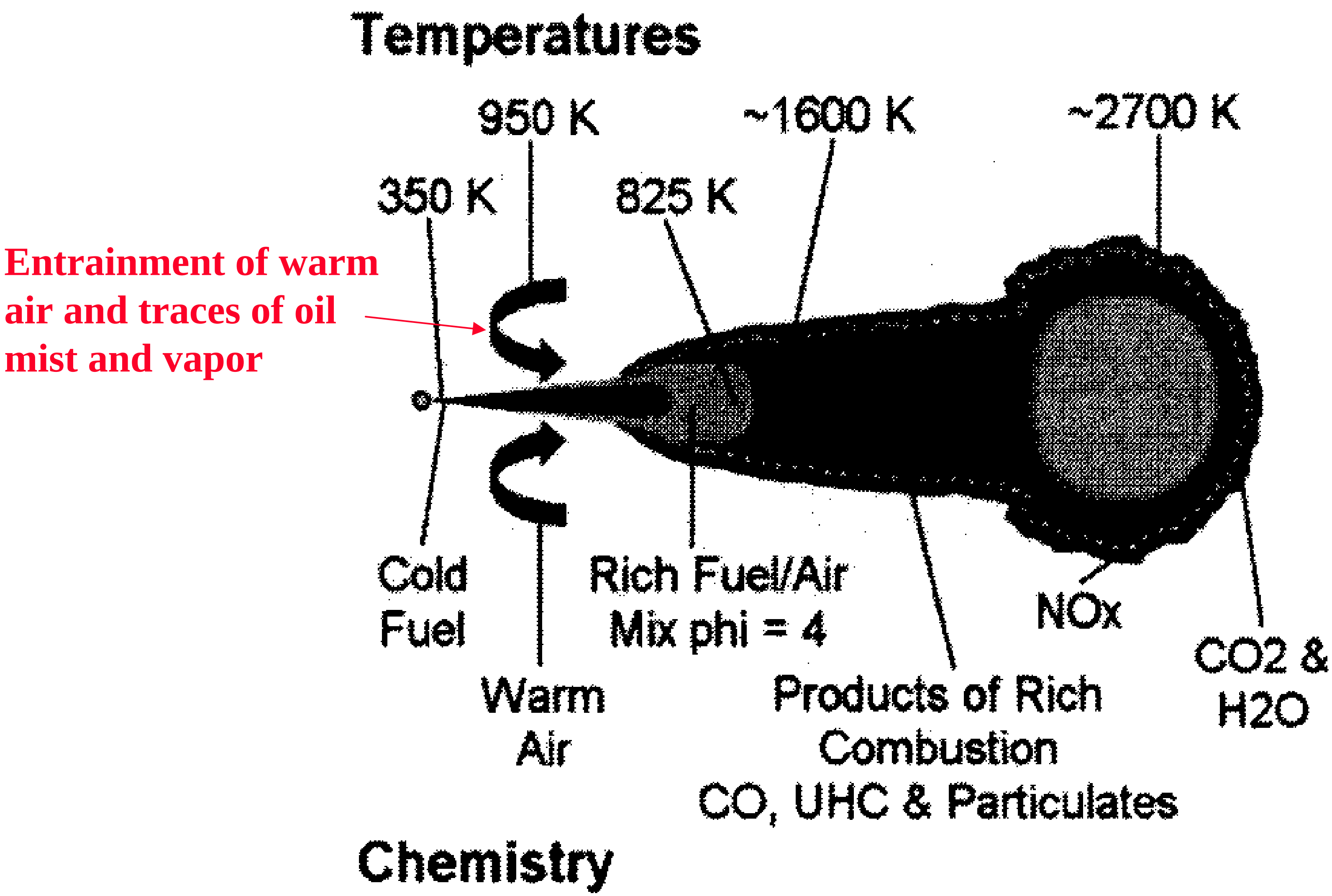
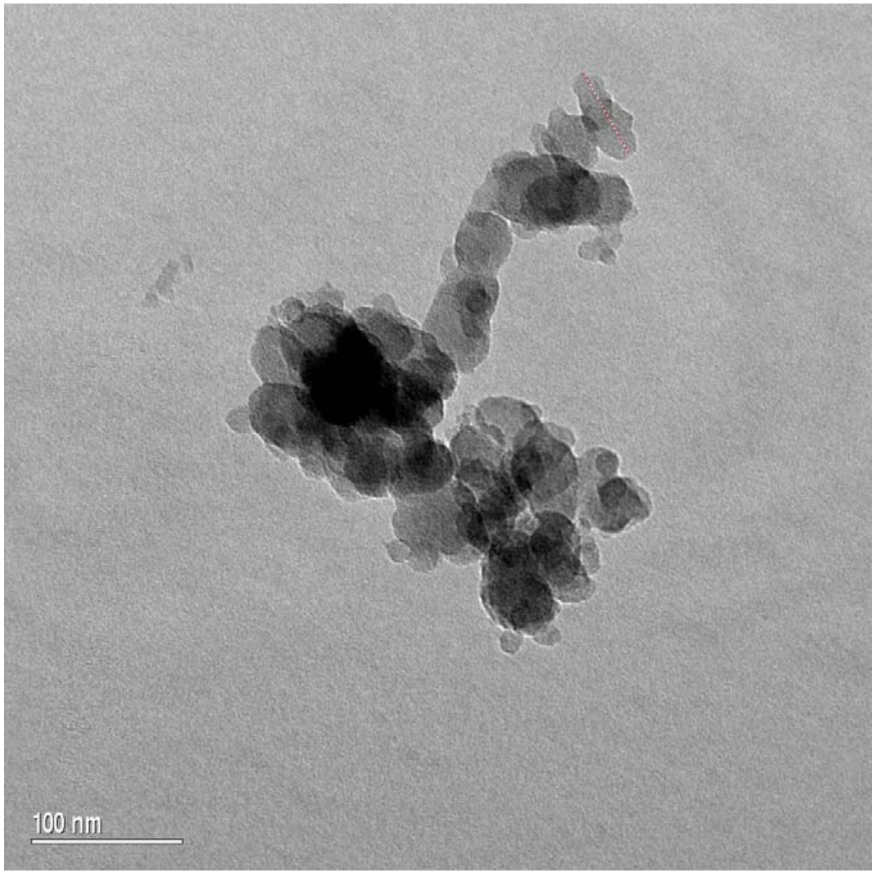
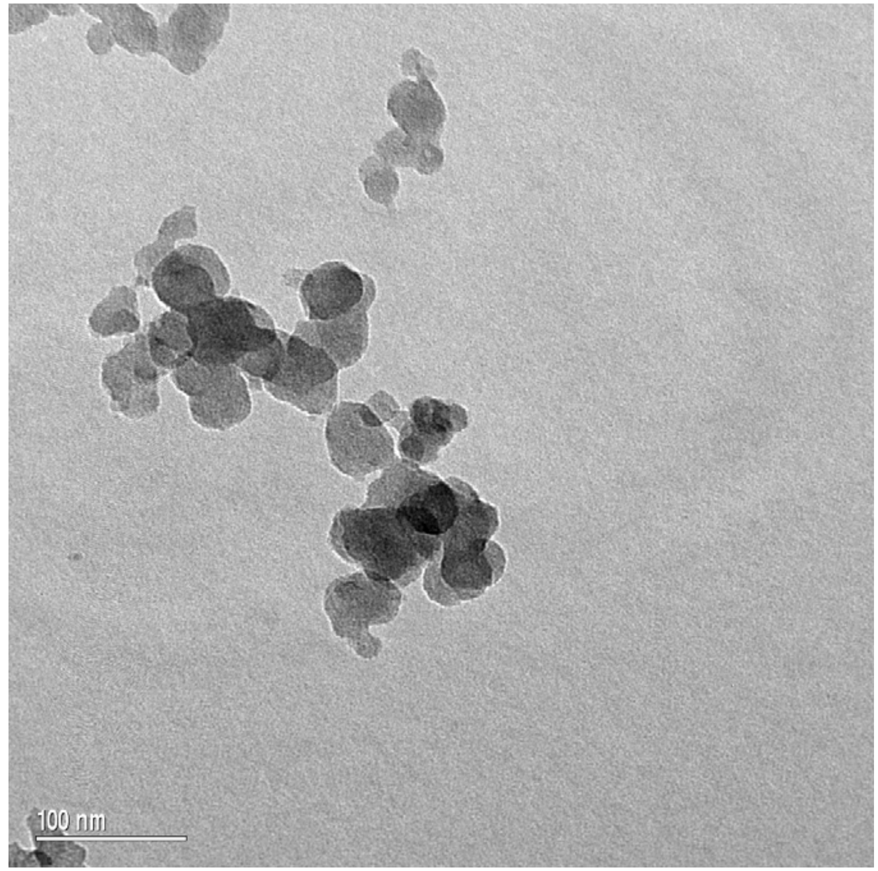
Combustion in Diesel Engines – burning jet, adapted from SAE 1999-01-0509



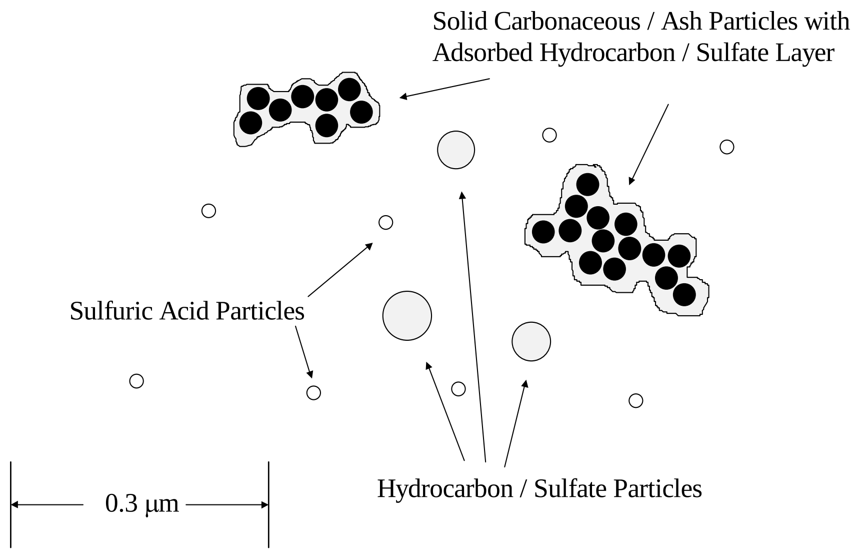
Carbonaceous Agglomerates Comprise Most of the Mass from Current Diesel Engines

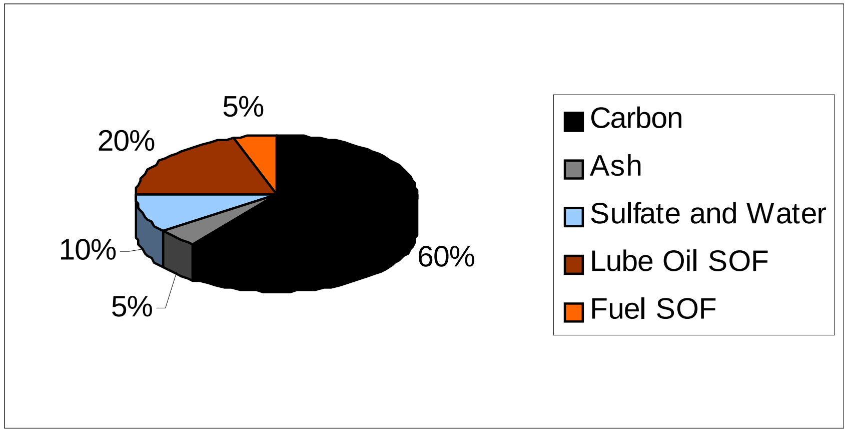




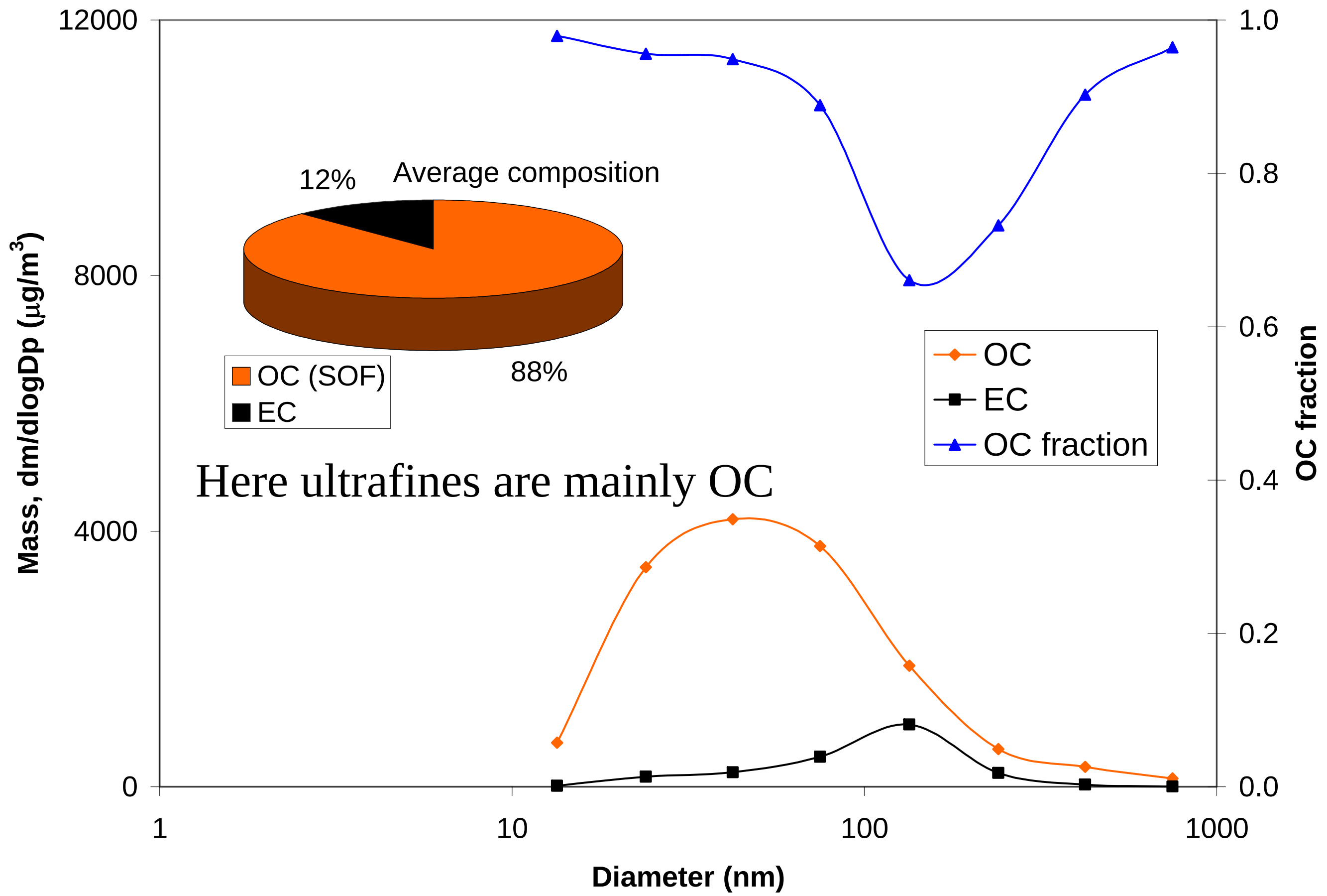
Typical composition and structure of diesel particulate matter – *heavy-duty, no aftertreatment*

- Solid particles are typically carbonaceous chain agglomerates (mainly elemental carbon, EC) and ash and usually comprise most of the particle mass
- Volatile or semi-volatile matter (sulfur compounds and organic carbon (SOF)) typically constitutes 35% (5-90%) of the particle mass, 90% (30-99%) of the particle number
- Carbon and sulfur compounds derive mainly from fuel
- SOF and ash derive mainly from oil
- Most of the volatile and semi-volatile materials undergo gas-to-particle conversion as exhaust cools and dilutes



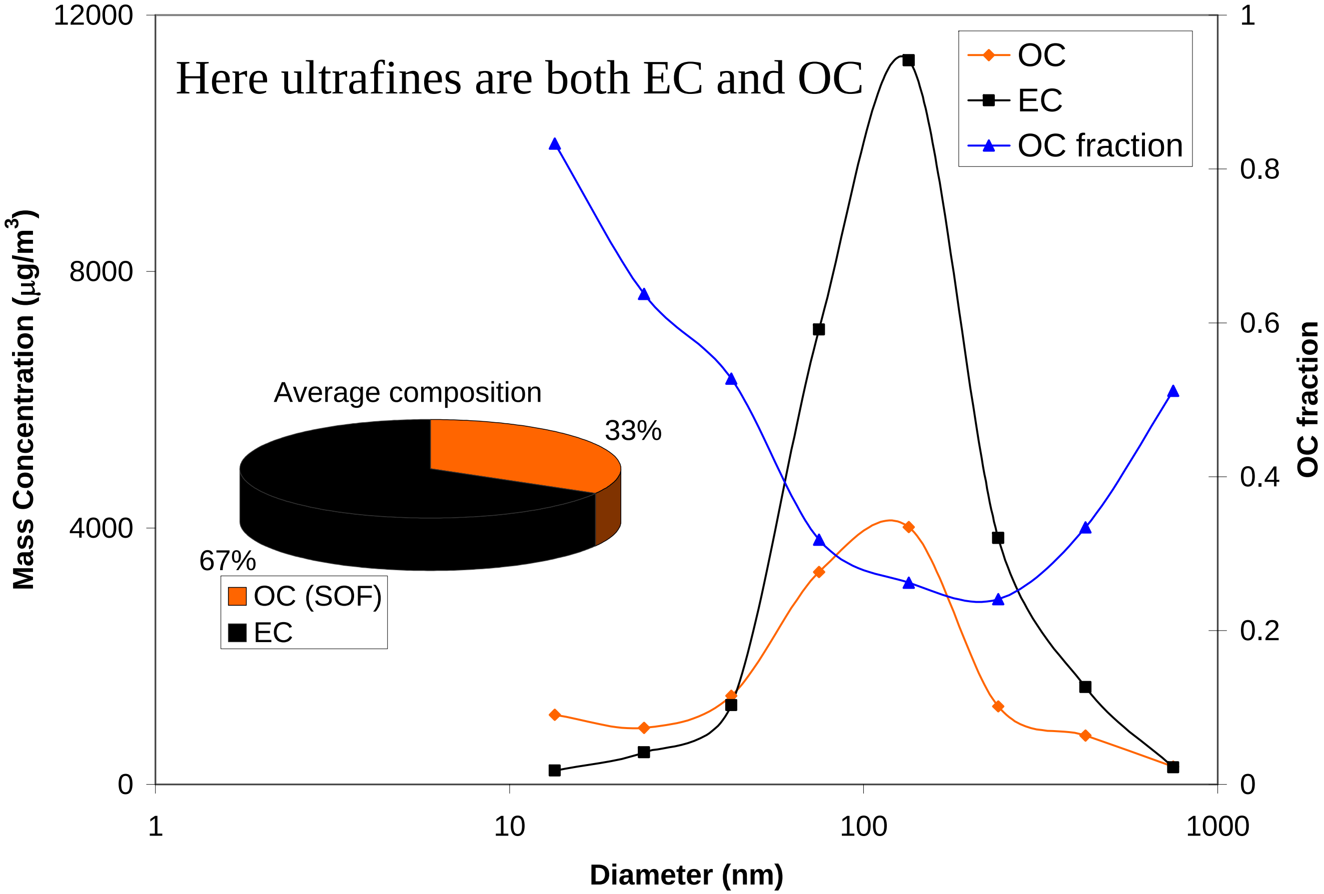


The composition of Diesel particles is very load and size dependent – slow traffic, light load, mainly OC



Barbara Zielinska, Wendy Goliff and Mark McDaniel, Desert Research Institute, Thomas Cahill, University of California, Davis, David Kittelson and Winthrop Watts, University of Minnesota, CHEMICAL ANALYSES OF COLLECTED DIESEL PARTICULATE MATTER SAMPLES IN THE E-43 PROJECT, Final Report Prepared for: National Renewable Energy Laboratory, Subcontract No. ACI-9-29099-01, January 2003

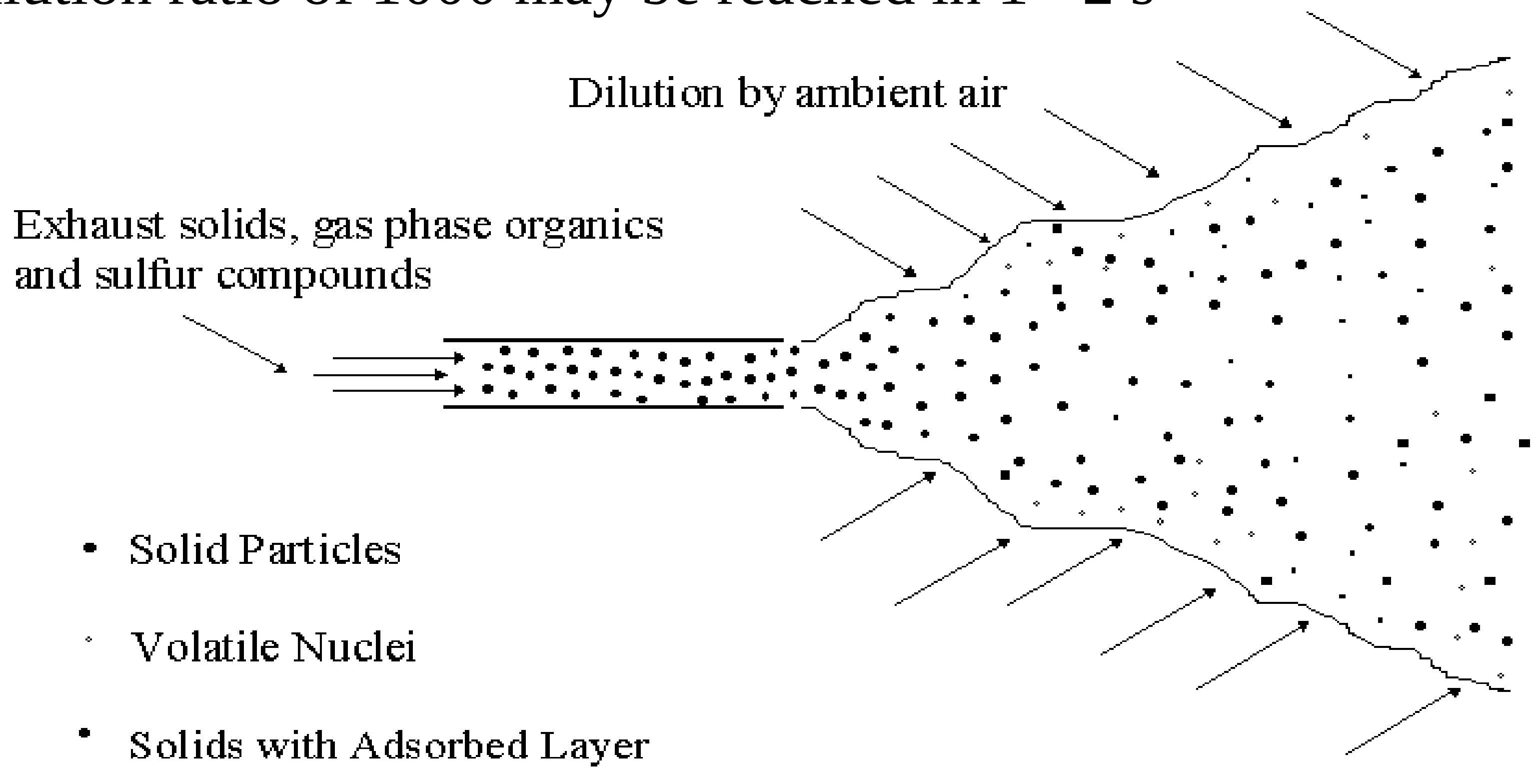
The composition of Diesel particles is very load and size dependent – highway cruise, mainly EC



Barbara Zielinska, Wendy Goliff and Mark McDaniel, Desert Research Institute, Thomas Cahill, University of California, Davis, David Kittelson and Winthrop Watts, University of Minnesota, CHEMICAL ANALYSES OF COLLECTED DIESEL PARTICULATE MATTER SAMPLES IN THE E-43 PROJECT, Final Report Prepared for: National Renewable Energy Laboratory, Subcontract No. ACI-9-29099-01, January 2003

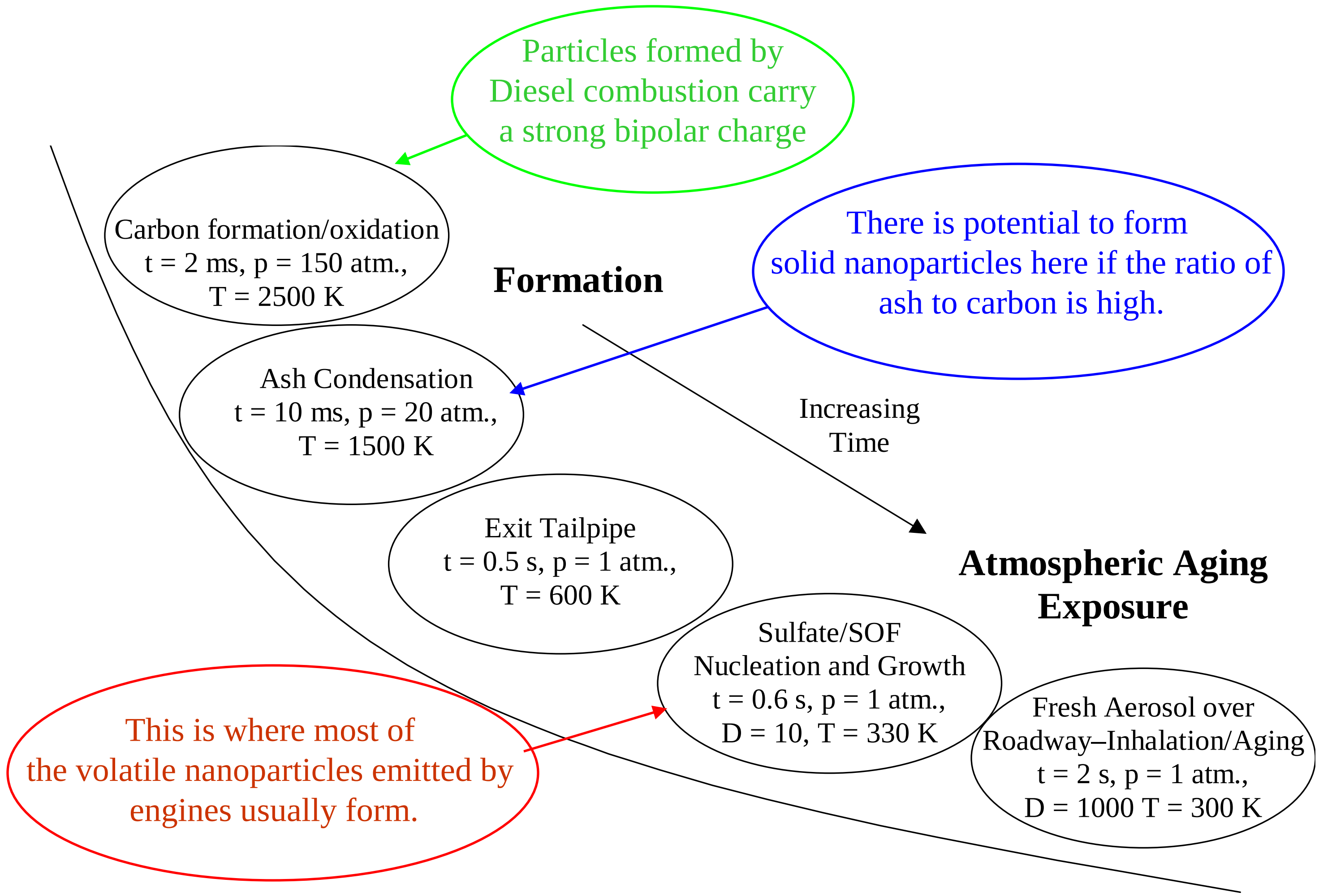
Atmospheric dilution leads to nucleation, absorption, and adsorption - in excess of 90 % of the particle number may form as the exhaust dilutes

A dilution ratio of 1000 may be reached in 1 - 2 s



Exhaust solids are mainly solid carbon (EC) and ash from lube oil
Volatiles include organic carbon (OC) and sulfuric acid

Particle formation history – 2 s in the life of an engine exhaust aerosol



Kittelson, D. B., W. F. Watts, and J. P. Johnson 2006. "On-road and Laboratory Evaluation of Combustion Aerosols Part 1: Summary of Diesel Engine Results," Journal of Aerosol Science, in press.

Nature of particles emitted by Diesel engines – *heavy duty without aftertreatment*

- Engines produce a bimodal size distribution in the submicron range with a nuclei mode containing most of the particle **number** in the 3-30 nm diameter range and an accumulation mode containing most of the particle **mass** in the 30-500 nm range
- The nuclei mode is nearly always in the ultrafine range, while the accumulation mode is partially fine, partially ultrafine. Perhaps it is better to think of modes rather than arbitrary size distinctions
- Nuclei mode particles form mainly from volatile precursors, mainly heavy hydrocarbons and sulfuric acid
  - Nuclei mode particles typically consist mainly of heavy hydrocarbons, however the formation of this mode is facilitated by sulfur in the fuel
  - Their formation is very dependent on dilution conditions, especially dilution rate and dilution air temperature
  - Their formation is favored by low carbon and high precursor concentrations
  - Although these particles are volatile they may be relatively insoluble – this could influence their behavior in biological systems

Nature of particles emitted by Diesel engines - *heavy duty without aftertreatment*

- Solid nuclei mode particles may form from metals in the lube oil under engine conditions that lead to little solid carbon formation. They also may form when metallic additives or other high metal fuels are used.
- The accumulation mode is where most “soot” or “smoke” resides
  - It consists primarily of carbonaceous agglomerates and adsorbed hydrocarbons
  - Particles in this mode are strongly light absorbing
  - The number and mobility size of accumulation mode particles are not strongly influenced by dilution conditions
  - Accumulation mode particles have been reduced sharply by better engine technology
- Solid particles may be nearly completely eliminated by filtration
- Filters cannot directly remove the gas phase precursors that lead to the formation of volatile nuclei mode particles
  - Precursors may be removed by adsorption on collected particles followed by..
  - Hydrocarbon precursors may be destroyed in catalyzed systems to the extent allowed by kinetics (mainly mass transfer) but sulfuric acid may be formed

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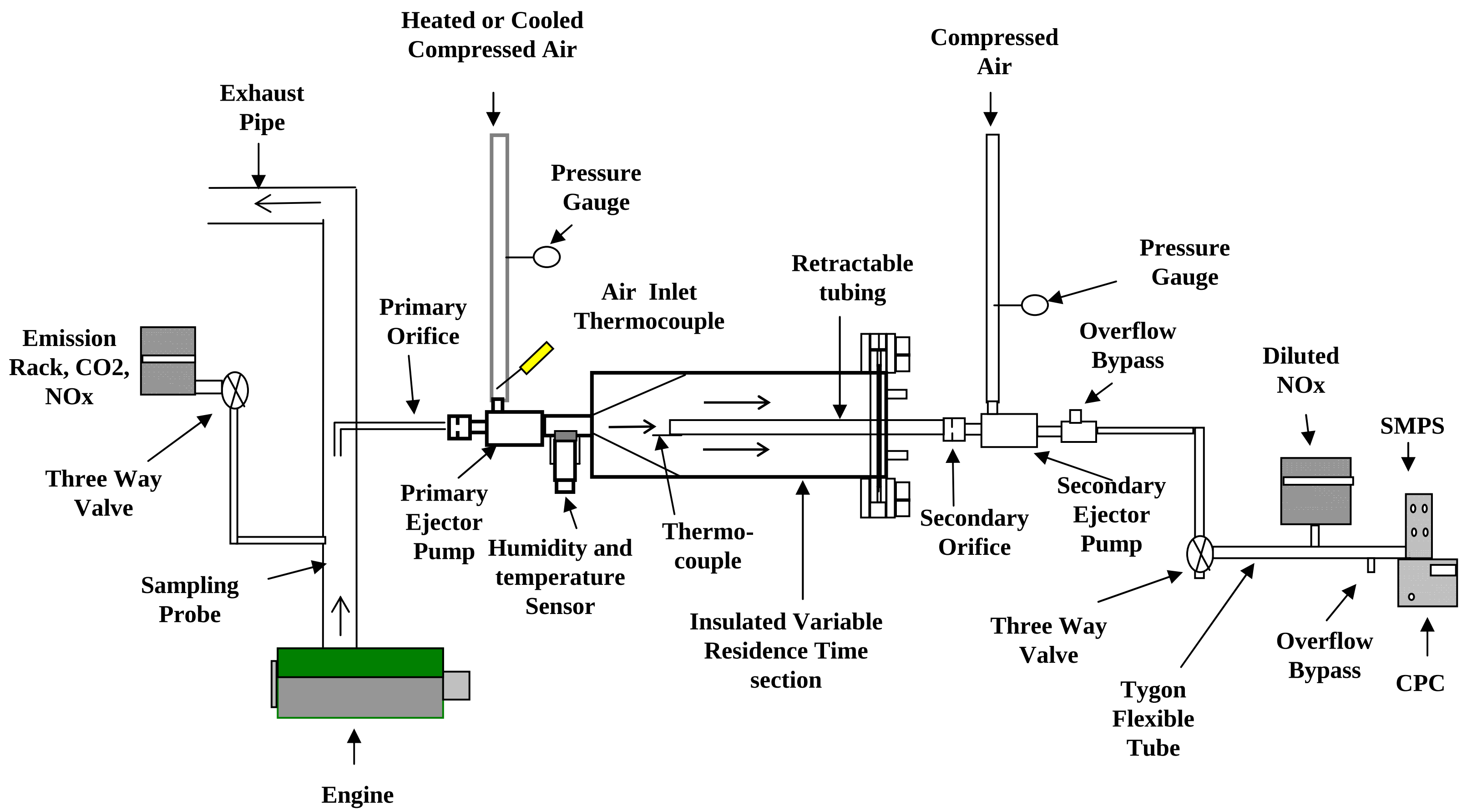
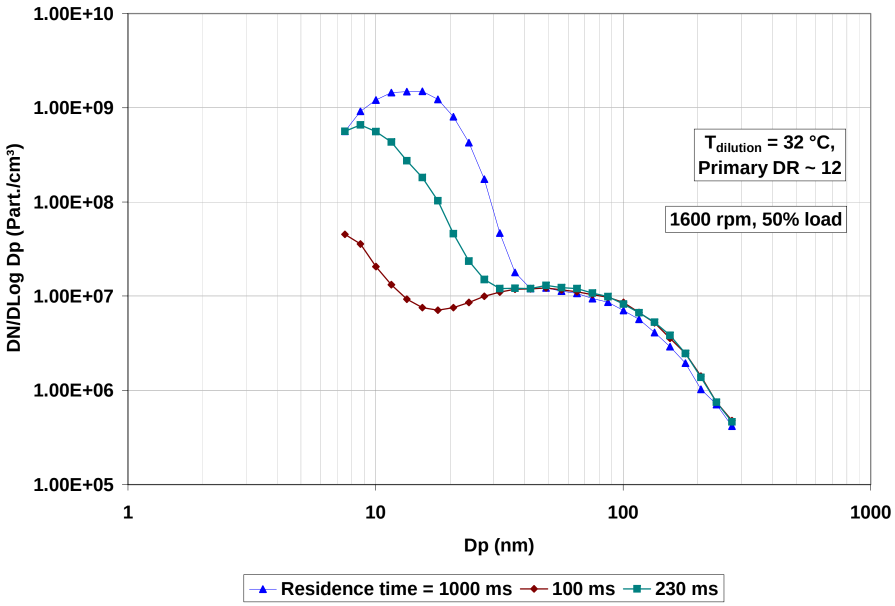
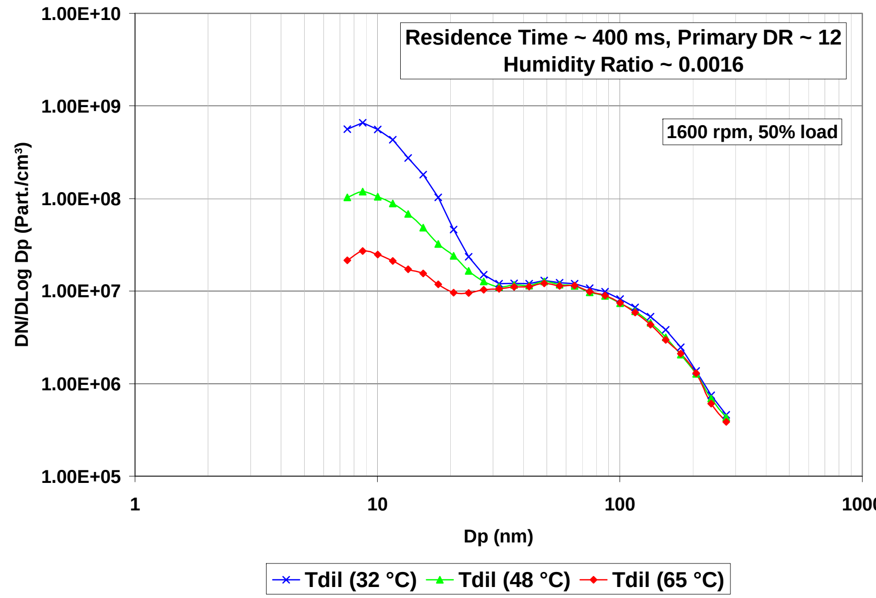
Studies of Diesel Nanoparticle Formation Using a Variable Residence Time Dilution System



Nuclei mode formation is extremely sensitive to sampling conditions

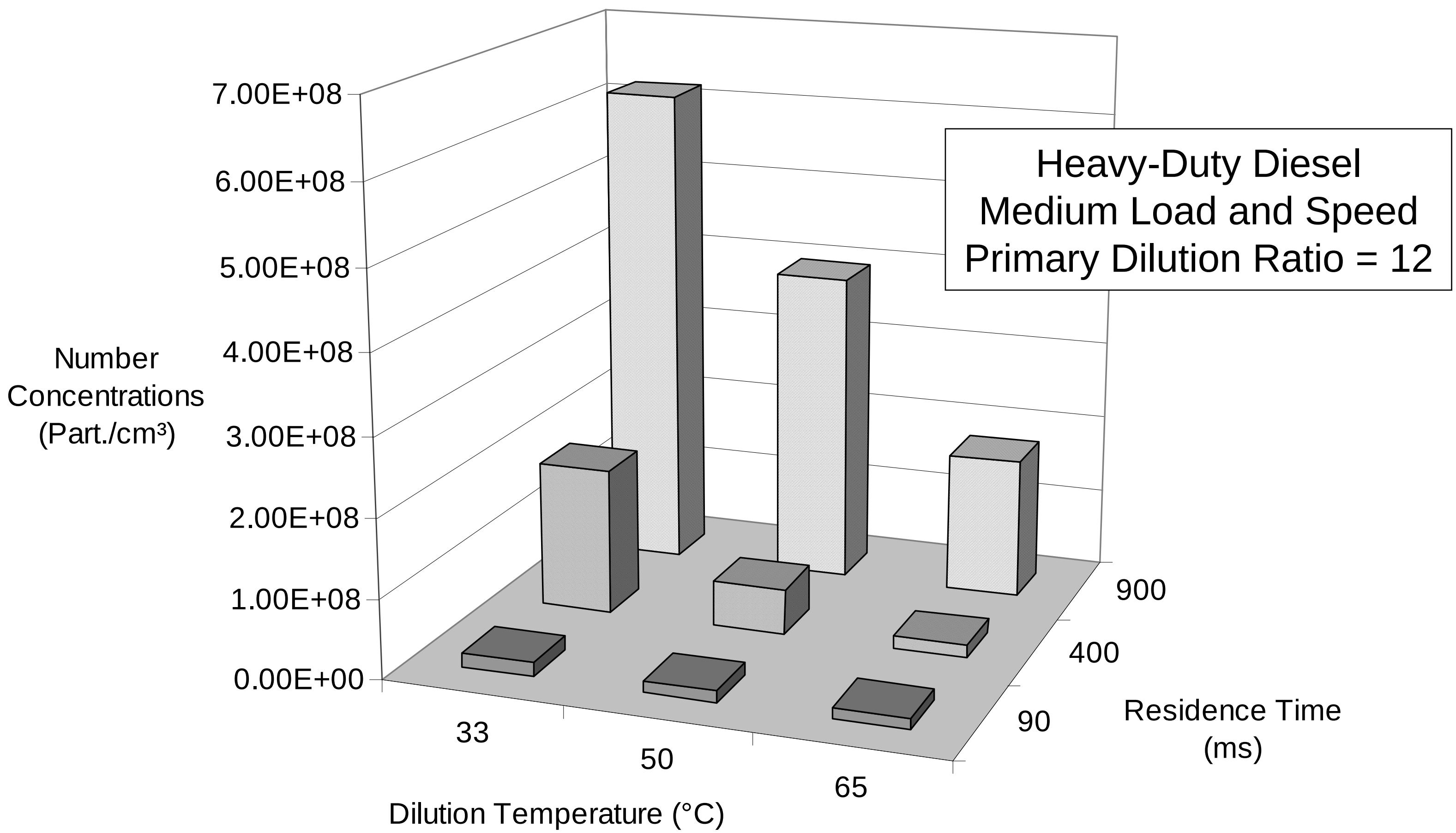




- Medium-duty Diesel engine running at medium speed and load
- Increasing residence time in the primary dilution chamber from 230 ms to 1 s increases the size of the nuclei mode by two orders of magnitude
- Decreasing the temperature in the primary dilution chamber from 66 to 32 °C increases the size of the nuclei mode by about one and one half orders of magnitude
- Concerns about sampling and dilution led to continued lab work under EMA/Caterpillar sponsorship and the on-road CRC E-43 program

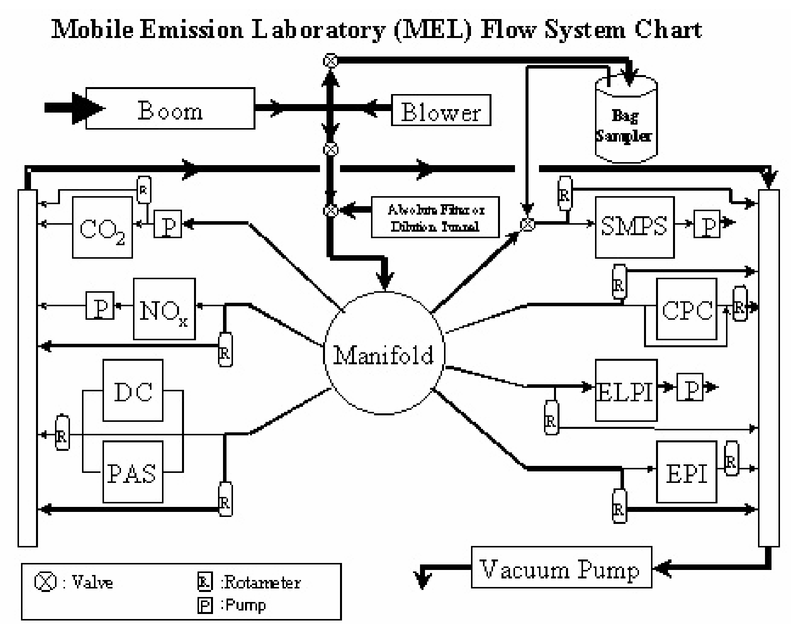
Abdul-Khalek, I., D.B. Kittelson, and F. Brear. 1999. “The Influence of Dilution Conditions on Diesel Exhaust Particle Size Distribution Measurements,” SAE Paper No. 1999-01-1142, 1999.

Sensitivity of Diesel Particle Number Emissions to Dilution Conditions - Residence Time and Temperature Effects



Abdul-Khalek, I., D.B. Kittelson, and F. Brear. 1999. “The Influence of Dilution Conditions on Diesel Exhaust Particle Size Distribution Measurements,” SAE Paper No. 1999-01-1142, 1999.

On-road measurements: U of M mobile laboratory built to study formation of nanoparticles in the atmosphere for the CRC E-43 project

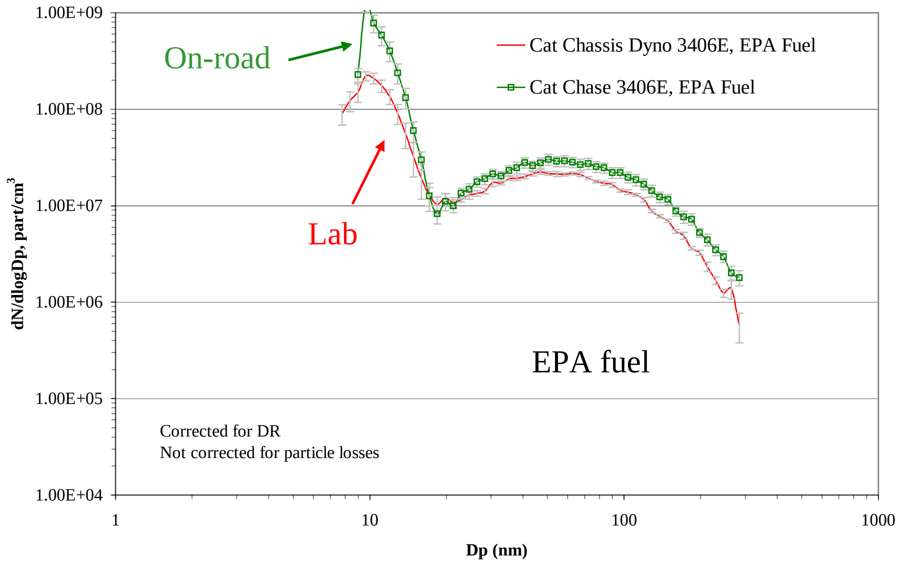


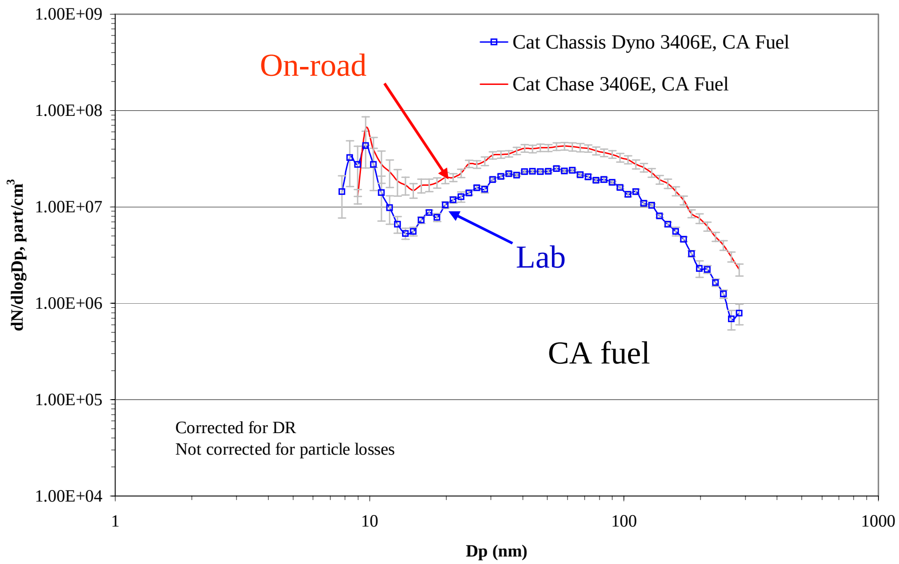
- Instruments (primary instruments highlighted in blue)
  - SMPS to size particles in 9 to 300 nm size range
  - ELPI to size particles in 30 to 2500 nm size range
  - CPC to count all particles larger than 3 nm
  - Diffusion Charger to measure total submicron particle surface area
  - Epiphaniometer to measure total submicron particle surface area
  - PAS to measure total submicron surface bound PAH equivalent
  - CO_2, CO, and NO analyzers for gas and dilution ratio determinations

On-road validation: CRC E-43 - nanoparticle measurements in on-road chase and lab

Here we have a 1999 highway tractor with its plume being characterized by the University of Minnesota Mobile Emission Laboratory

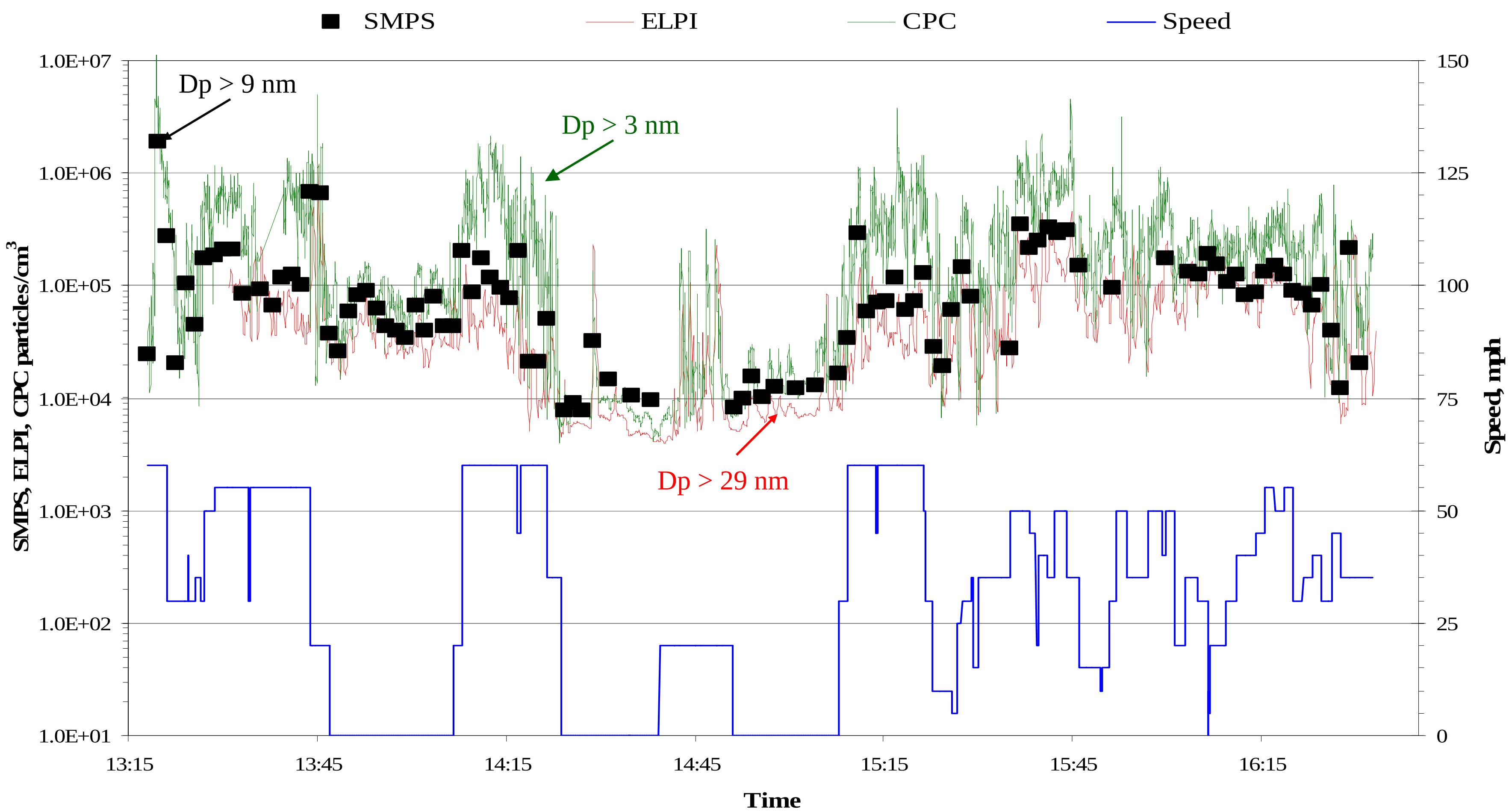
The CRC E-43 Program compared size distributions measured in the laboratory with those measured on-road





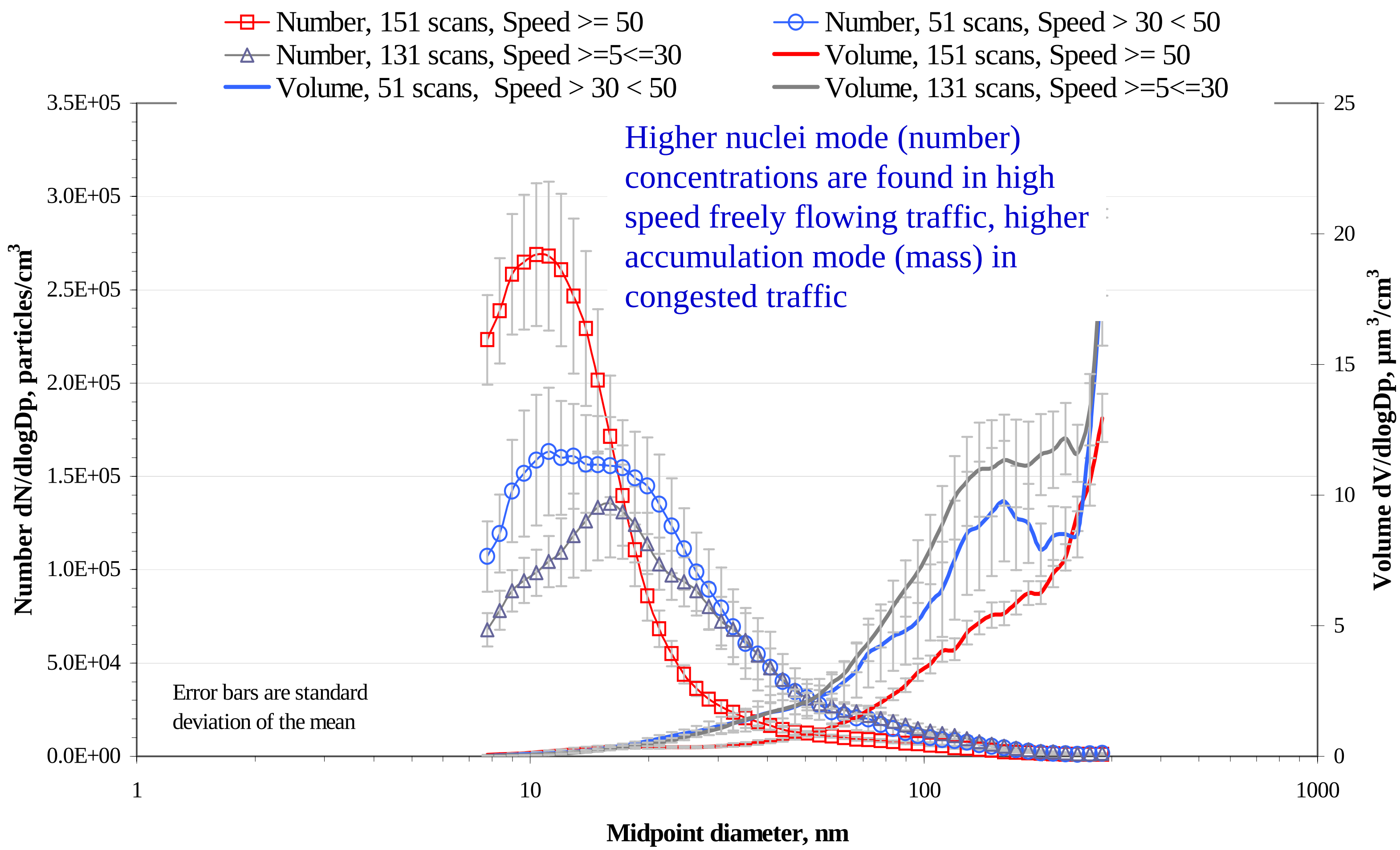
- Results shown are composite highway cruise for a modern heavy-duty Diesel engine with full electronic engine control – no aftertreatment
- A volatile nuclei mode is present on-road
- The relative sizes of the two modes are more significant than the absolute levels – due to uncertainty in on-road dilution ratios
- In general the CA fuel produced a smaller nuclei mode than EPA fuel
- A two-stage, porous tube / ejector dilutor could simulate on-road nuclei mode formation for composite, summertime highway conditions
- These results show that it is possible to simulate the tendency to form a nuclei mode under carefully defined on-road conditions
- At present, it is unclear which on-road conditions should be simulated. There are many variables including
  - Temperature
  - Previous operating history
  - Road speed
  - Exhaust system design
  - Others ….
- More recent work shows that with aftertreatment lab tests may underestimate nuclei mode
- On-road validation highly desirable!

On-road number measurements showing the role of congestion on ultrafine concentration



Kittelson, D. B., W. F. Watts and J. P. Johnson, 2004. “Nanoparticle Emissions on Minnesota Highways,” Atmospheric Environment, 38, 9-19.

High speed traffic favors ultrafine formation, but congestion leads to higher total volume (~ fine PM)



Kittelson, D. B., W. F. Watts and J. P. Johnson, 2004. “Nanoparticle Emissions on Minnesota Highways,” Atmospheric Environment, 38, 9-19.

On-road exposure experiments
EPA/U of Rochester/U of Minnesota

- The next slide shows overall average fall 2002 on-road size distribution
  - Sampled 6 hours per day for 10 days on New York rural freeway
  - Drove in Diesel truck traffic and sample aerosol to which truckers are exposed
- Clear bimodal structure with consistent formation of nuclei mode
- A thermal denuder (TD) used to remove volatile particles
  - 96% reduction in nuclei mode region
  - 65% reduction in accumulation mode region
  - Nuclei mode or nanoparticles are nearly all volatile – as expected from laboratory tests

Kittelson, D. B., W. F. Watts, J. P. Johnson, M. L. Remerowki, E. E. Ische, G. Oberdörster, R. M. Gelein, A. C. Elder, and P. K. Hopke, 2004. "On-Road Exposure to Highway Aerosols: 1. Aerosol and Gas Measurements," Inhalation Toxicology, 16(suppl. 1):31–39

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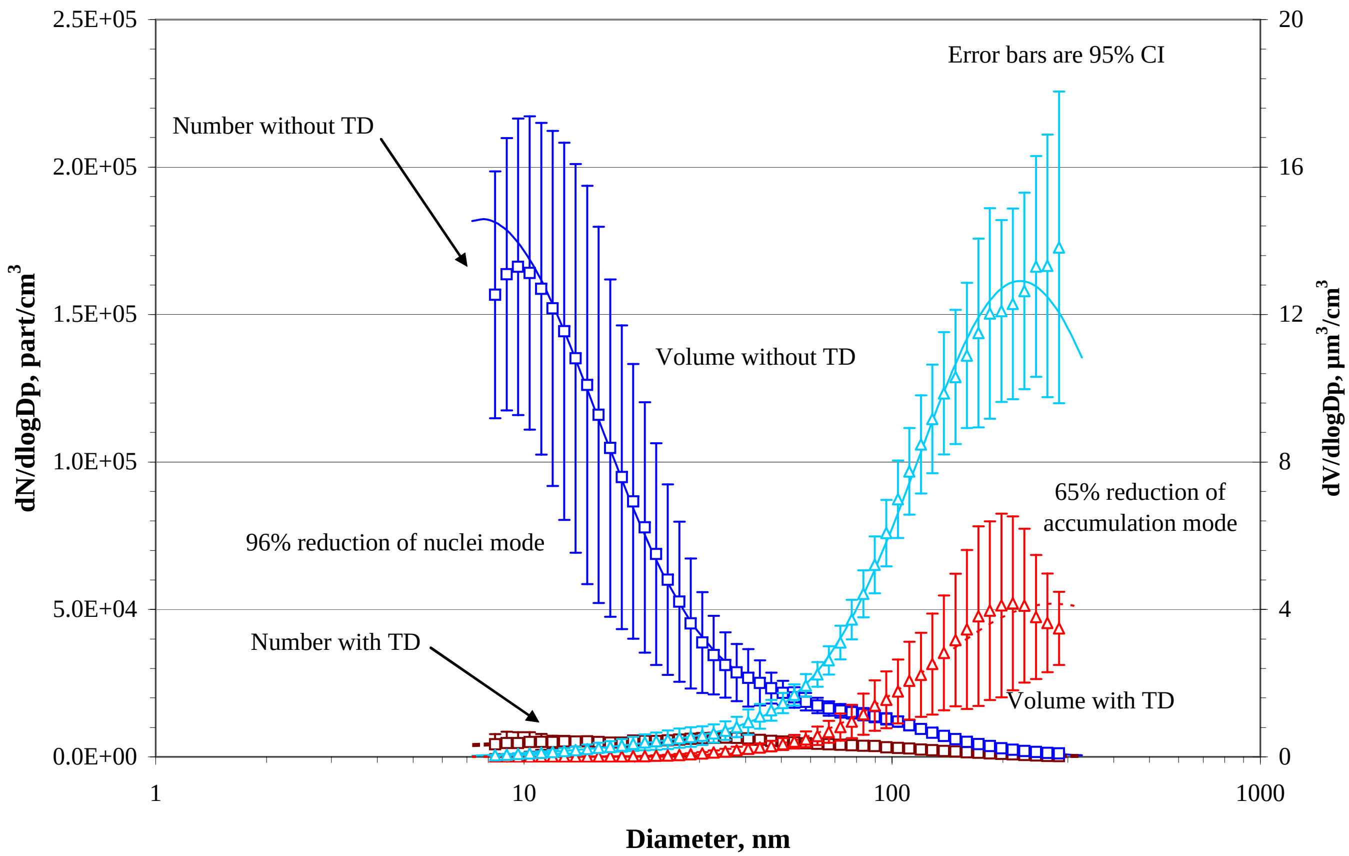

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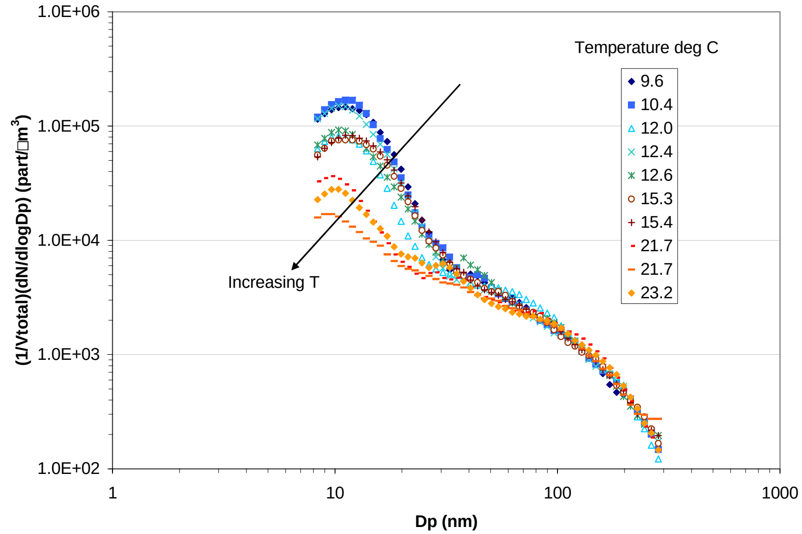
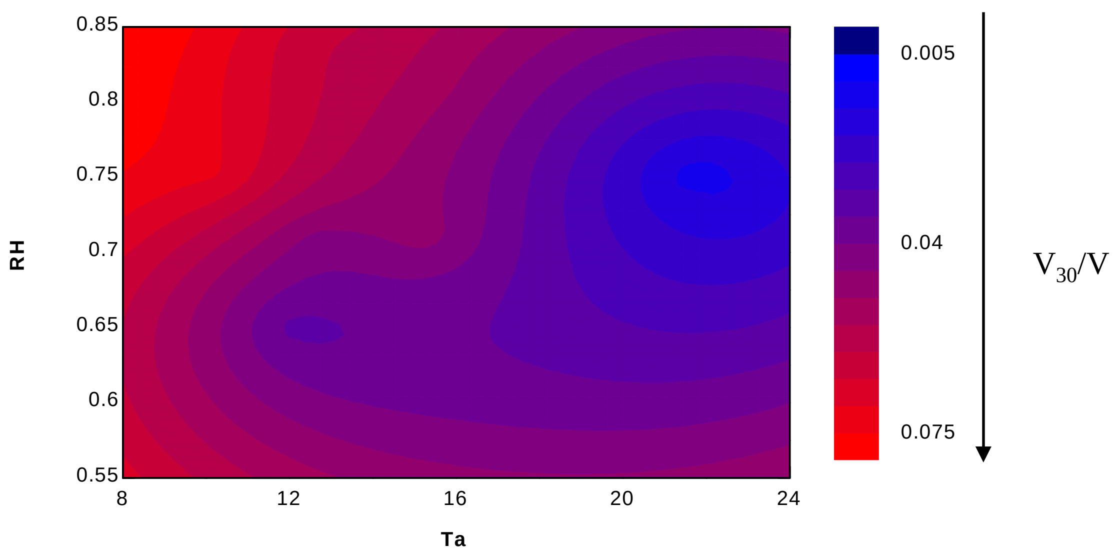
Ambient temperature (mainly) and humidity influence size of nuclei mode - U of Rochester / EPA





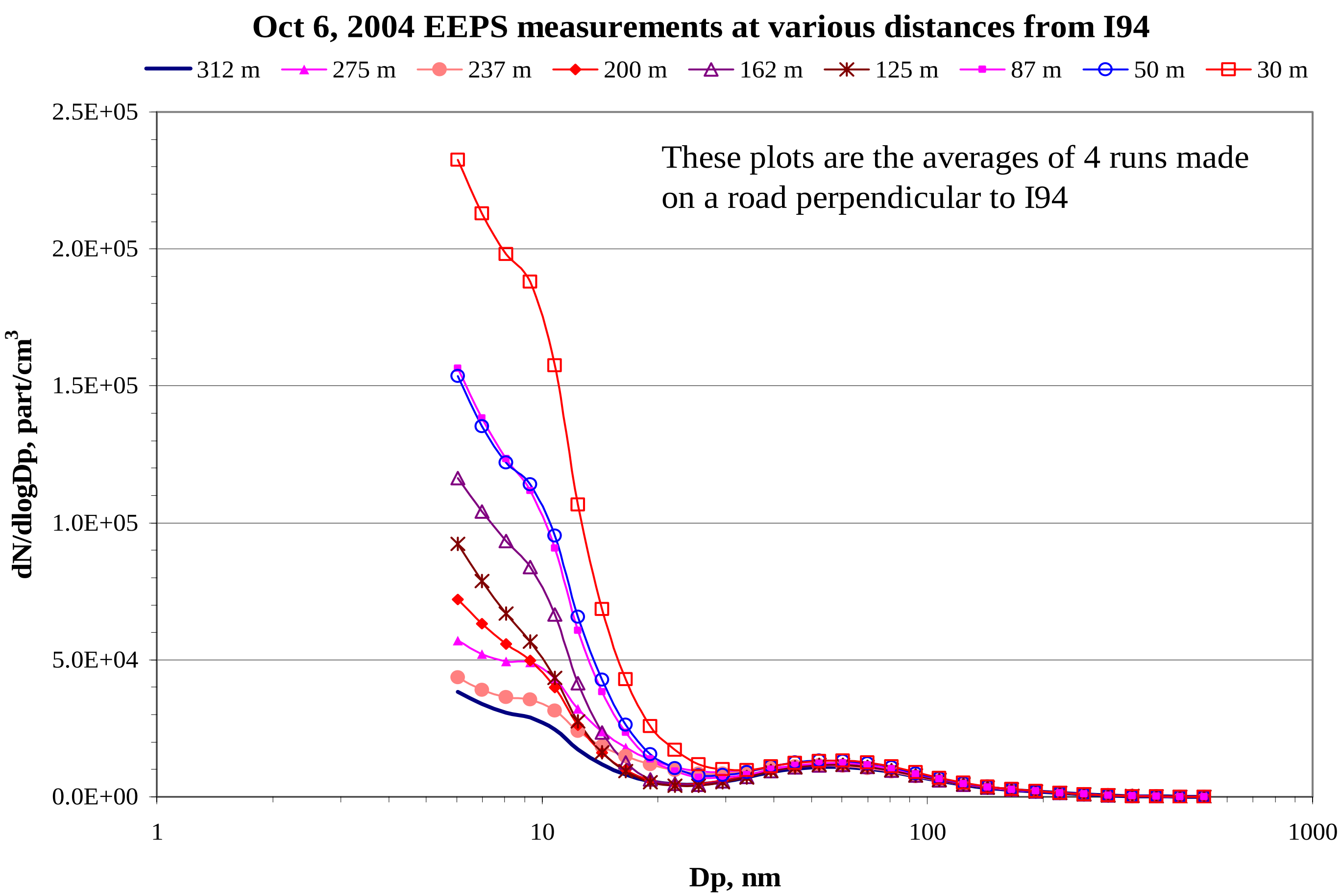
Daily average results for fall 2003 study - 60 hrs (10 days 6 hrs/day)

V_{30}/V is the fraction of aerosol volume smaller than 30 nm and is an estimate of the volume (and mass) fraction in the nuclei mode

V_{30}/V increases by an order of magnitude as ambient temperature falls from about 23 to 10 °C

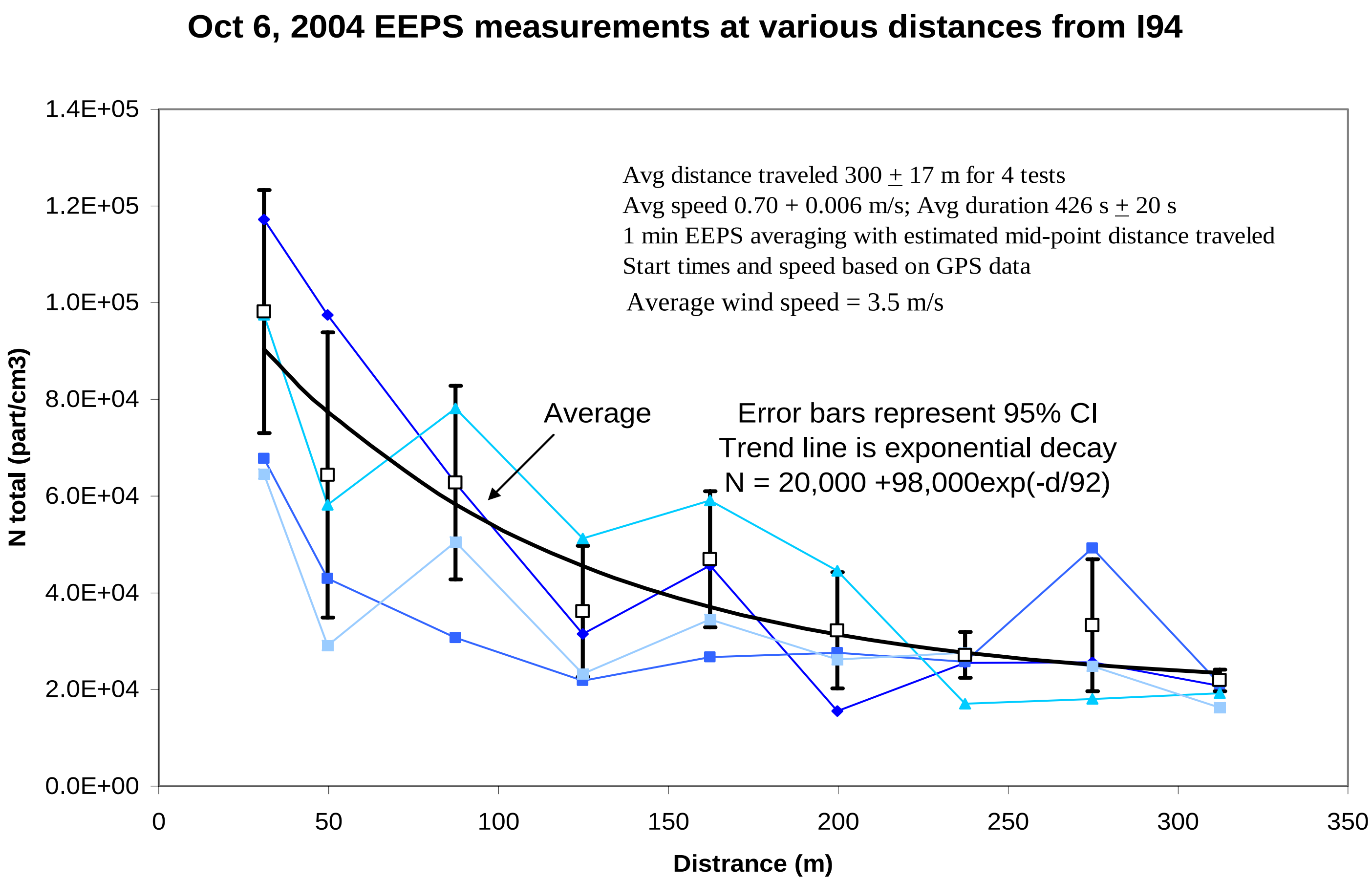
Measurements of the decay of nanoparticles downwind of a major rural roadway

EEPS measurements show nuclei mode decays quickly downwind of rural roadway



These measurement are described and modeled in: Jacobson, M. Z., D. B. Kittelson, and W. F. Watts. 2005. "Enhanced Coagulation Due to Evaporation and its Effect on Nanoparticle Evolution," Environmental Science and Technology, v 39, n 24, p 9486-9492

Integrated EEPS number measurements downwind of rural freeway show rapid decay



These measurement are described and modeled in: Jacobson, M. Z., D. B. Kittelson, and W. F. Watts. 2005. “Enhanced Coagulation Due to Evaporation and its Effect on Nanoparticle Evolution,” Environmental Science and Technology, v 39, n 24, p 9486-9492

Conclusions –on-road measurements of nuclei mode and ultrafines

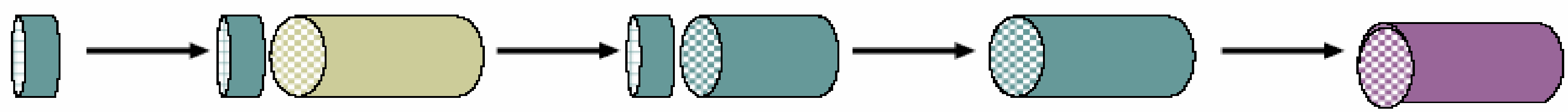
- Very large concentrations of nucleation mode particles are found under realistic on-road conditions
- The nucleation mode consists mainly of volatile particles
- Formation for the nucleation mode is favored by high speed traffic and low temperatures
- The nucleation mode decays very rapidly downwind of roadways
  - Characteristic distance 90 m
  - Characteristic time – 30 s
- Nucleation mode particles likely to be mainly an issue on and near roadways – but in CA more than 50% of PM exposure takes place while commuting

Outline

- Introduction
  - Emission standard
  - Typical engine and atmospheric size distributions
  - Why do we care about particle size
- Particle Formation by Diesel Engines
  - Structure and composition of ultrafine and nanoparticles
  - Particle formation during dilution
- Dilution and Sampling issues
  - Laboratory measurements
  - On-road measurement
- Diesel particle removal systems
  - Description
  - On-road evaluation
- Particles from gasoline spark ignition engines
- Future issues and conclusions

Possible Diesel Emission Control Pathway

OEM Emission System Strategies



DOCs only

- Minimum current diesel system: DOCs for odor control
- Vehicles are able to meet EU IV legislation through engine management.

DOCs + uncatalyzed filters (DPF)

- First system (1999); Incremental improvements in the FBC formulation and delivery and increased DPF ash storage capacity are keeping this competitive.

DOCs + catalyzed filters

- Catalyst on filter improves regeneration while DOC reduces HC, CO and NOx.
- Expands range of passive regeneration, reduces complexity.

Catalyzed filters only

- Target system for many OEMs: Further complexity reduction and cost.

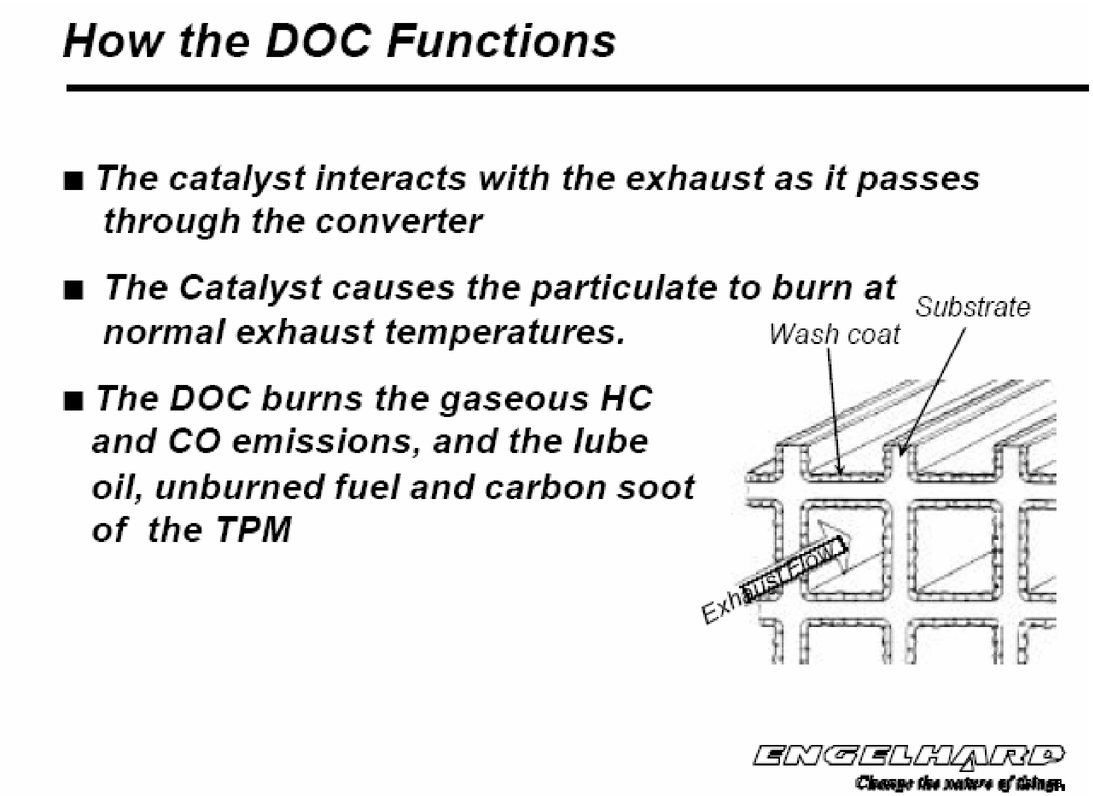
PM and NOx solution

- Mixed-mode combustion synergies enable this cost saving integration

CORNING

Courtesy: Tim Johnson, Corning

Diesel oxidation catalyst (DOC)



- Typical performance
  - ~90% CO reduction
  - ~70% gaseous hydrocarbon reduction
  - 25-30% PM reduction mainly by OC oxidation
  - Slight EC reduction
  - May increase sulfate emissions at high load

Diagram courtesy Engelhard

Diesel Particulate Filter

- Controls PM and HC, CO (Catalyzed DPF)
- Extremely high removal efficiencies
- Technology challenges
  - Regeneration strategies
    - » Passive
      - Catalyzed soot filter (Engelhard)
      - CRT, CCRT (JM)
      - Fuel borne catalyst
      - NO_2 and H_2SO_4 formation are concerns
      - Exhaust temperature may be inadequate in many applications
    - » Active – passive plus
      - Engine management (post injection, etc.)
      - Combustion or electric heating
  - Ash accumulation
    - » Lube oil
    - » Fuel additives
  - Durability, cost
  - Nuclei mode formation downstream of DPF

Wall flow particle filter, the most common exhaust filtration technology

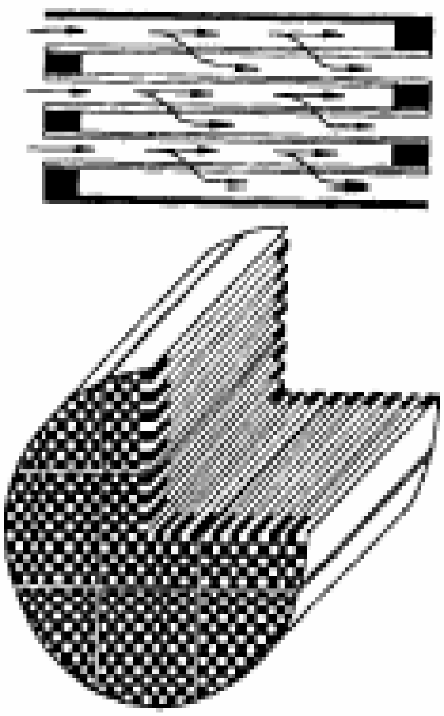


Fig.5: Monolithic ceramic cell filter

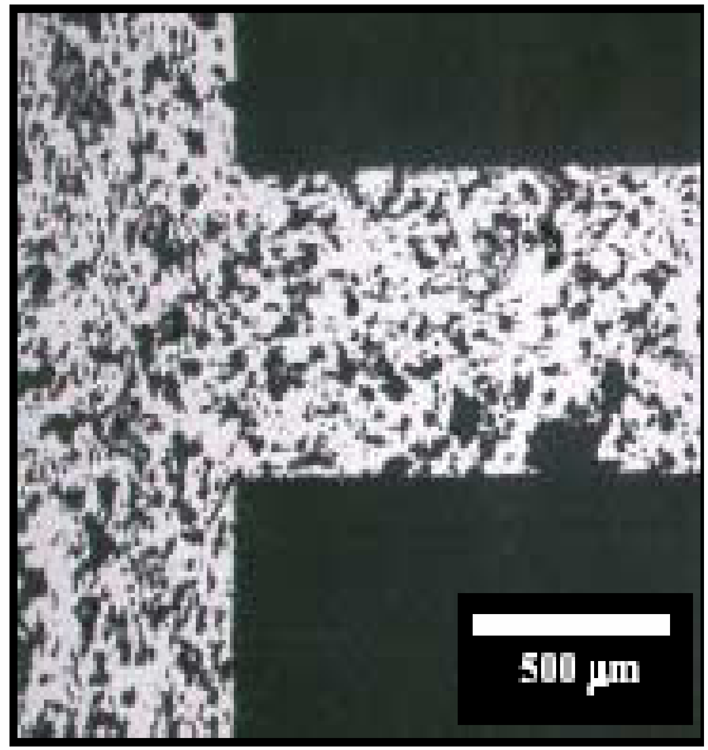
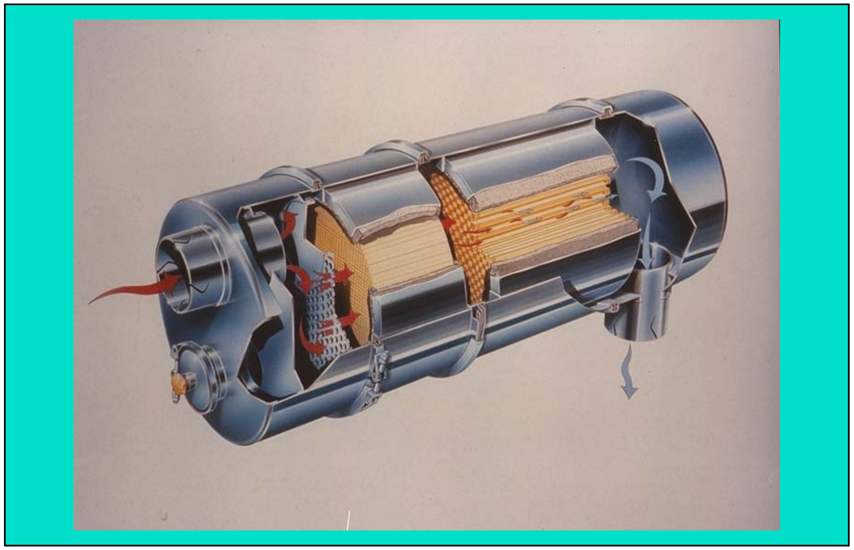


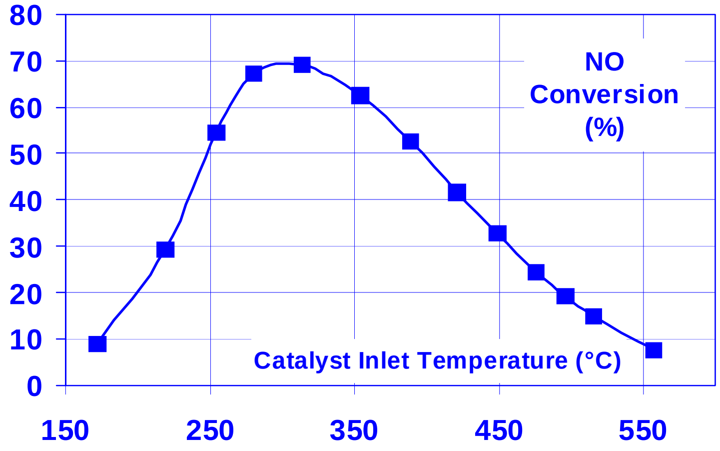
Fig.6: Pore structure of a ceramic filter. CORNING, NGK

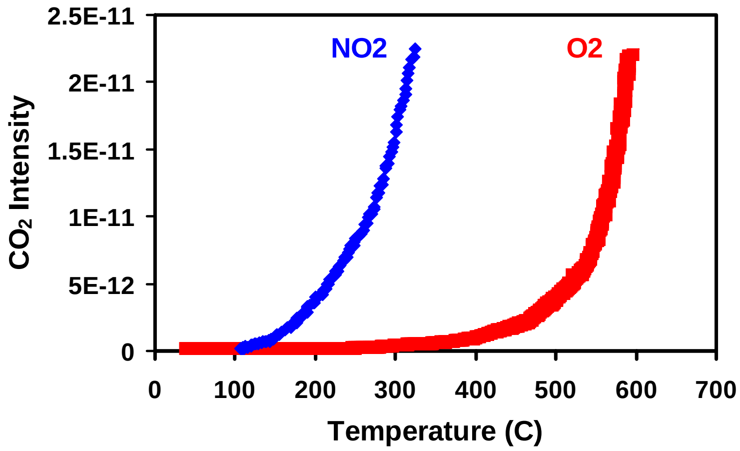
From - A. Mayer, TTM PARTICULATE-FILTER-SYSTEMS, PARTICLE TRAPS

CRT® reduces regeneration temperature by producing NO_2 upstream of filter



- NO_2 enables low temperature soot combustion - but engine-out NO_x is predominantly NO
- Oxidation catalyst converts NO into NO_2 with high efficiency





Courtesy Johnson-Matthey

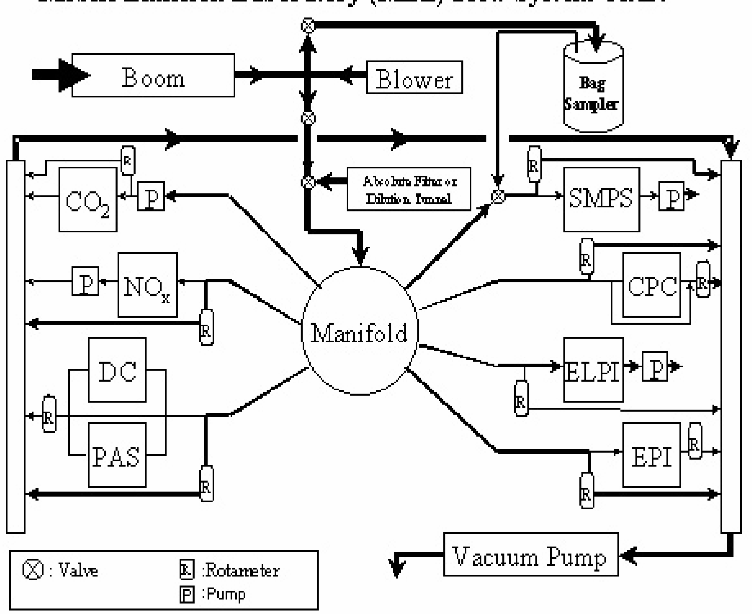
Filter mass measurements with low emission engines - issues

- Very difficult to accurately measure filter mass at low levels
- For volatile particles, filter mass does not adequately represent suspended mass (what we breathe)
  - DPF performance measured with filters very different from that measured by instruments that measure suspended particles (VERT, SWRI, Ford,..)
  - Absolute suspended mass measurements made with aerosol centrifuge show that filters may significantly overstate the mass of volatile particles[1]
  - Sampling and dilution may strongly influence results – consequently on-road measurements are useful
- Other measures may better predict environmental impact
  - Number, Surface area, Black carbon
- The EU is considering a solid particle number standard
  - A sampling and measurement procedure has been developed as part of the EU Particulate Measurement Program (PMP)
  - Swiss ministry suggests 10^{11} part/km (50 – 100 μg/km)

1 - Park, Kihong, David B. Kittelson, and Peter H. McMurry, 2003. "A Closure Study of Aerosol Mass Concentration Measurements: Comparison of Values Obtained with Filters and by Direct Measurements of Mass Distributions," Atmospheric Environment, 37, 1223-1230.

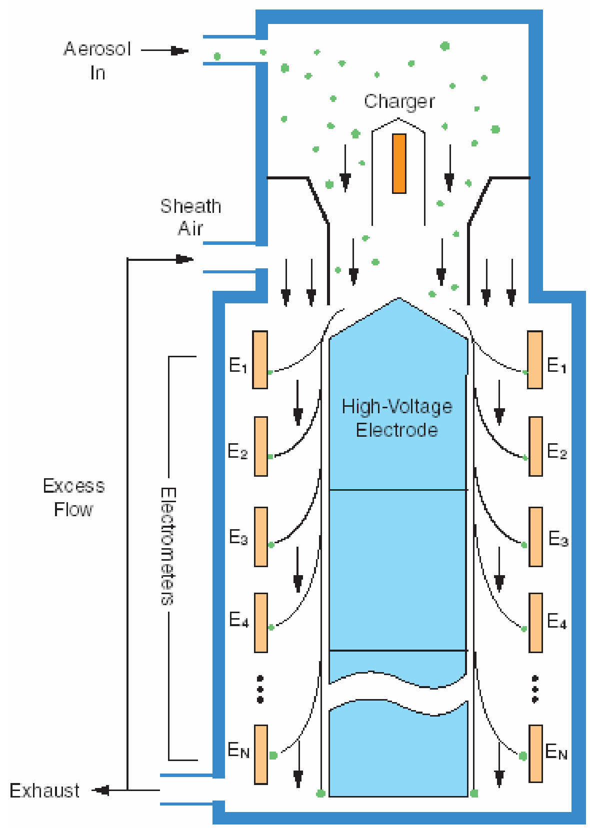
On-road exhaust filter evaluations the MEL

Mobile Emission Laboratory (MEL) Flow System Chart



- Instruments (primary instruments in this work highlighted in blue)
  - SMPS to size particles in 9 to 300 nm size range, $\tau = 60$ s
  - EEPS 3090 that sizes particles in the 5.6 to 560 nm range, $\tau < 1$ s
  - 3025 CPC to count all particles larger than about 3 nm, $\tau \sim 1$ s
  - Diffusion Charger to measure total submicron particle surface area
  - PAS to measure total submicron surface bound PAH equivalent
  - CO_2 , CO, NO and NO_2 analyzers for gas and dilution ratio determinations

The TSI 3090 EEPS is another fast response electrical mobility based instrument



Preliminary Specifications

3090 Engine Exhaust Particle Sizer™ Spectrometer

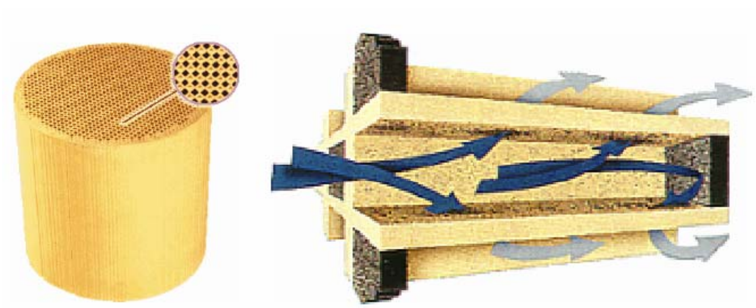
Particle Size Range	5.6 to 560 nm
Particle Size Resolution	16 channels per decade (32 total)
Electrometer Channels	22
Charger Mode of Operation	Unipolar diffusion charger
Inlet Cyclone 50% Cutpoint	1 µm
Time Resolution	10 size distributions per second
Flow Rates	
Aerosol	10 L/min
Sheath Air	40 L/min
Inlet Aerosol Temperature	10 to 52°C
Operating Temperature	0 to 40°C

Sizing range 5.6-560 nm

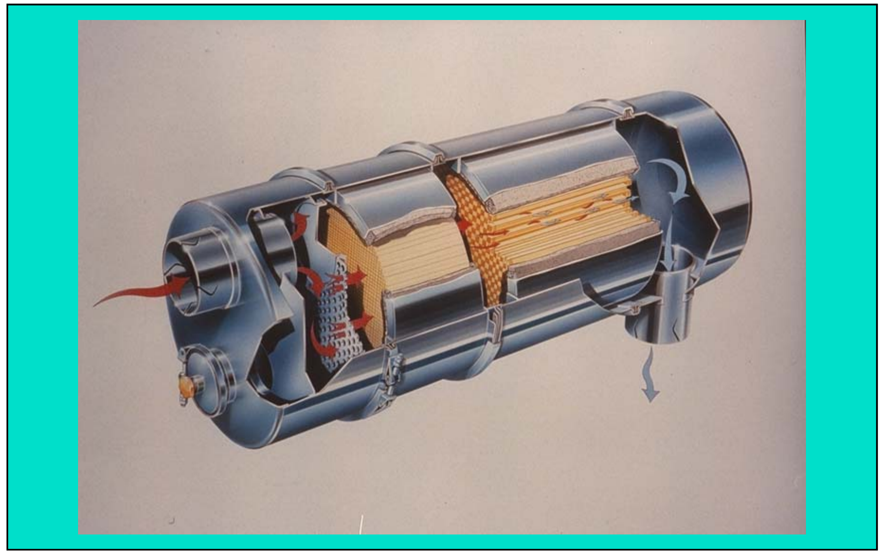
Response time ~1 s

Johnson, Tim, Robert Caldow, Arndt Pöcher, Aadu Mirme, and David Kittelson, 2004. “A New Electrical Mobility Particle Sizer Spectrometer for Engine Exhaust Particle Measurements,” SAE paper number 2004-01-1341

Particle removal by exhaust filters – On road evaluations of CRT® and CCRT®



Figures courtesy Corning and Johnson-Matthey



- Most PM filtration systems being considered for 2007 are the wall flow type shown on the left. Without regeneration to oxidize soot these devices quickly plug.
- Catalyzed filtration systems like the J-M CRT® shown on the right reduce regeneration temperature by producing NO_2 from exhaust NO in an oxidizing catalyst upstream of filter
- The J-M CCRT® has a catalyzed washcoat on the filter as well to further reduce regeneration temperature
- NO_2 in the exhaust is an issue
- In most applications active regeneration is also required

On-road evaluations of exhaust particle filters – plume sniffing of MEL with CRT, CCRT

Kittelson, D. B., W. F. Watts, J. P. Johnson, C. Rowntree, M. Payne, S. Goodier, C. Warrens, H. Preston, U. Zink, M. Ortiz, C. Goersmann, M. V. Twigg, A. P. Walker, and R. Caldow. 2006. On-Road Evaluation of Two Diesel Exhaust Aftertreatment Devices, Journal of Aerosol Science, in press.

Test conditions for on-road filter evaluations

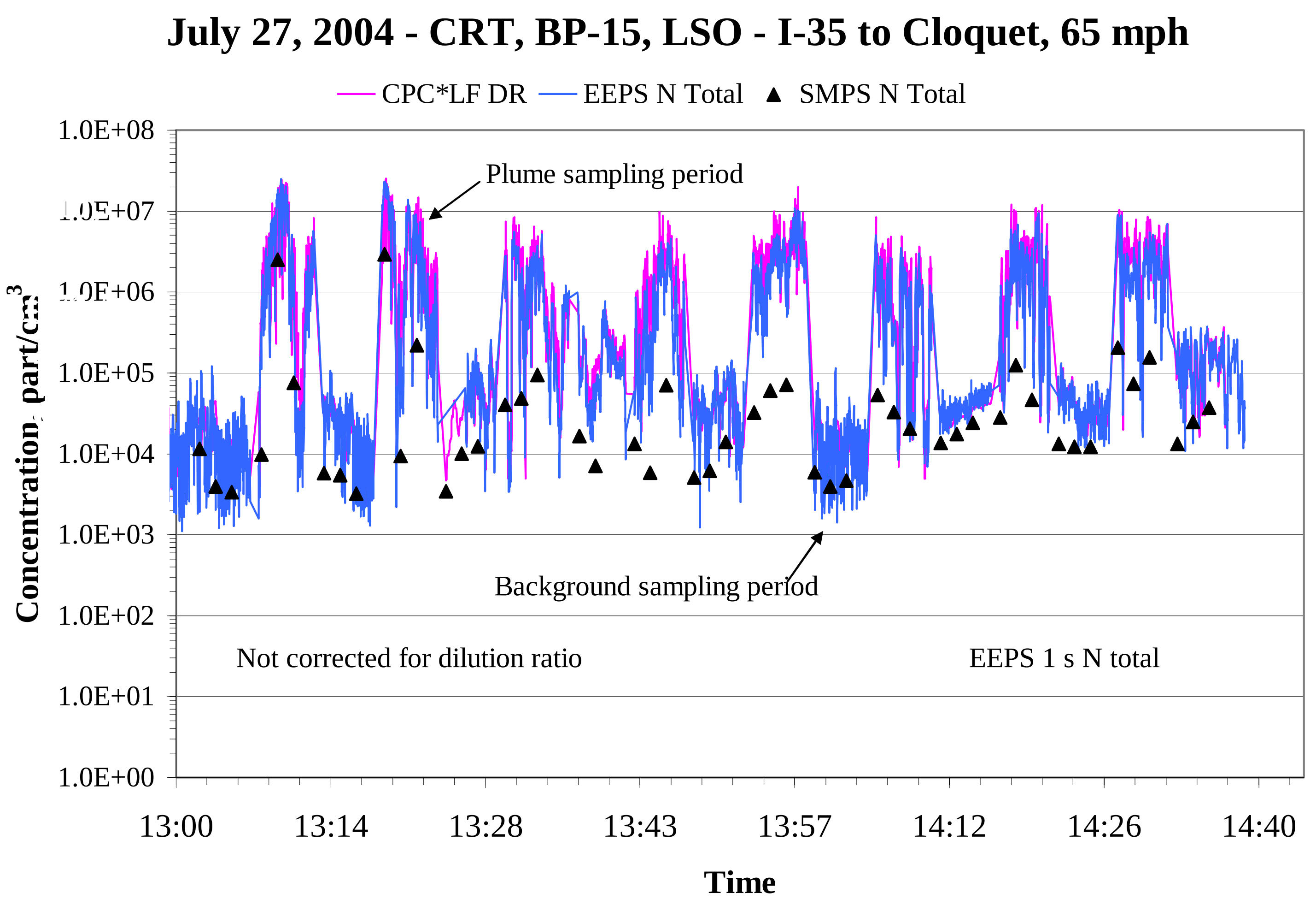
- Tests run with J-M CRT and CCRT
  - CRT consist of oxidizing catalyst plus wall flow filter
  - CCRT consist of oxidizing catalyst plus catalyzed wall flow filter
- BP15 fuel (2007 compliant)
- Castrol low S lube oil (~1500 ppm)
- 65 mph cruise on Minnesota rural freeway
- Load and exhaust temperature varied with grade, headwind, tailwind

Date[a]	Source	N[b]	CO_2, ppm		Exhaust CO_2, %		Exhaust temp, C		Ambient temp, C		Speed, km/hr	
			Avg	Std	Avg	Std	Avg	Std	Avg	Std	Avg	Std
7/27/2004	Background	5730	371	9	6.4	1.1	317	27	25.6	1.4	107	2
7/27/2004	Plume	5182	527	88	6.4	1.1	318	27	25.6	1.3	108	2
7/29/2004	Background	5580	386	13	6.4	1.1	312	33	21.4	2.2	107	2
7/29/2004	Plume	4963	494	100	6.4	1.1	312	29	21.2	2.2	107	2
8/5/2004	Background	5924	395	12	6.3	1.1	312	19	22.8	1.6	106	2
8/5/2004	Plume	5272	625	99	6.3	1.1	311	20	22.8	1.6	106	2
8/11/2004	Background	3980	380	11	6.5	1.0	313	24	16.1	0.9	107	2
8/11/2004	Plume	3290	520	102	6.3	1.2	312	28	16.2	0.9	107	3
8/12/2004	Background	6134	386	9	6.3	0.9	317	19	19.6	1.5	109	2
8/12/2004	Plume	5274	588	95	6.3	0.9	317	19	19.6	1.5	109	4

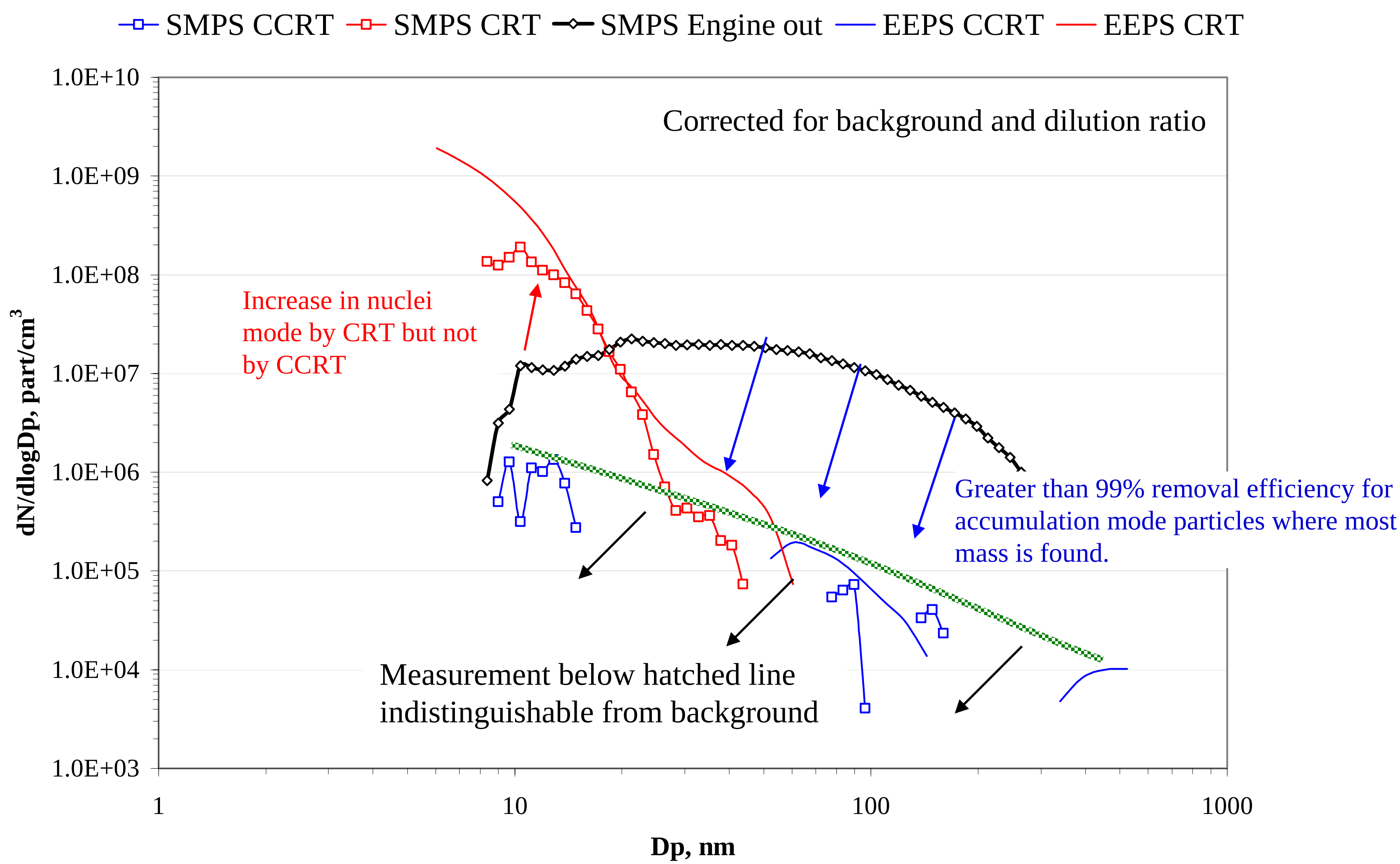
[a] 7/27 and 7/29 a CRT was used; 8/5, 8/11,8/12 a CCRT was used

[b] N is the number of measurements recorded by the data logger at approximately 1 second intervals

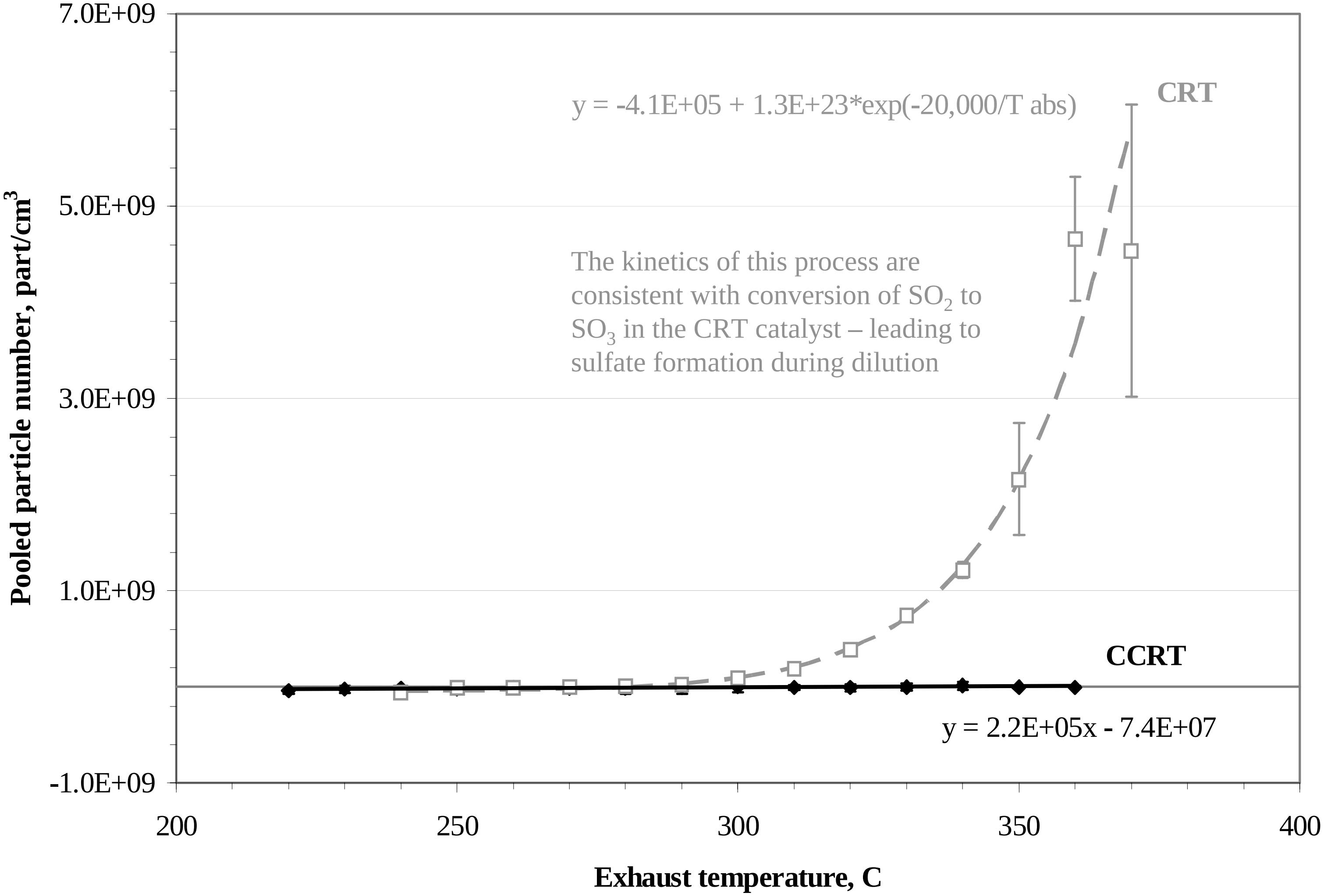
Sampling pattern – background, plume, background



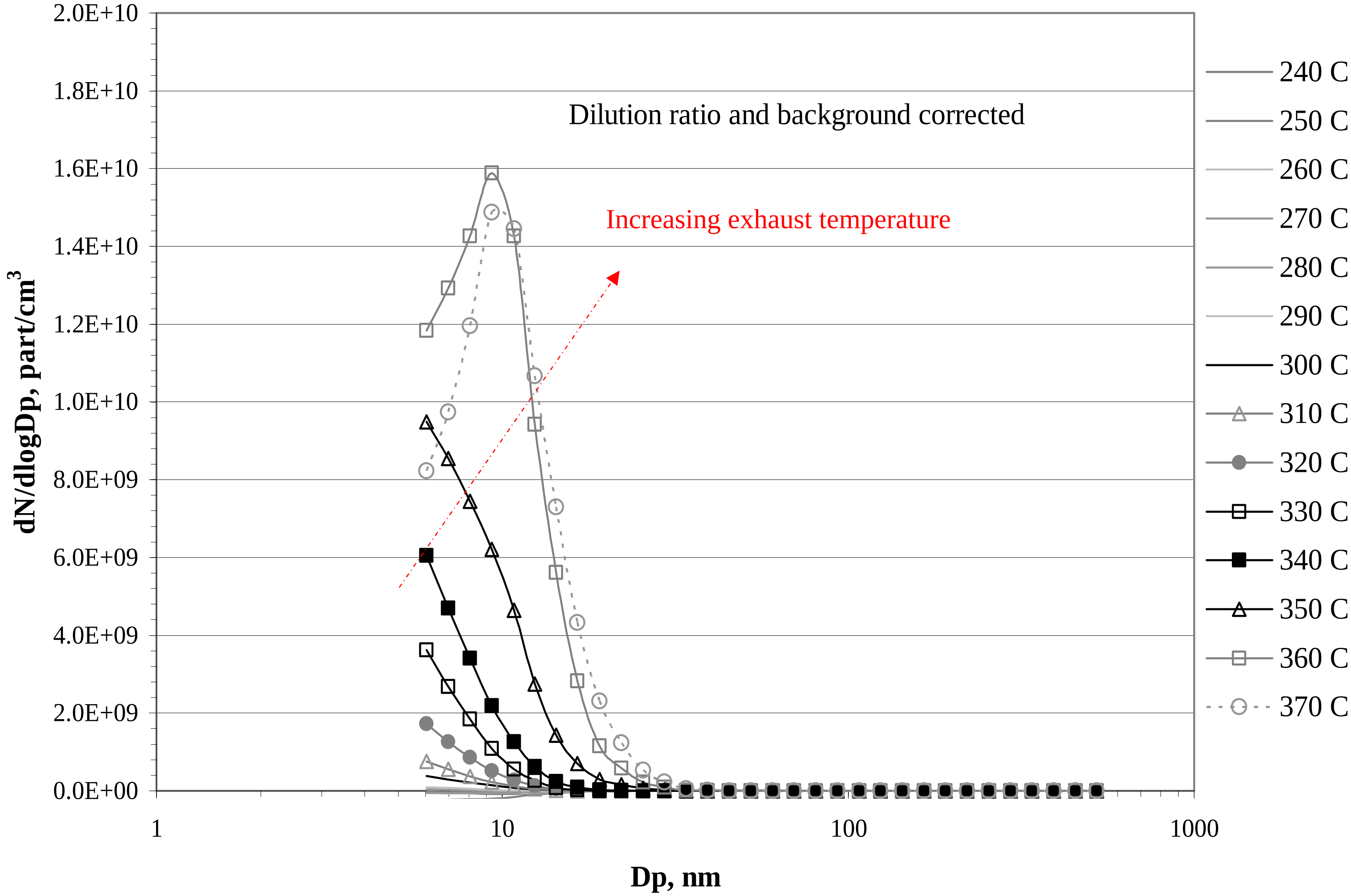
Plume – background size distributions corrected for dilution ratio - BP15 fuel and LSO



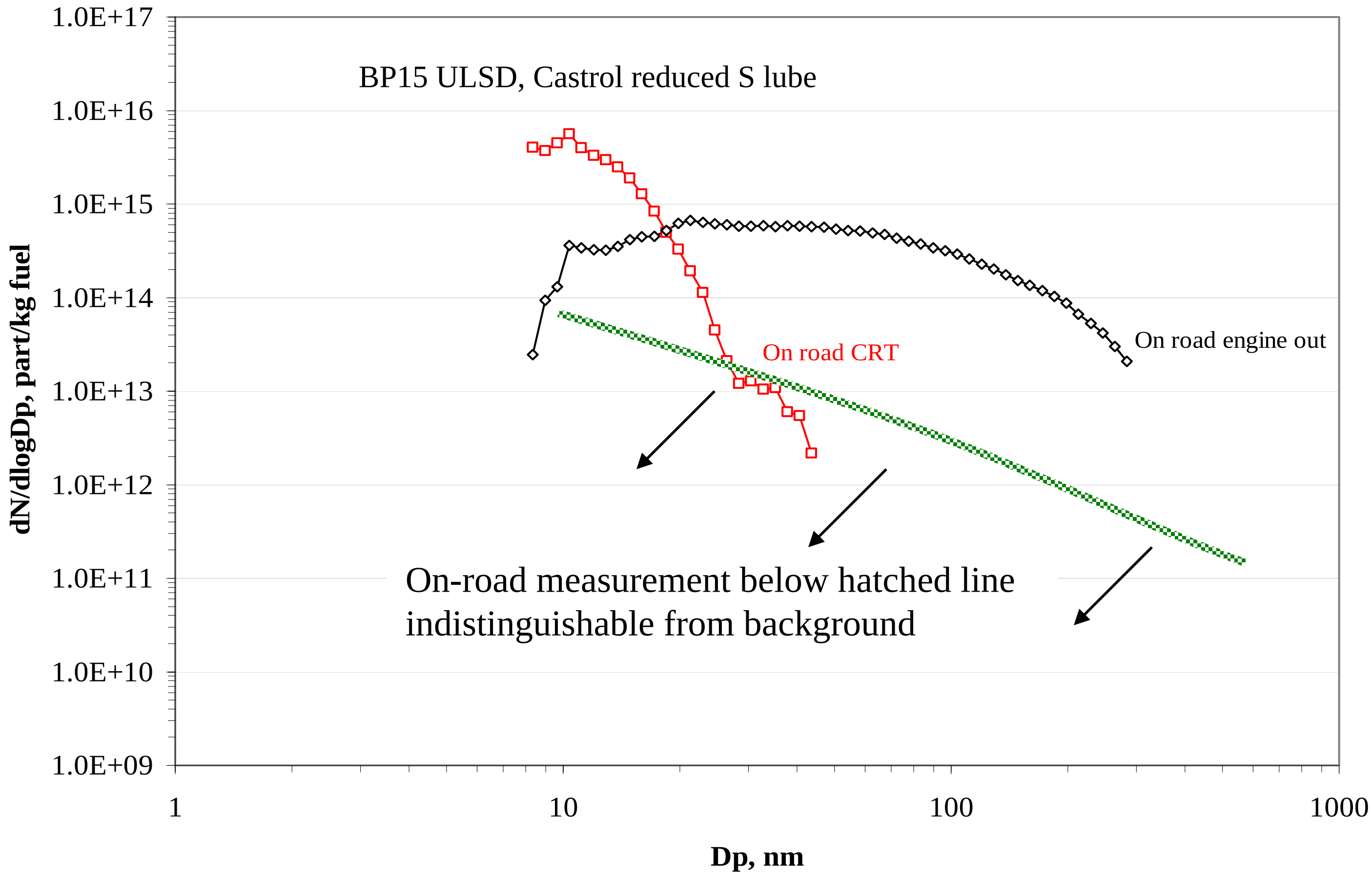
The CRT showed strongly temperature dependent number emissions but the CCRT showed no detectable emissions



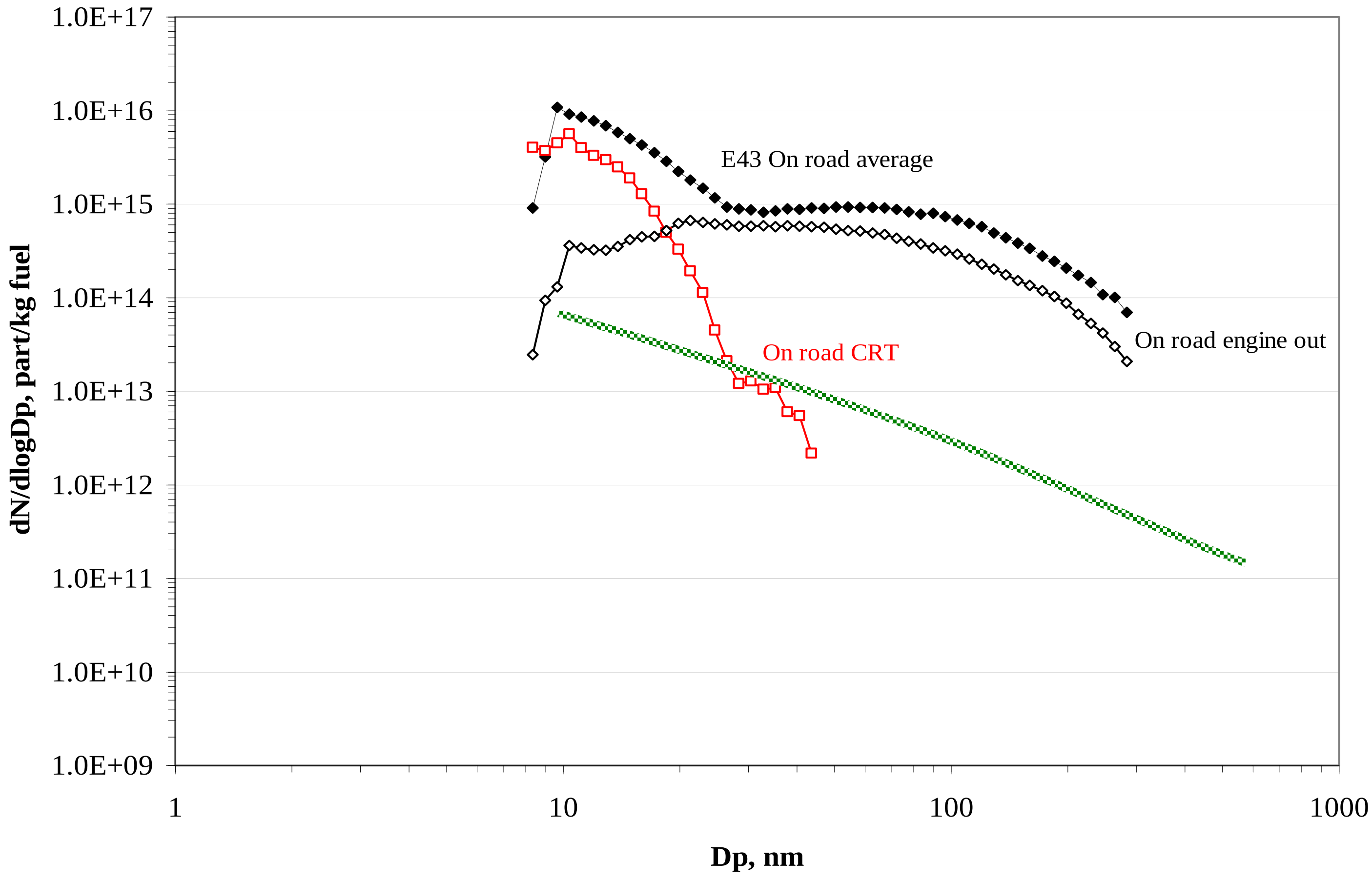
Nearly all particles downstream of CRT were in nucleation mode and strongly temperature dependent



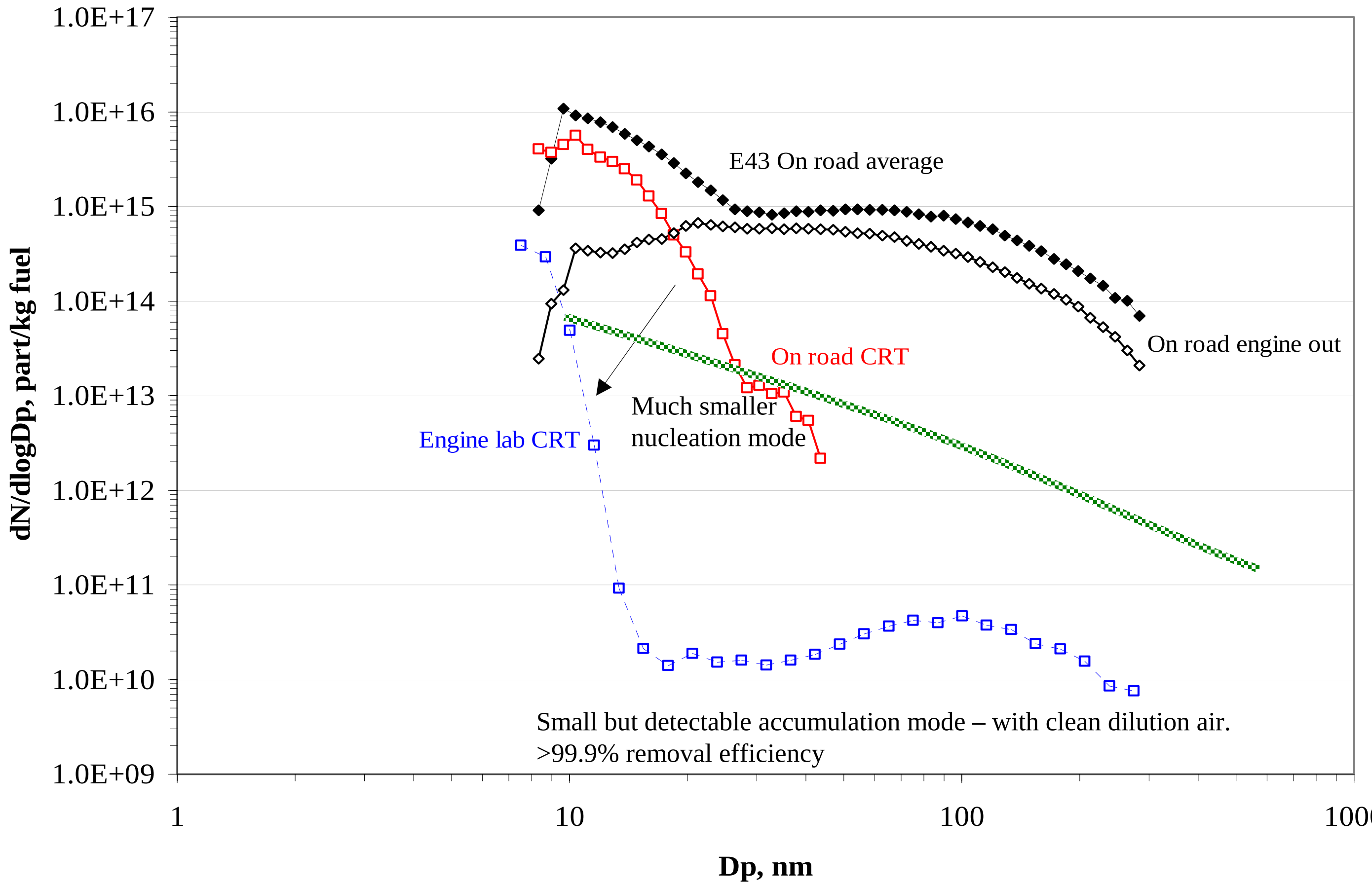
Here the results are put into a fuel specific form so that they may be compared with other studies



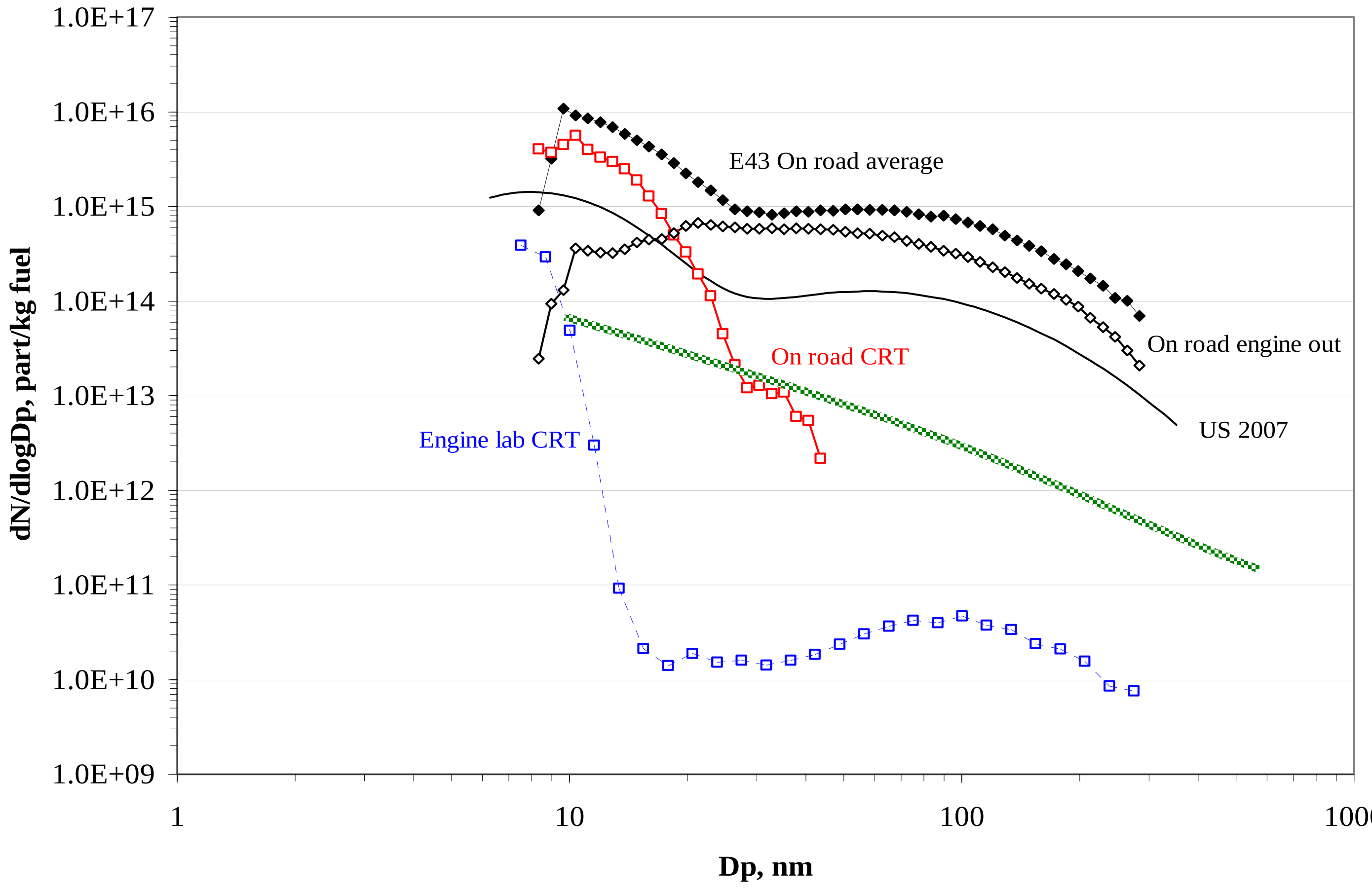
Here we compare with the on road fleet tested in the E43 program – engine out ~350 ppm S fuel



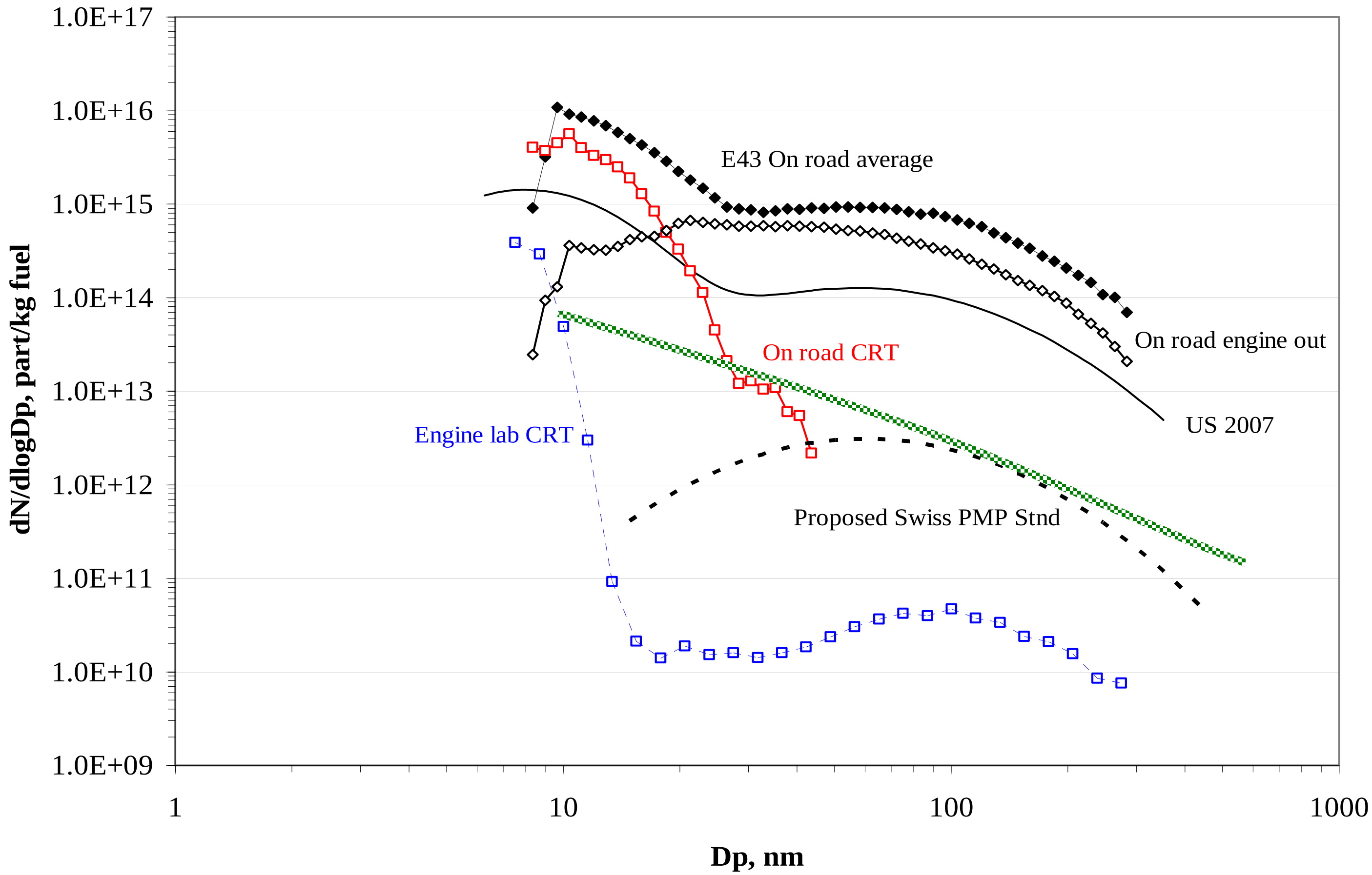
What if we test the CRT in the lab – same BP15 fuel and operating condition



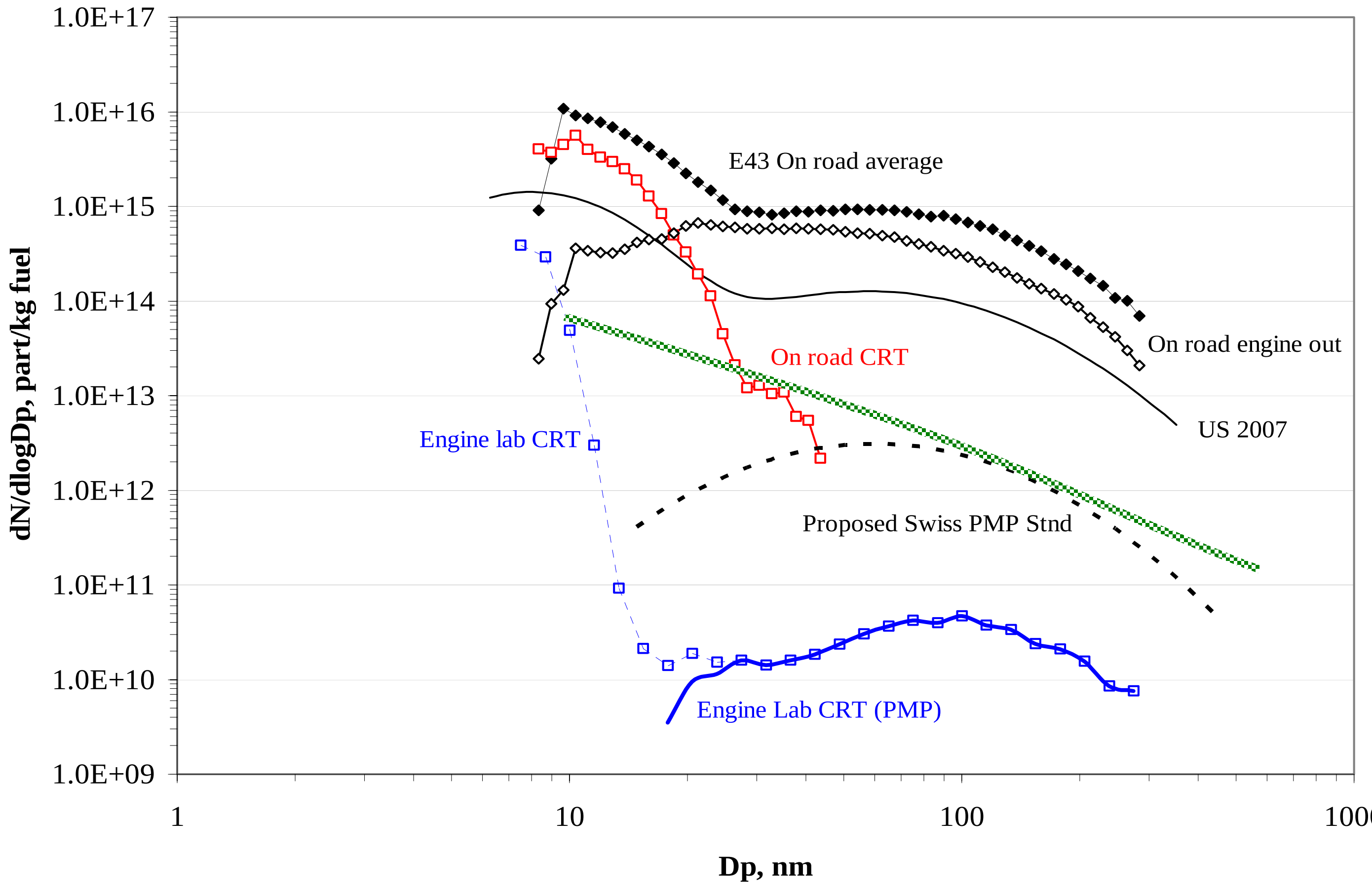
CRT accumulation mode well below the US 2007 standard (mass converted to equivalent number)



Here the an estimate of the proposed Swiss and EU number standard is added



Here the lab measurement has been treated in the manner of the PMP program removing nuclei mode



Conclusions - On-road CRT and CCRT measurements - 1

- CRTs and CCRTs tested on-road under relatively light load conditions
- In the accumulation mode size range where most of the mass is found:
  - Neither the CRT nor the CCRT emitted concentrations significantly above background ambient air.
  - This corresponds to > 99% removal efficiency
- Significant number emissions were observed with the CRT
  - The particles are extremely small nucleation mode particles
  - These particles represent nearly no mass
  - Number emissions are extremely exhaust temperature dependent
  - The particles are believed to be mainly sulfuric acid
- CCRT number emissions could not be distinguished from ambient air
  - This effect is not fully understood
  - Apparently particle precursors are stored in catalyzed filter section

Conclusions - On-road CRT and CCRT measurements - 2

- Both systems meet all current and proposed particle emission standards, however..
  - Operating conditions where different from those of certification tests
    - » Continuous high speed operation
    - » No cold start
    - » Passive regeneration
  - US 2007 mass standards have been converted to equivalent number
    - » Proposed EU PMP standard 1 to 2 orders of magnitude more stringent than US 2007
    - » It is unlikely that any filter mass based measurement system would be able to make meaningful measurements at the PMP level
- However, it should be noted that even under more difficult transient conditions of the EPA certification test 2007 engines are typically more than 5 times below the EPA standard
- Long term durability is still and issue

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- Introduction
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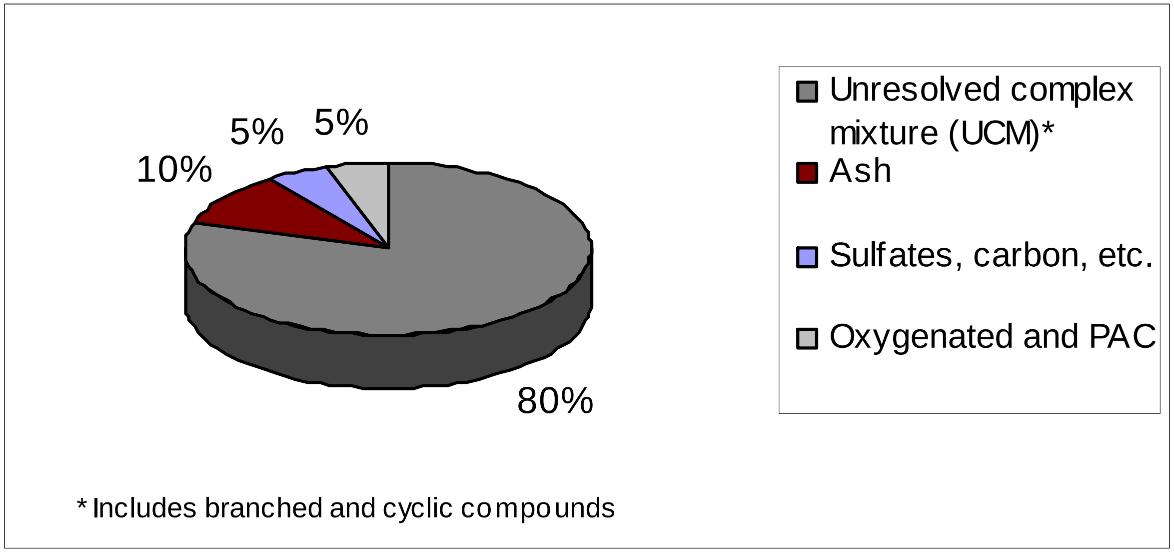
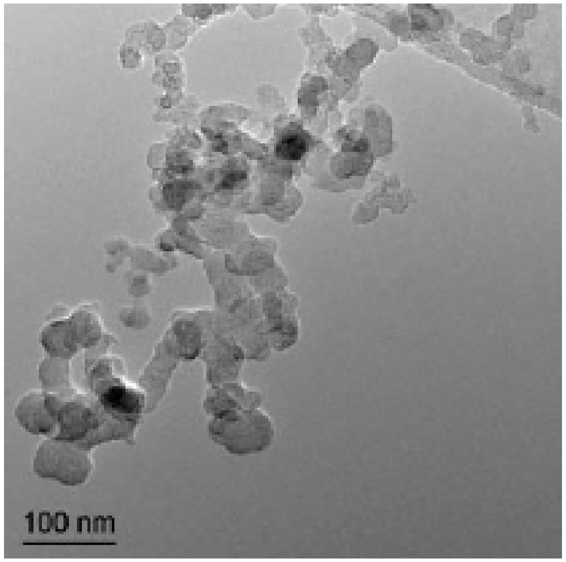
  - Structure and composition of ultrafine and nanoparticles
  - Particle formation during dilution
- Dilution and Sampling issues
  - Laboratory measurements
  - On-road measurement
- Diesel particle removal systems
  - Description
  - On-road evaluation
- Particles from gasoline spark ignition engines
- Future issues and conclusions

Summary - Particle Emissions from Gasoline Spark Ignition Engines (SI) (not including GDI)

- SI engine exhaust particles consist of similar materials and have similar morphology to Diesel particles
- However there are important differences
  - They usually smaller
  - They are composed primarily of volatile materials
  - Formation is generally more dependent on operating conditions than for Diesel engine
  - Perfectly premixed chemically correct combustion should not produce particles
    - » Formation likely to be associated by local inhomogeneous conditions - big droplets, crevices
    - » Lube oil may play an important role – especially with worn engines

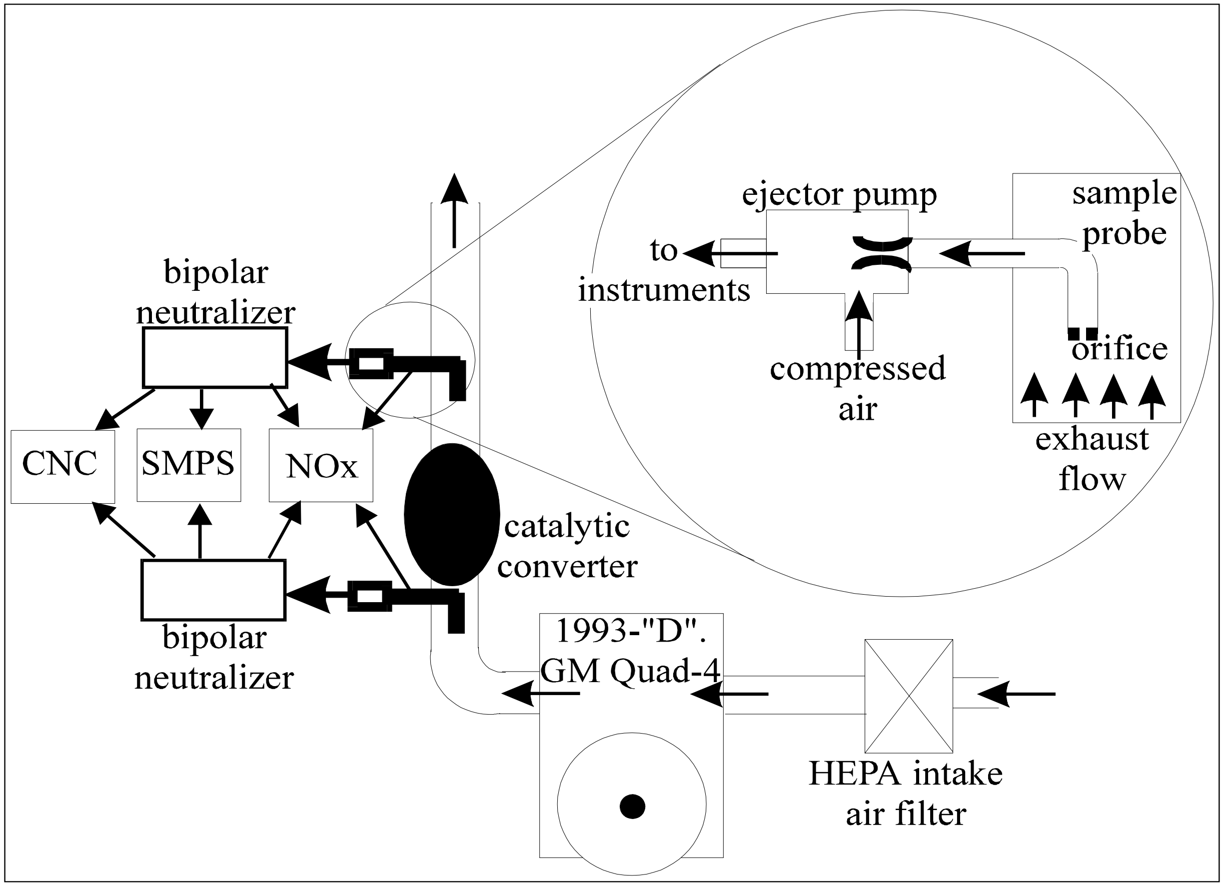
Typical Composition and Structure of Gasoline Exhaust Particulate Matter





- Composition data courtesy Ricardo
  - Much more OC (UCM) than Diesel
  - UCM might be described as little tarry balls
- TEM photo from report by Blom and Nolan, Oak Ridge National Laboratory
  - Particles from gasoline SI engine have similar morphology to Diesel
  - Particles from high emitters – oil burners – show more liquid like structures

Dilution System Used for SI Engine Exhaust Particle Measurements



Adapted from:

Graskow, B.R., D.B. Kittelson, M.R.Ahmadi, and J.E. Morris. 1999. "Exhaust Particulate Emissions from Two Port Fuel Injected Spark Ignition Engines," SAE Paper No. 1999-01-1144, 1999.

Graskow, B.R., D.B. Kittelson, I.S. Abdul-Khalek, M.R. Ahmadi, and J.E. Morris. "Characterization of Exhaust Particulate Emissions from a Spark Ignition Engine," SAE Paper No. 980528 and SP-1326 also in 1998 Transactions of the Society of Automotive Engineering, Vol. 3, *Engine, Fuels and Lubricants*, 1998.

SI Engine Particle Emissions - Influence of Load and Additives

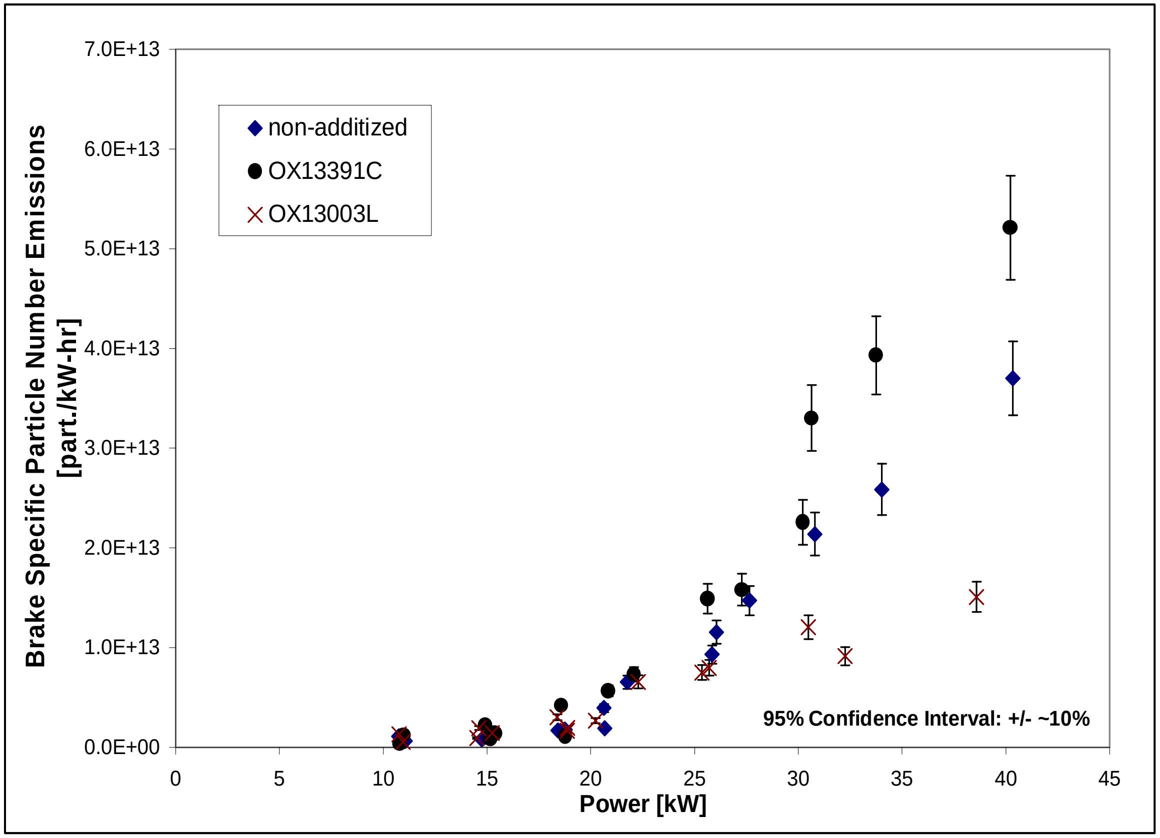


Figure 2. Brake Specific Particle Number Emissions as a Function of Power with 95% Confidence Intervals

Adapted from:

Graskow, B.R., D.B. Kittelson, M.R.Ahmadi, and J.E. Morris. 1999. "Exhaust Particulate Emissions from Two Port Fuel Injected Spark Ignition Engines," SAE Paper No. 1999-01-1144, 1999.

Graskow, B.R., D.B. Kittelson, I.S. Abdul-Khalek, M.R. Ahmadi, and J.E. Morris. "Characterization of Exhaust Particulate Emissions from a Spark Ignition Engine," SAE Paper No. 980528 and SP-1326 also in 1998 Transactions of the Society of Automotive Engineering, Vol. 3, *Engine, Fuels and Lubricants*, 1998.

Port Fuel Injected SI Engine - Influence of Additives on Size Distributions

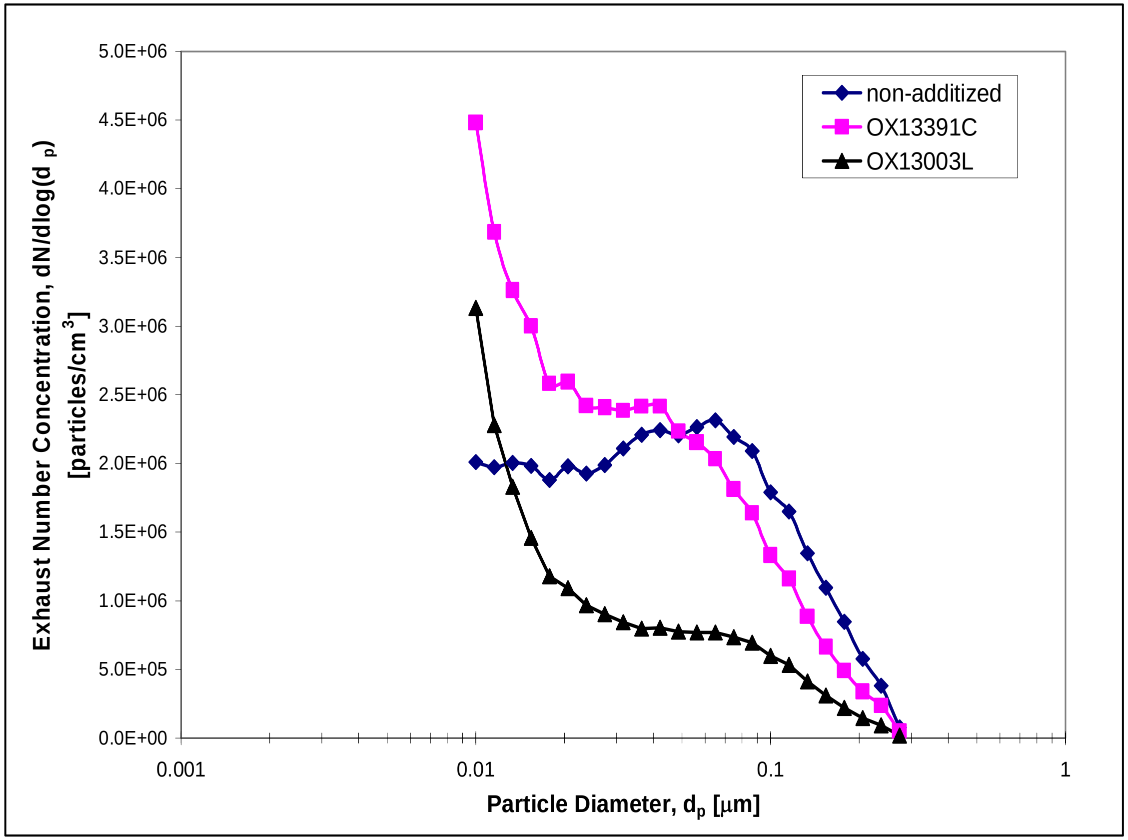


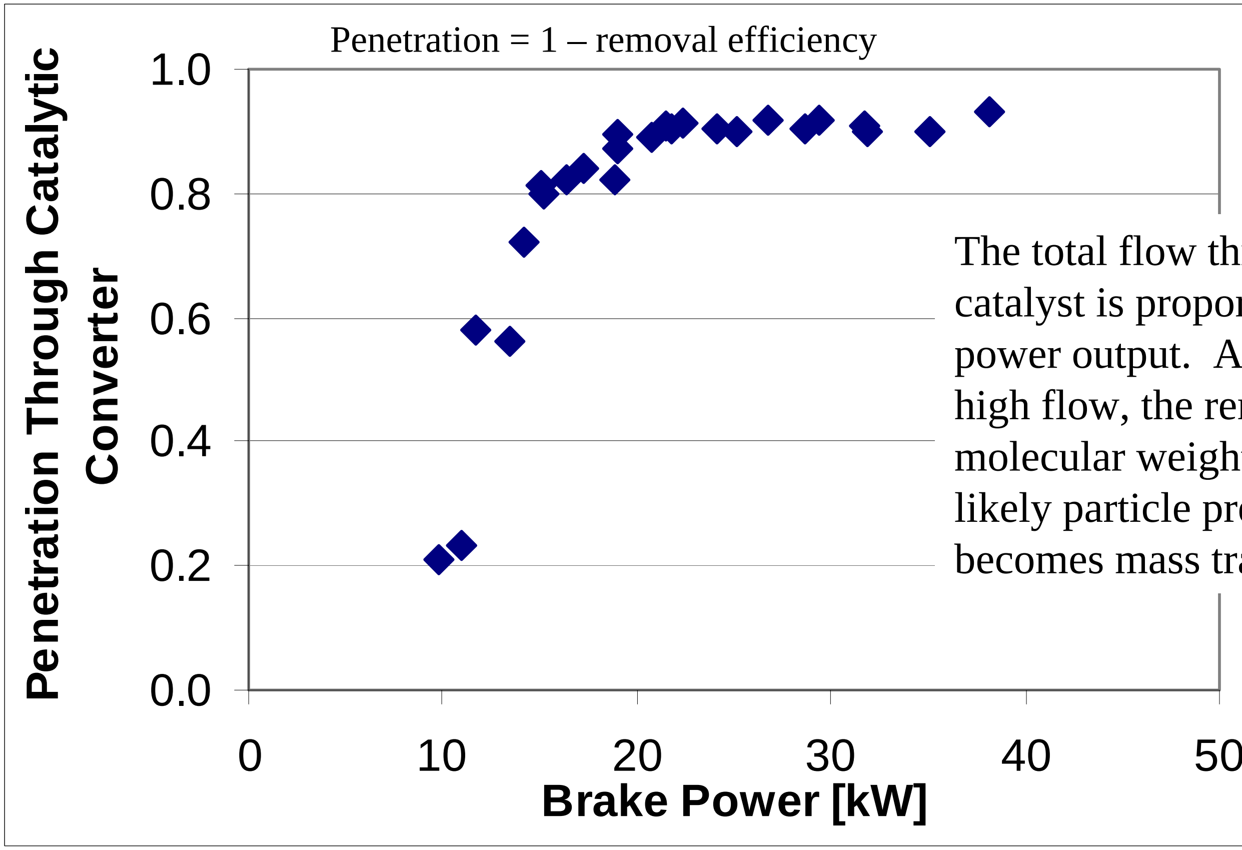
Figure 3. Representative Baseline Size Distributions for the OX13391 and OX13003 Additives [2500 RPM, 90 kPa]

Adapted from:

Graskow, B.R., D.B. Kittelson, M.R.Ahmadi, and J.E. Morris. 1999. “Exhaust Particulate Emissions from Two Port Fuel Injected Spark Ignition Engines,” SAE Paper No. 1999-01-1144, 1999.

Graskow, B.R., D.B. Kittelson, I.S. Abdul-Khalek, M.R. Ahmadi, and J.E. Morris. “Characterization of Exhaust Particulate Emissions from a Spark Ignition Engine,” SAE Paper No. 980528 and SP-1326 also in 1998 Transactions of the Society of Automotive Engineering, Vol. 3, *Engine, Fuels and Lubricants*, 1998.

Particle Number Penetration through the Catalytic Converter (Quad-4)



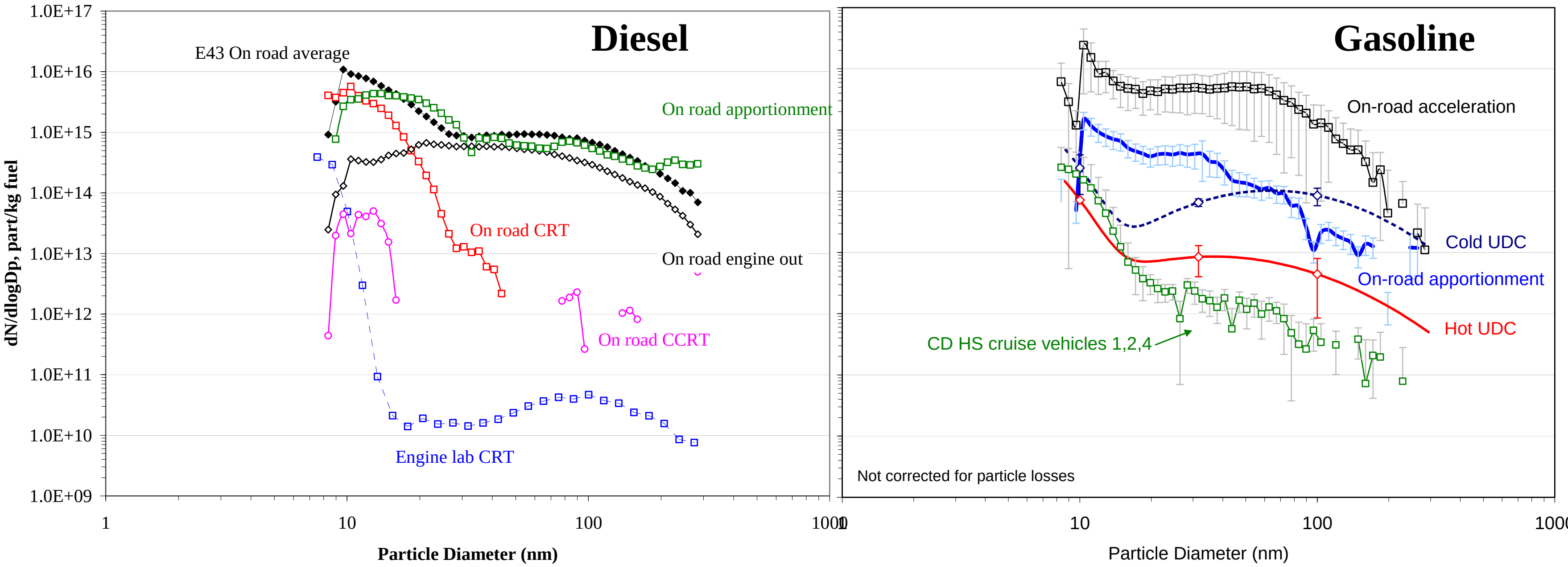
The total flow through the catalyst is proportional to the power output. At high power, high flow, the removal of high molecular weight hydrocarbons, likely particle precursors, becomes mass transfer limited.

Adapted from:

Graskow, B.R., D.B. Kittelson, M.R.Ahmadi, and J.E. Morris. 1999. "Exhaust Particulate Emissions from Two Port Fuel Injected Spark Ignition Engines," SAE Paper No. 1999-01-1144, 1999.

Graskow, B.R., D.B. Kittelson, I.S. Abdul-Khalek, M.R. Ahmadi, and J.E. Morris. "Characterization of Exhaust Particulate Emissions from a Spark Ignition Engine," SAE Paper No. 980528 and SP-1326 also in 1998 Transactions of the Society of Automotive Engineering, Vol. 3, *Engine, Fuels and Lubricants*, 1998.

On-road and lab experiments – comparison of Diesel and gasoline SI emission



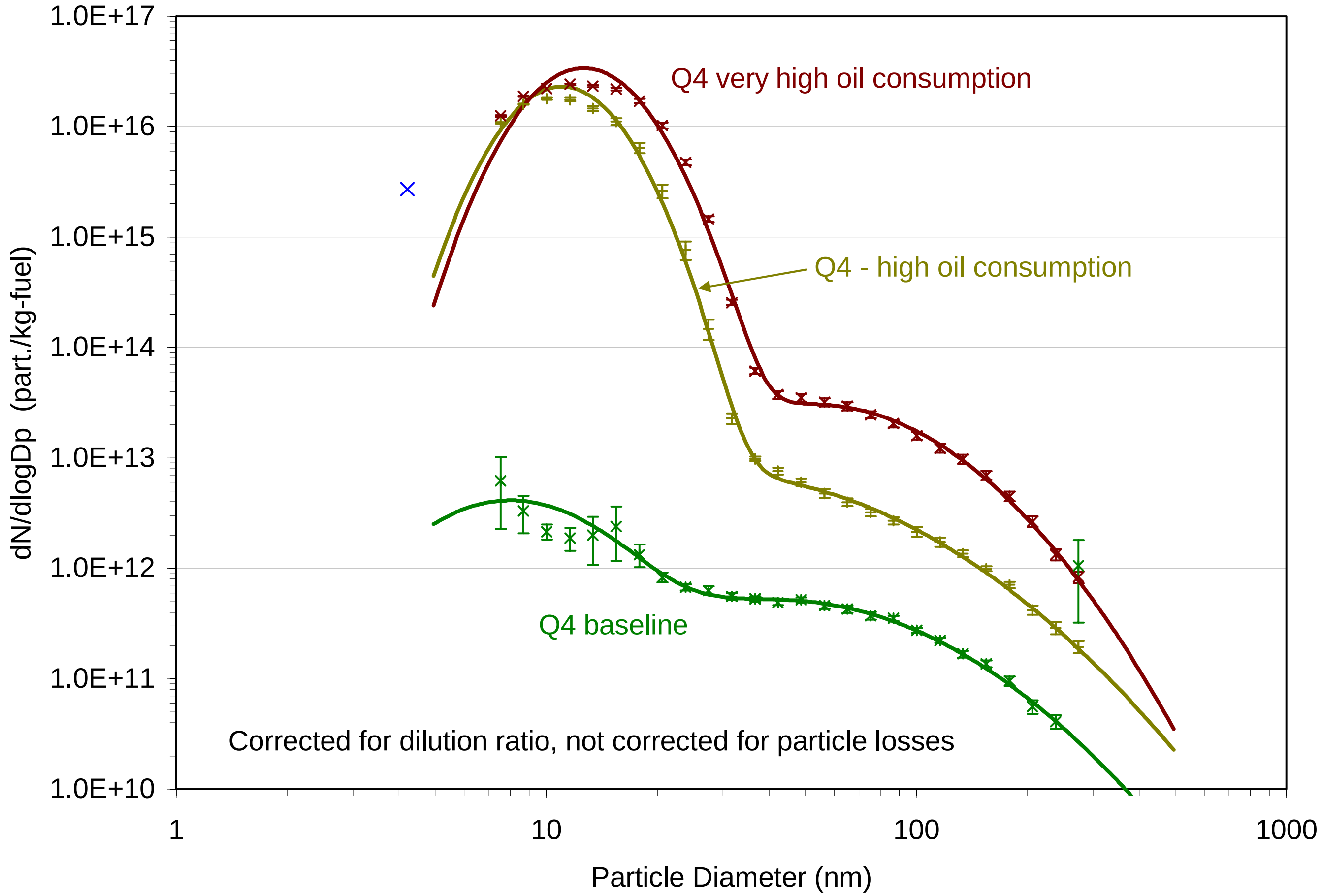
- SI emissions are much more load dependent than Diesel
- During highway cruise SI emissions are significantly lower than Diesel
- However, during hard accelerations, size distributions for gasoline light-duty vehicles were surprisingly similar to modern heavy-duty Diesel vehicles
- Diesel with CRT or CCRT has lowest emissions

Johnson, Jason P., David B. Kittelson, Winthrop F. Watts, 2005. “Source Apportionment of Diesel and Spark Ignition Exhaust Aerosol Using On-Road Data from the Minneapolis Metropolitan Area,” Atmospheric Environment 39, 2111–2121.
Kittelson, D. B., W. F. Watts, J. P. Johnson, J. Schauer, and D. R. Lawson 2006. “On-road and Laboratory Evaluation of Combustion Aerosols Part 2: Summary of Spark Ignition Engine Results,” Journal of Aerosol Science, in press.
Kittelson, D. B., W. F. Watts, J. P. Johnson, C. J. Rowntree, S. P. Goodier, M. J. Payne, W. H. Preston, C. P. Warrens, M. Ortiz, U. Zink, C. Goersmann, M. V. Twigg and A. P. Walker, 2006. “Driving Down On-Highway Particulate Emissions,” SAE paper number 2006-01-0916

Simulation of a gasoline high emitter – "Smoker"

- Most PM emissions from spark ignition engines do not come from well maintained engines running under cruise conditions
  - Cold start and hard acceleration account for most of the emissions from well maintained engines
  - Worn gasoline engines may be a major source of on-road PM
- The objective of this experiment was to simulate the behavior of a worn SI engine with high oil consumption under controlled conditions and measure its emissions
- A worn engine was simulated by the introduction of used lube oil onto the intake valve stems under controlled laboratory conditions. Leaky valve seals are a common cause for high oil consumption
- Properties and characteristics of the exhaust aerosol that were characterized included particle number and length concentrations, and the aerosol number and mass size distributions.

Tests of simulated gasoline high emitter – high oil consumption due to leaky valve seals



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  - Structure and composition of ultrafine and nanoparticles
  - Particle formation during dilution
- Dilution and Sampling issues
  - Laboratory measurements
  - On-road measurement
- Diesel particle removal systems
  - Description
  - On-road evaluation
- Particles from gasoline spark ignition engines
- Future issues and conclusions

Particles from future engines

- Diesel engines with exhaust filters
  - Solid particles in both the nuclei and accumulation modes may be nearly completely eliminated by exhaust filtration
    - » Carbonaceous particles removed from filter by regeneration
    - » Ash particles from lube oil eventually plugs filters
  - If exhaust filters remove nearly all of the solid particles the only thing left will be volatile particles in the nuclei mode
    - » Exhaust filters cannot directly remove the gas phase precursors that lead to the formation of nuclei mode particles
    - » Hydrocarbon precursors may be destroyed in catalyzed systems to the extent allowed by kinetics (mass transfer) but sulfuric acid may form
    - » Some catalyzed systems appear to trap sulfates (CCRT)
    - » Filters must be regenerated, actively or passively. Care must be taken to avoid particle release and possible hotspots

Particles from future engines

- Diesel and other engines without exhaust filters or with low efficiency filters
  - With very clean Diesel combustion systems, particles from lube oil will become more important
  - Other engine cycles and fuels may also have difficulties with particles from lube oil
    - Gaseous fueled engines
    - DME
    - Low exhaust T associated with lean burn or high EGR in new low temperature combustion engines (HCCI) will make aftertreatment to control volatile lube oil related particles difficult
  - Off cycle operation of 3-way catalyst SI engines may lead to high particle emissions
  - Perhaps the most important characteristic of future engines will be how they perform as they wear out

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Some slides have been added and modified. If you wish an updated copy contact me at kitte001@umn.edu