Ultrafine Particle Formation Mechanisms

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

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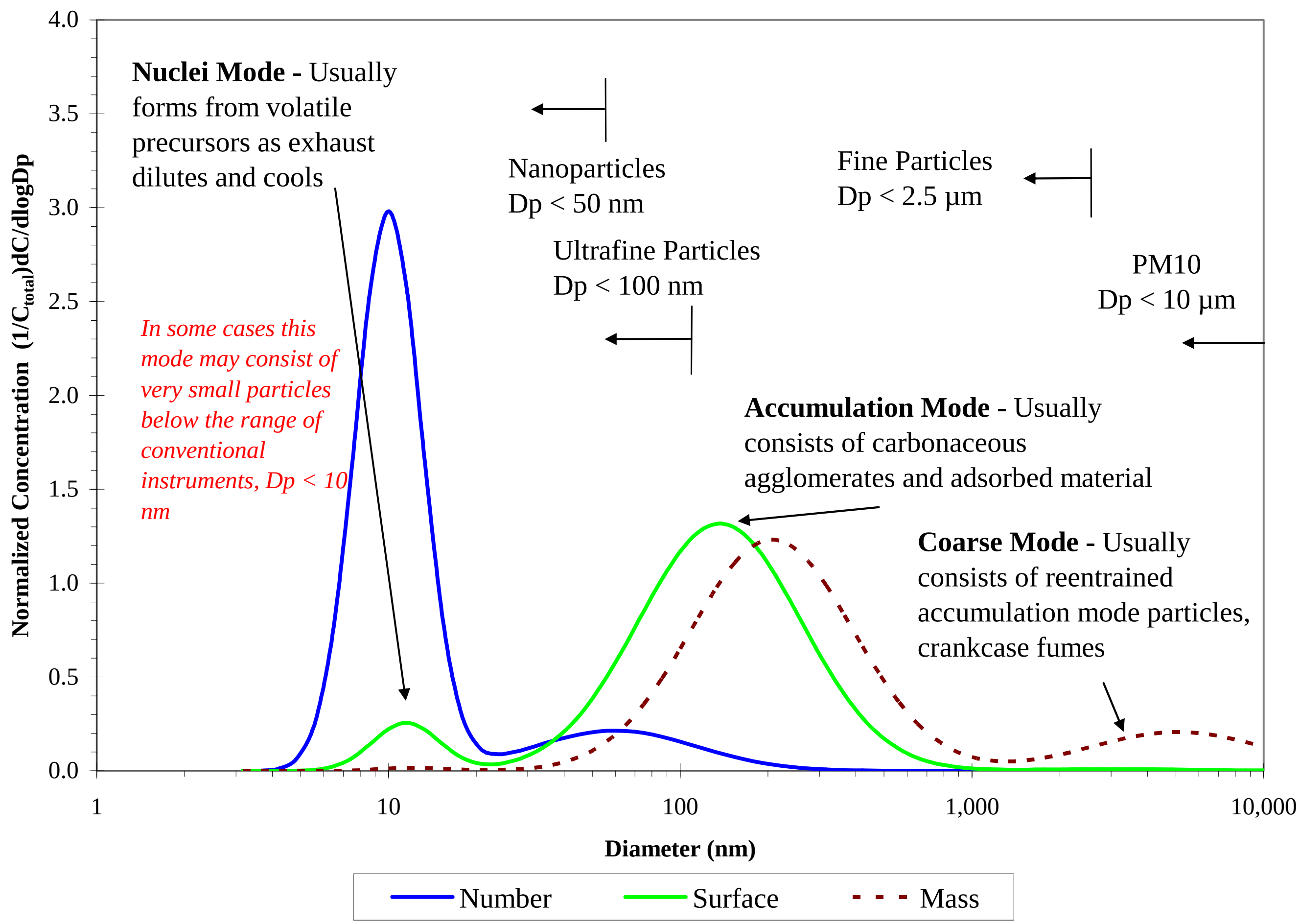
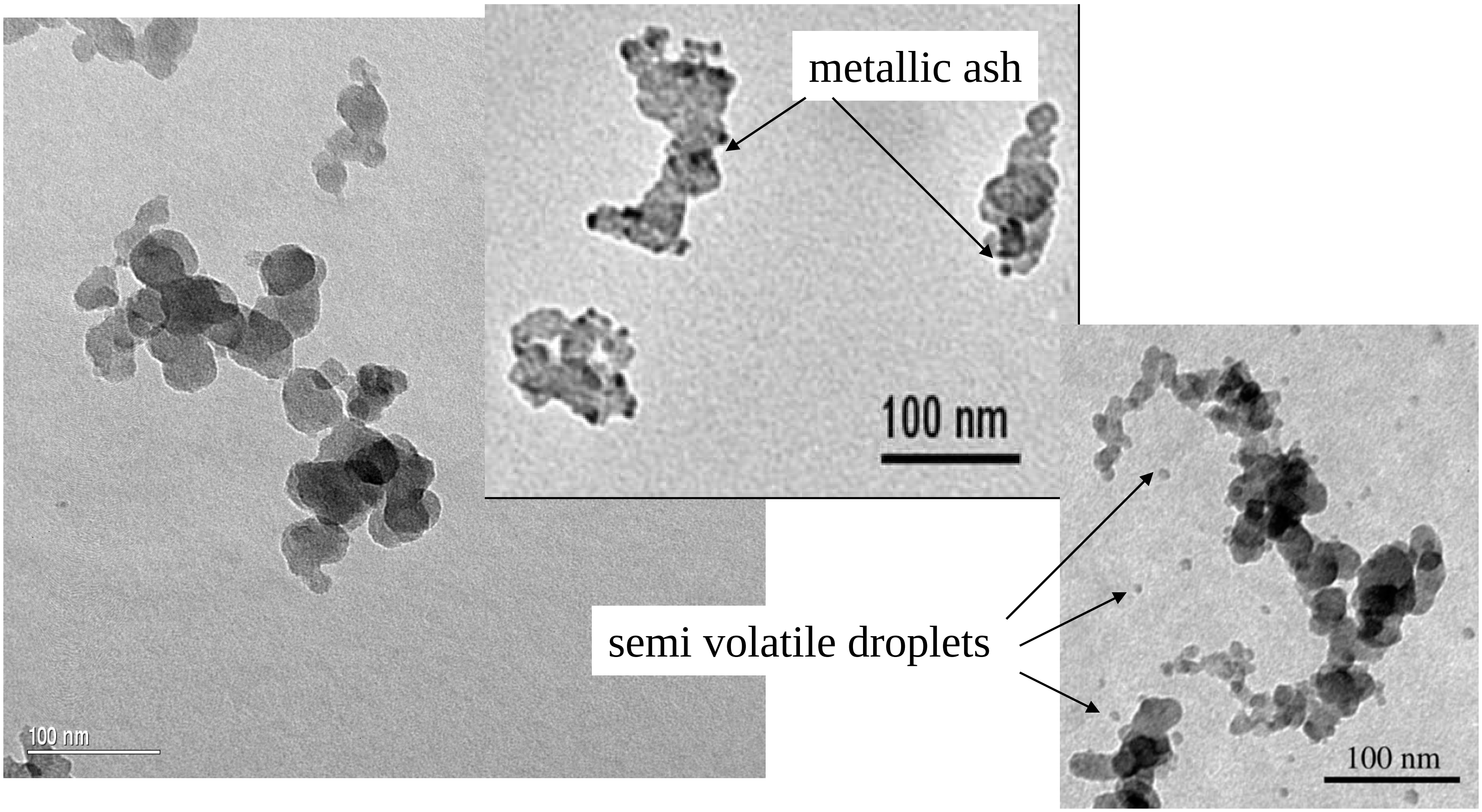
Typical engine exhaust particle size distribution by mass, number and surface area



Outline

- Particle Formation by Diesel Engines
  - Particle formation by combustion
  - Structure and composition of ultrafine and nanoparticles
  - Particle formation during dilution
- Particles from gasoline spark ignition (SI) engines
- On-road measurements of gasoline and Diesel fleet emission factors
- Other recent Diesel and SI emission measurements
  - Diesel
    - » Light and heavy duty, biodiesel
    - » Aftertreatment
    - » Solid and volatile particles
  - Gasoline SI
  - Comparison
- Future issues and conclusions

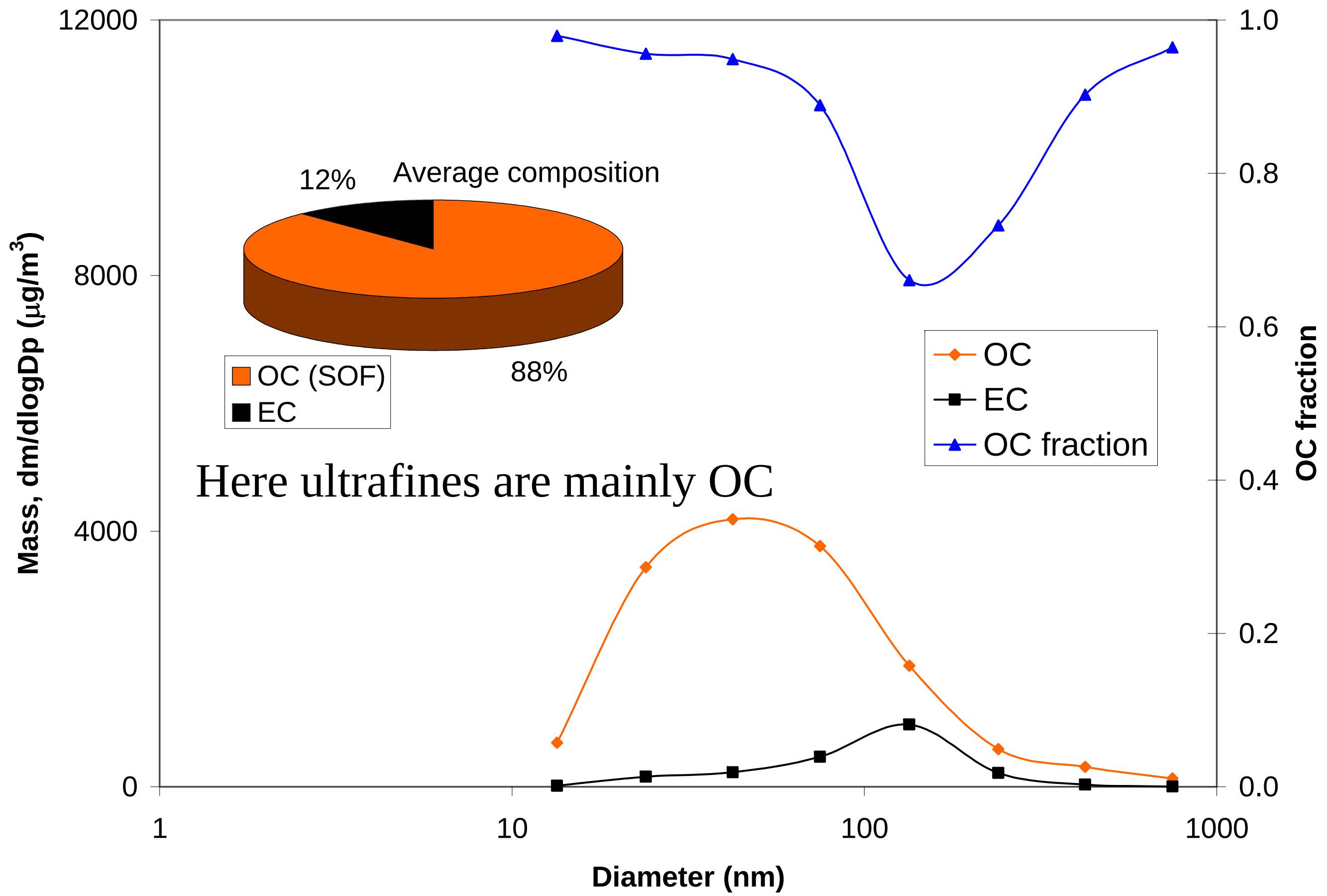
Carbonaceous agglomerates comprise most of the mass from current Diesel engines but different structures are evident



Particles from Diesel engines – without aftertreatment

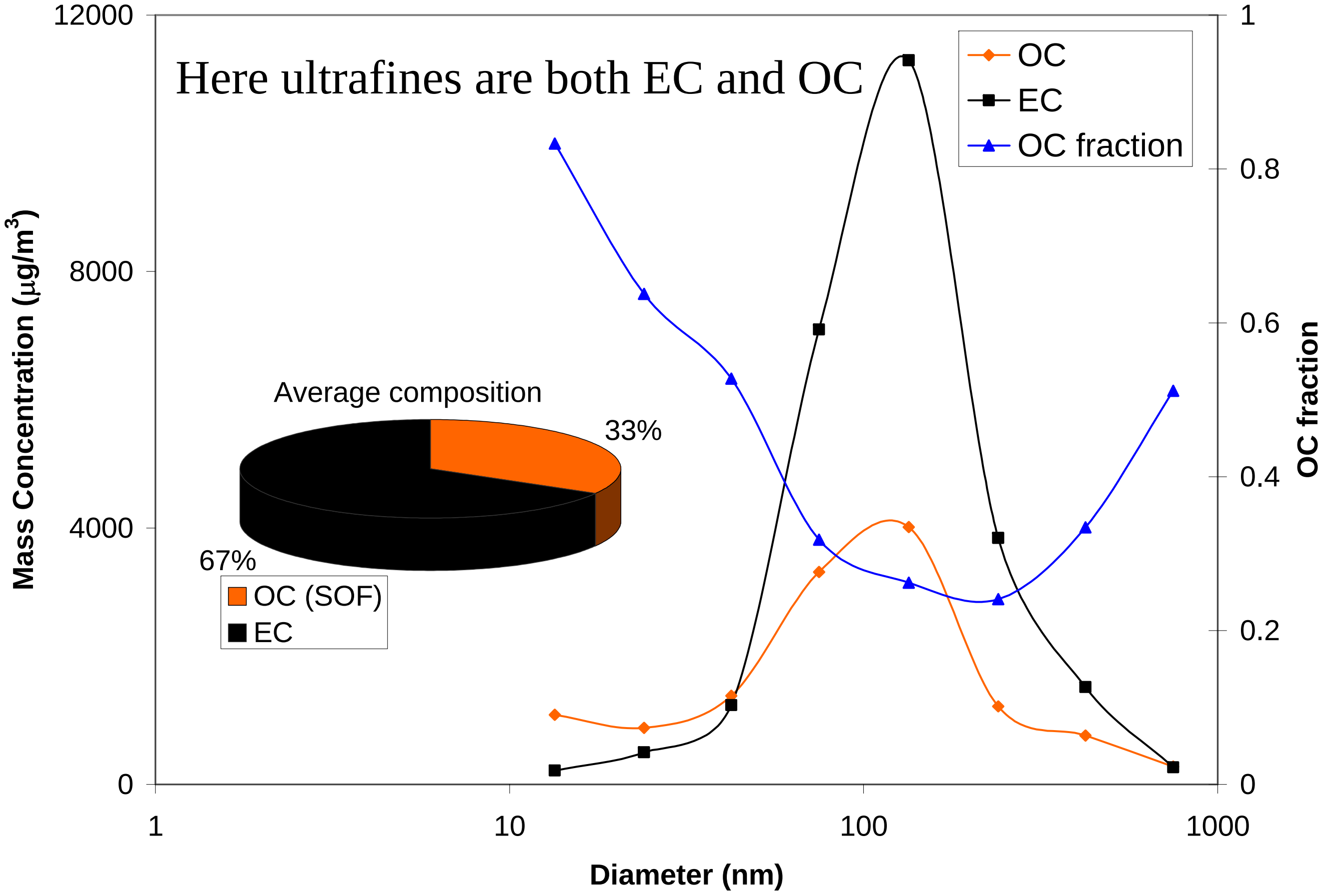
- Formed by combustion
  - Carbonaceous agglomerates (soot)
  - Metallic ash
    - » From lubricating oil – typically ~1% metal
    - » Wear related
  - Precursors to particle formation during dilution
    - » SO_3 from S in fuel and lube oil – most of S leaves as SO_2 but 2–4% is converted to SO_3
    - » Unburned and partially burned hydrocarbons from fuel and lube oil
- Formed by gas to particle formation during dilution
  - Sulfuric acid and other sulfates
  - Heavy hydrocarbons and derivatives
  - Usually most of these materials adsorb onto carbonaceous agglomerates during dilution
  - However a small fraction of these materials nucleate to form ultrafine nucleation mode particles

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



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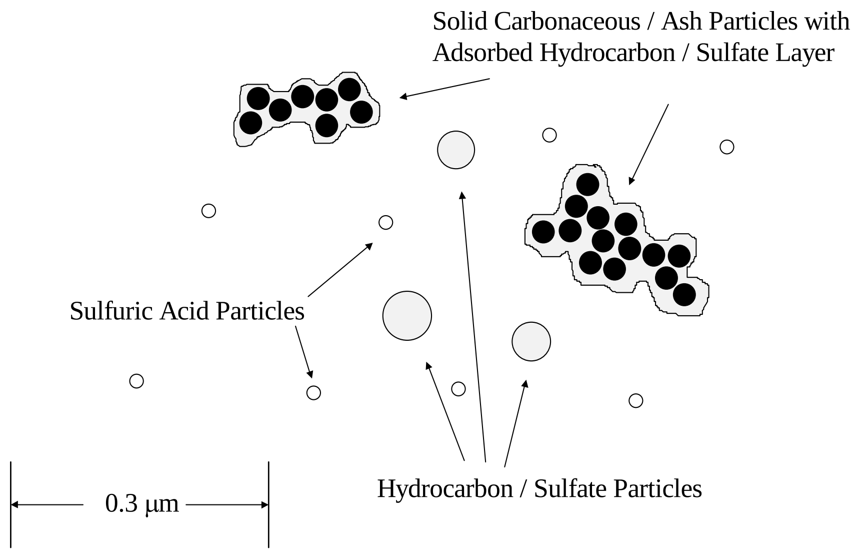
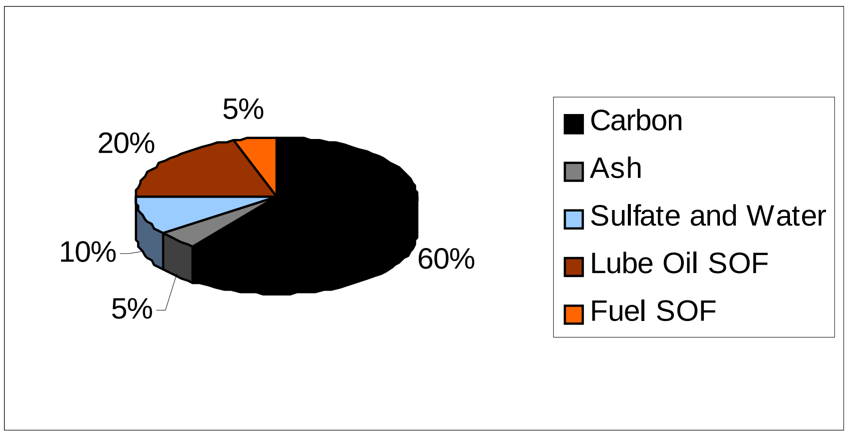
Typical composition and structure of diesel particulate matter – *heavy-duty, no aftertreatment*

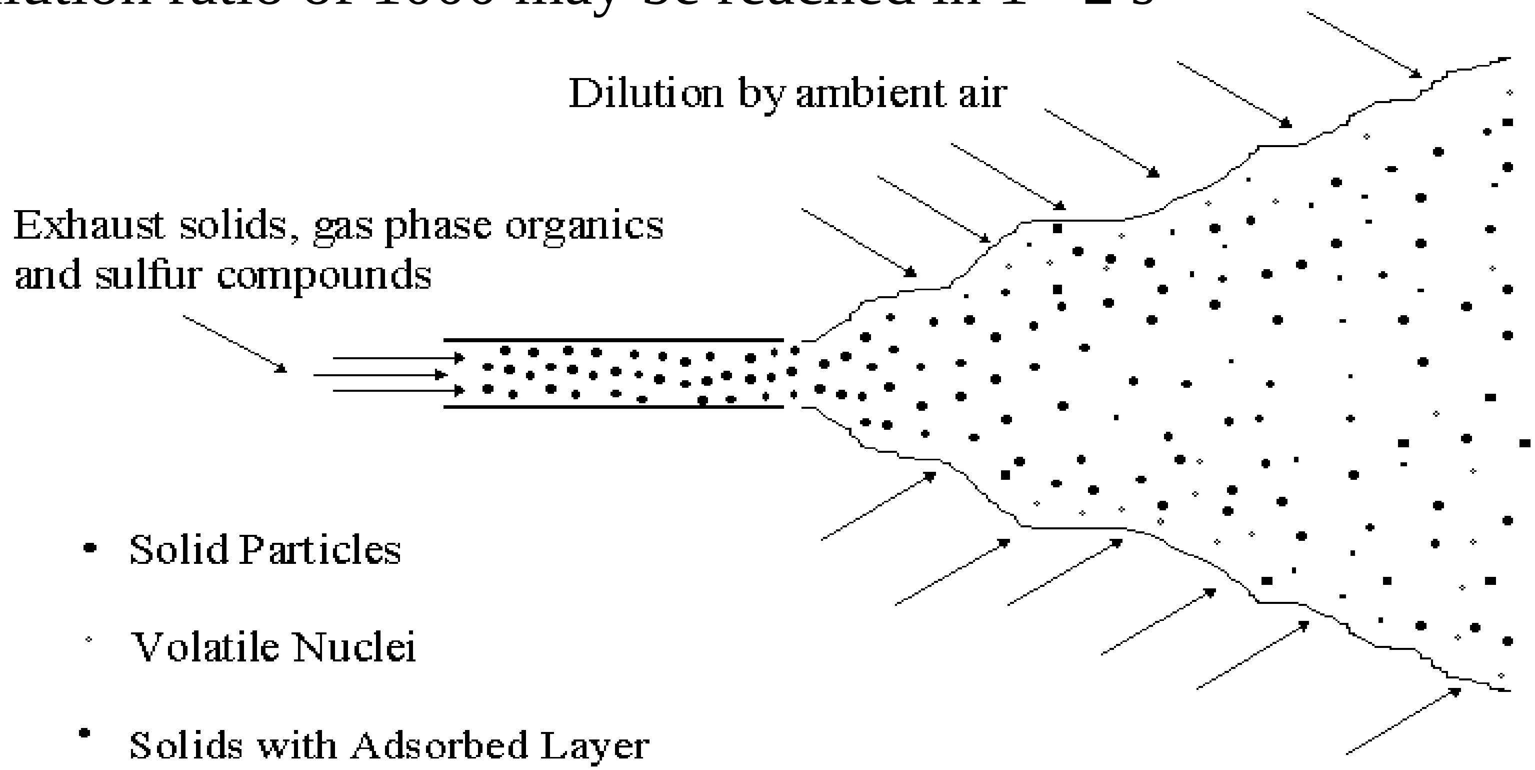
- Solid particles are typically carbonaceous chain agglomerates (mainly elemental carbon, EC) and ash and usually comprise most of the particle mass
- Volatile or semi-volatile matter (sulfur compounds and organic carbon (SOF)) typically constitutes 35% (5-90%) of the particle mass, 90% (30-99%) of the 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





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

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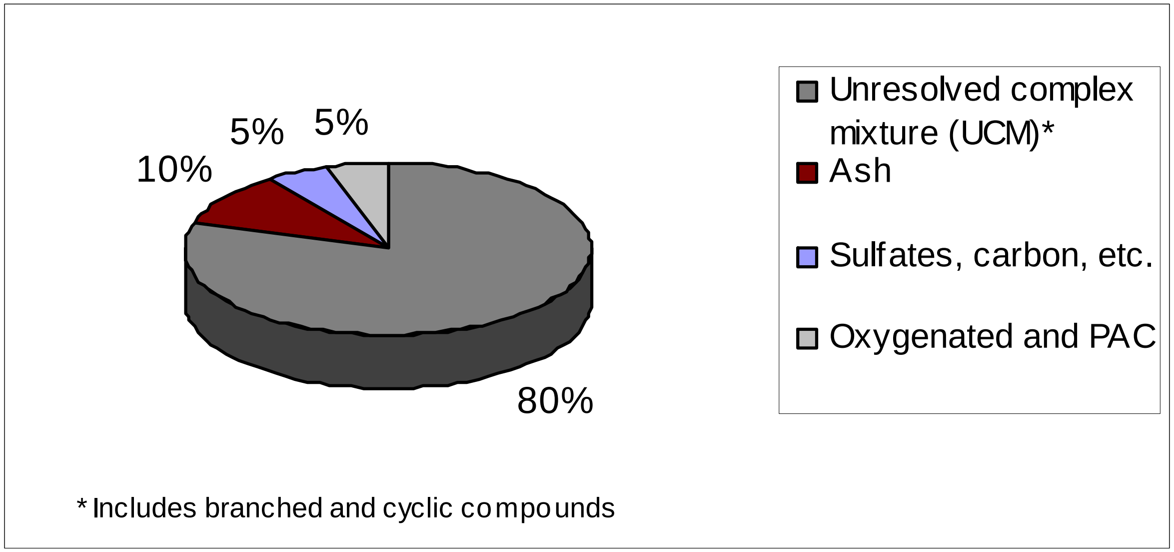
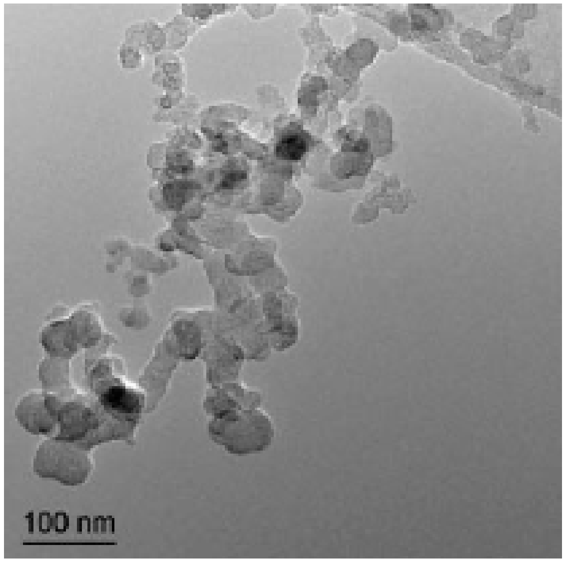
Particle Emissions from Gasoline Spark Ignition Engines (SI) (not including GDI)

- 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

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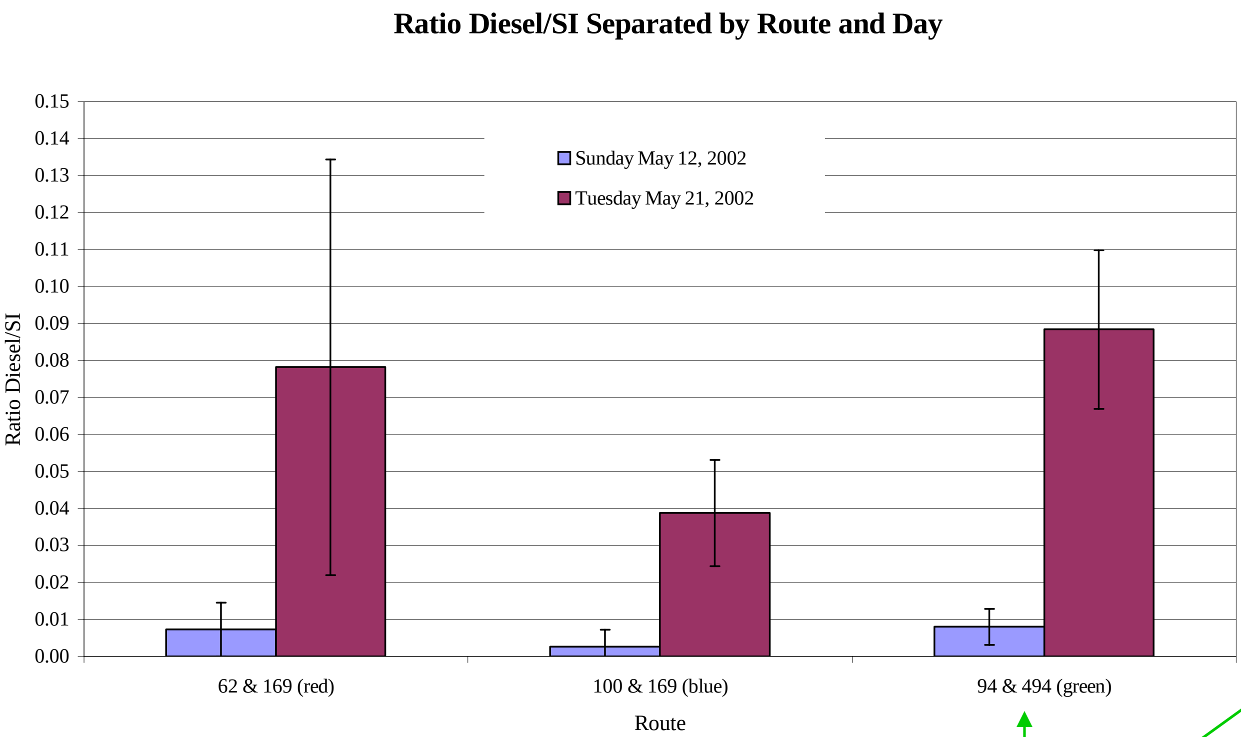
Characterization of real world fleets: weekday / weekend on-highway apportionment experiments

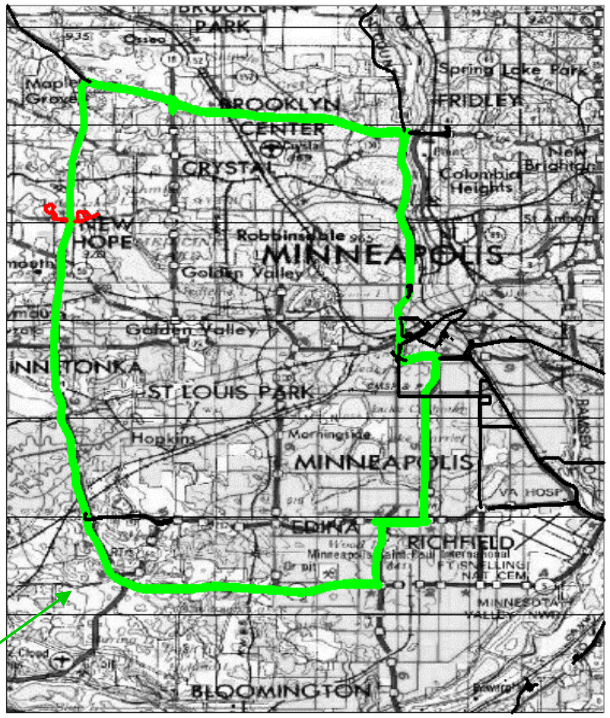
- Summertime urban freeway measurements
- Over-the-road aerosol, corrected for the background is contributed by vehicles in proportion to their traffic volume.
- Measuring traffic volumes and aerosol concentrations on days with differing SI to Diesel ratios gives a system of equations that can be solved for average Diesel and SI contribution on a per unit traffic volume basis
- Presented on a fuel specific (per kg of fuel) basis
- Principal uncertainties are in traffic counts and background corrections

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, D. Zarling, A. Kasper, U. Baltensperger, H. Burtscher, J. J. Schauer, C. Christenson, and S. Schiller. 2003. Gasoline vehicle exhaust particle sampling study. Contract Final Report U. S. Department of Energy Cooperative Agreement DE-FC04-01Al66910.

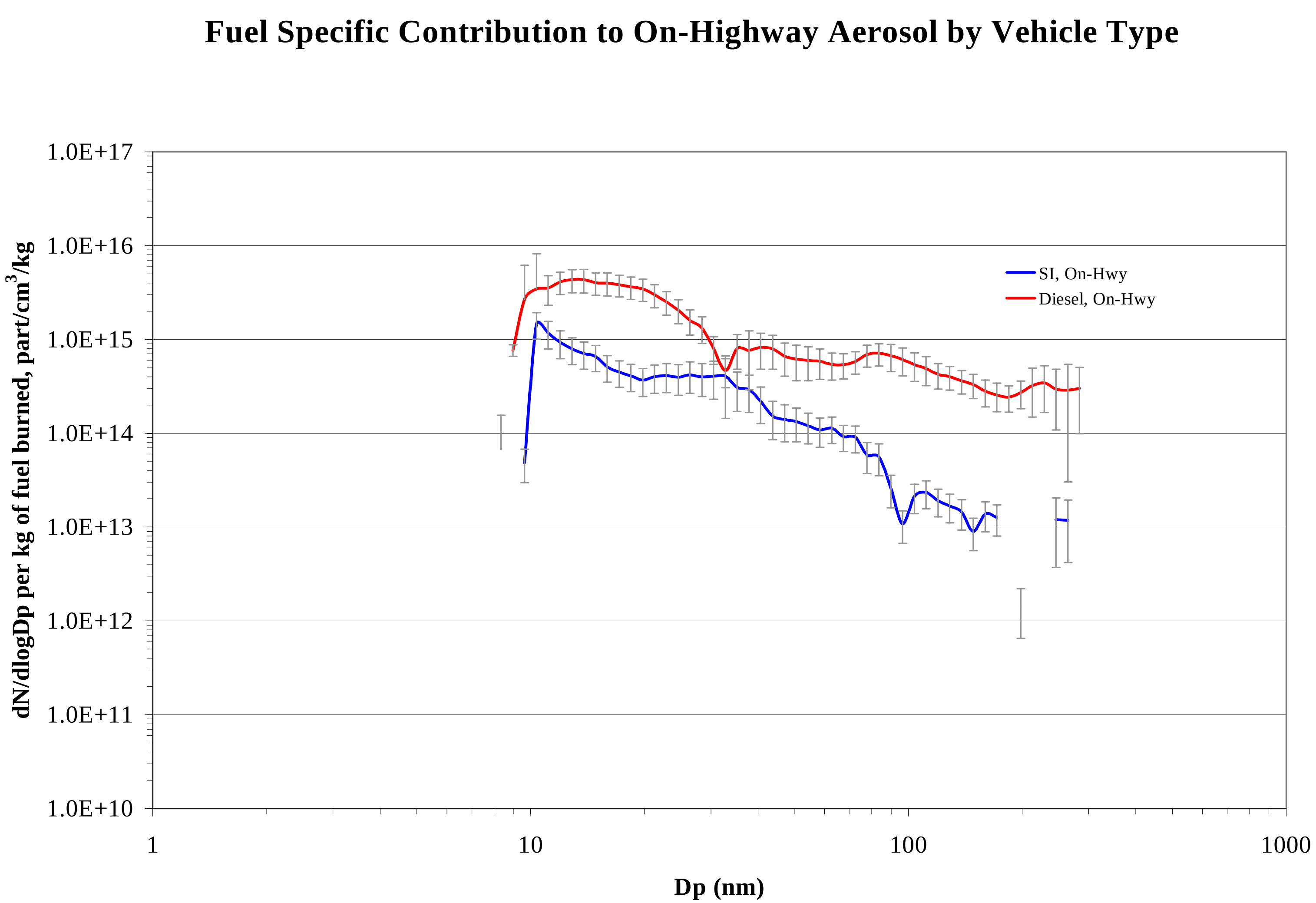
Diesel/gasoline (SI) ratio by route and day





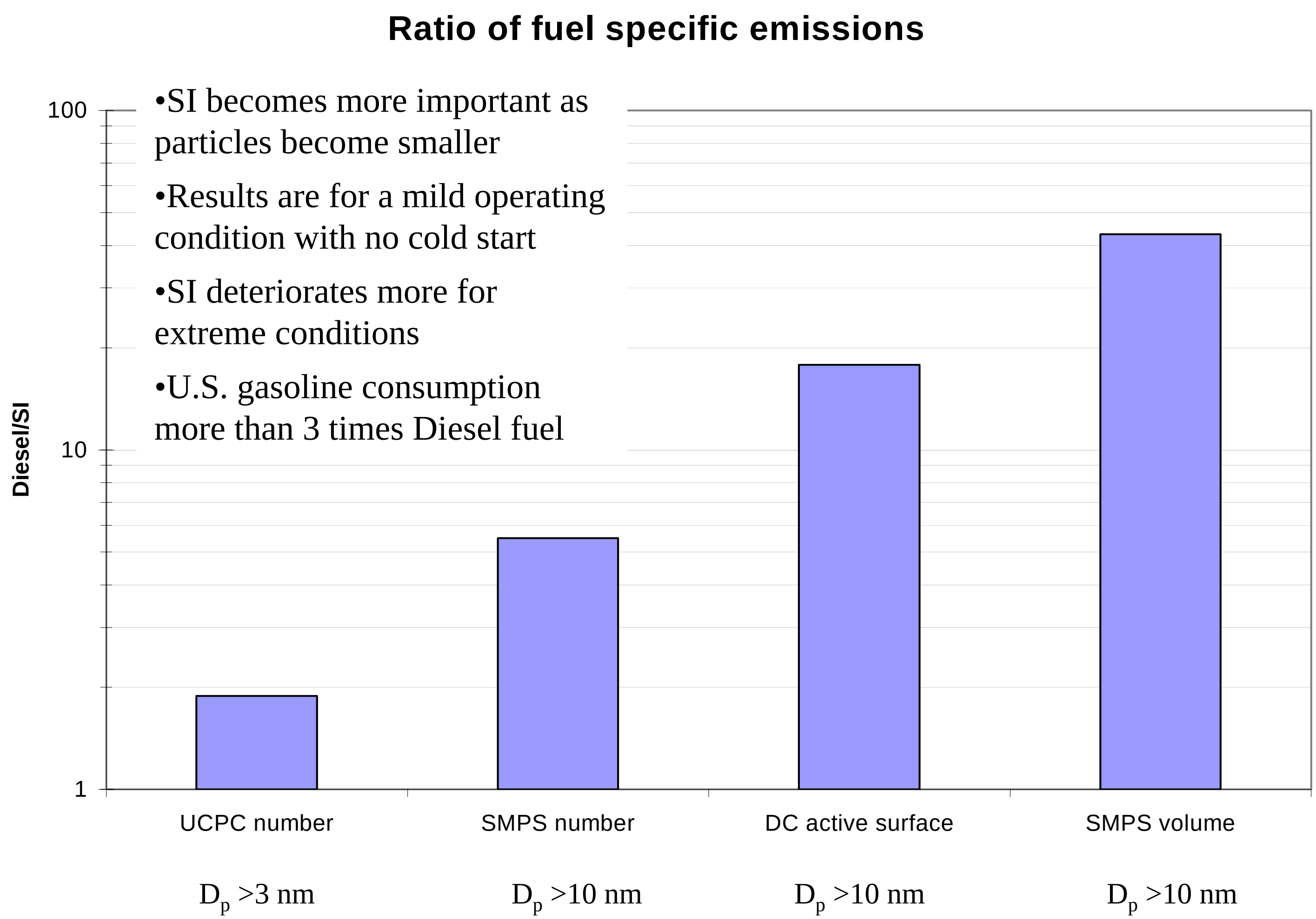
Route selected

Diesel and SI apportioned size distributions on a fuel specific basis



Fuel specific emissions – Diesel and SI summertime highway cruise emission ratios

- •SI becomes more important as particles become smaller
- •Results are for a mild operating condition with no cold start
- •SI deteriorates more for extreme conditions
- •U.S. gasoline consumption more than 3 times Diesel fuel



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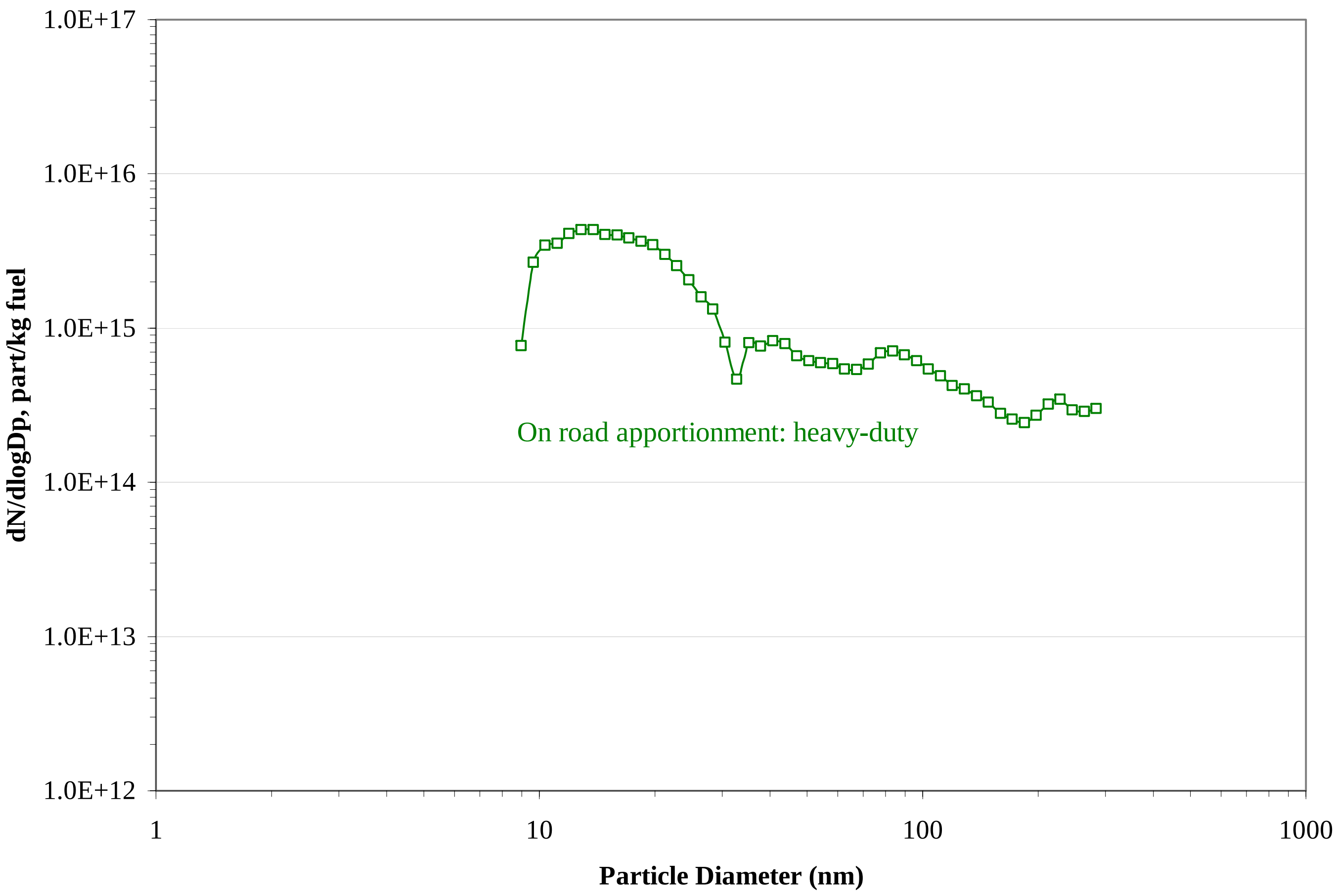
Comparison of light-duty and heavy-duty Diesel



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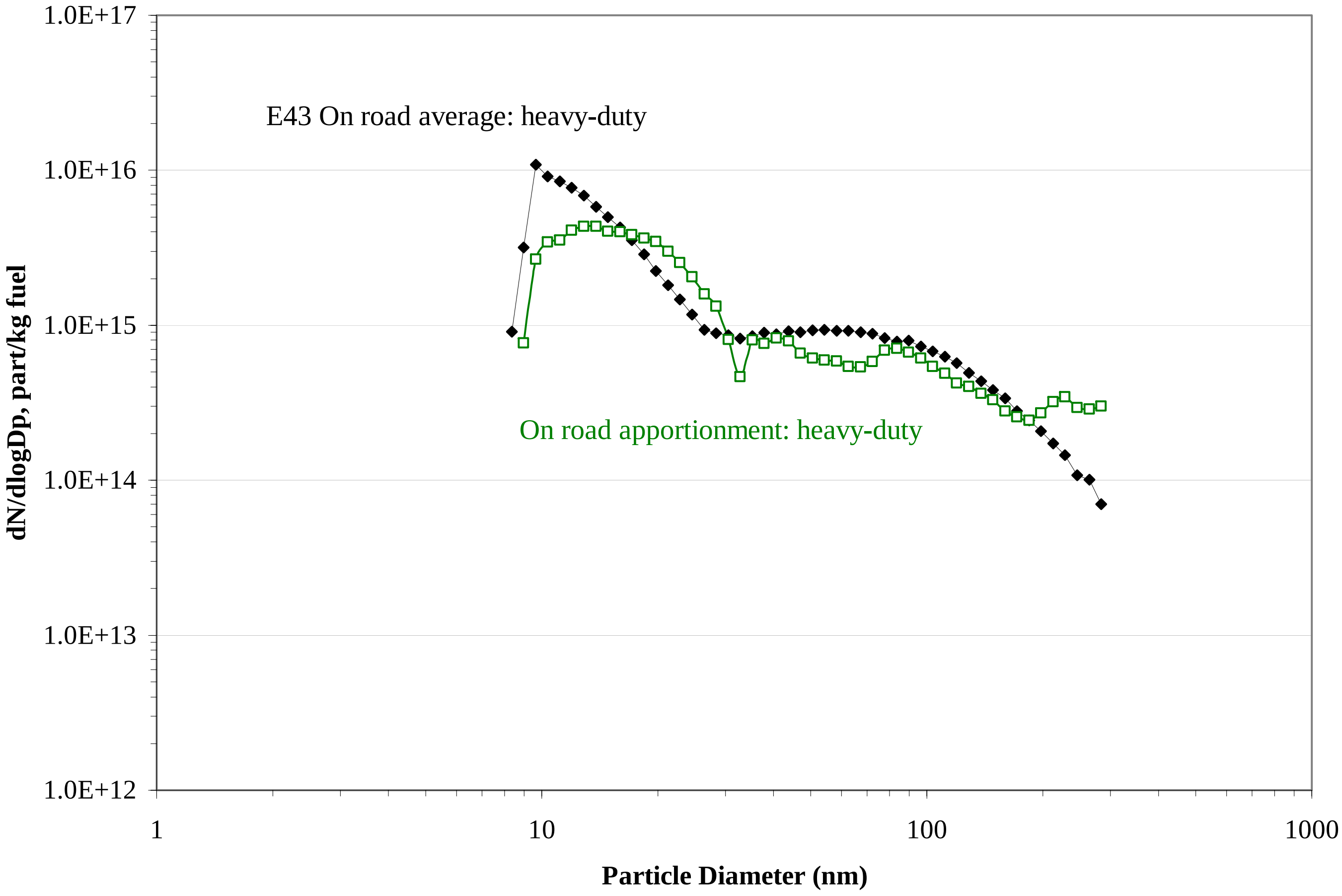

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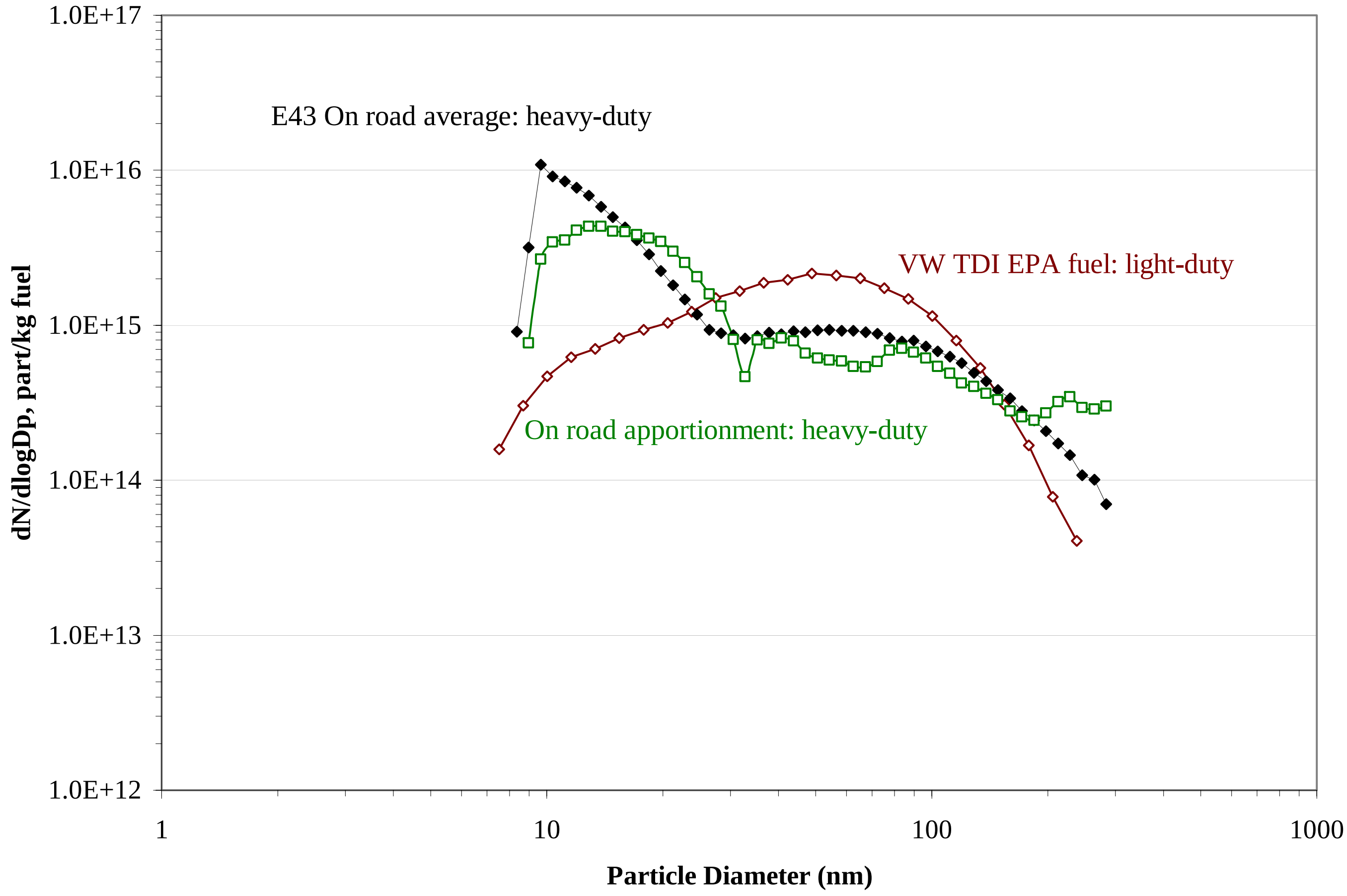
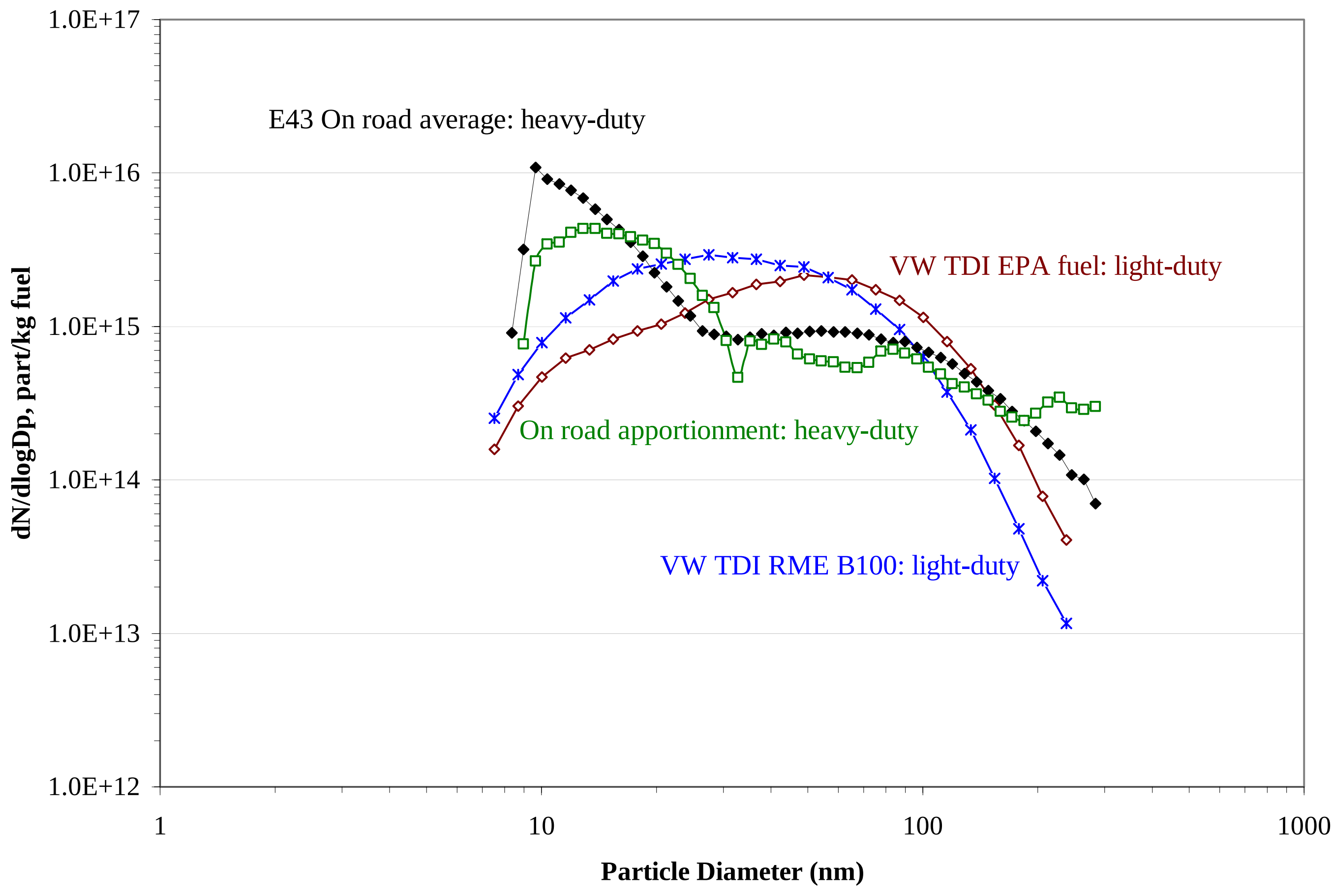
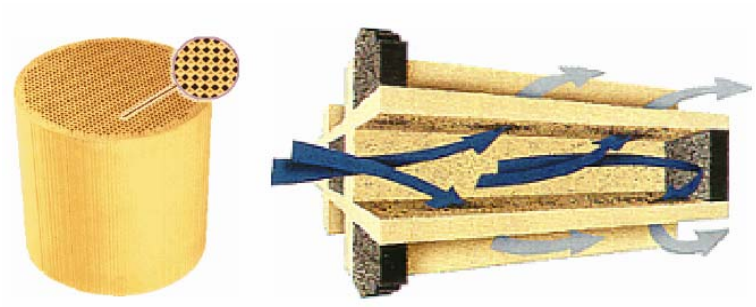


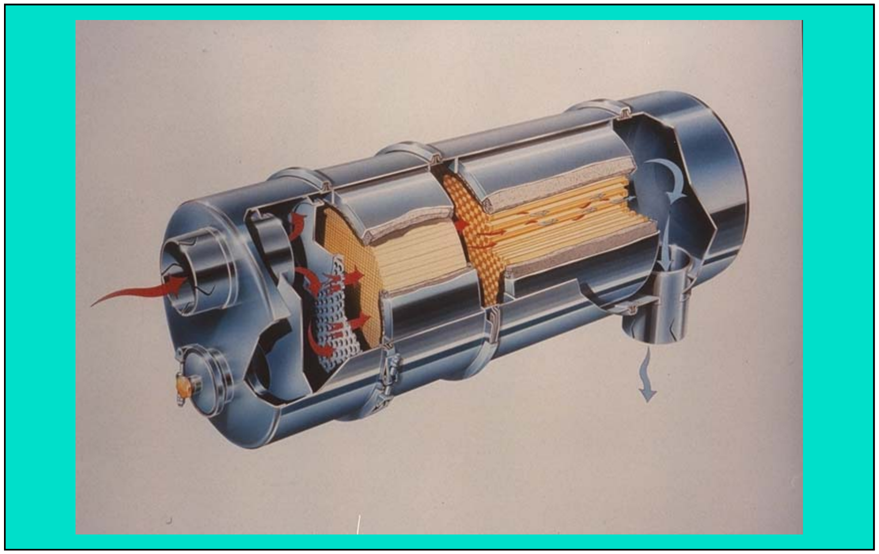
Comparison of light-duty and heavy-duty Diesel – and biodiesel



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



Figures courtesy Corning and Johnson-Matthey

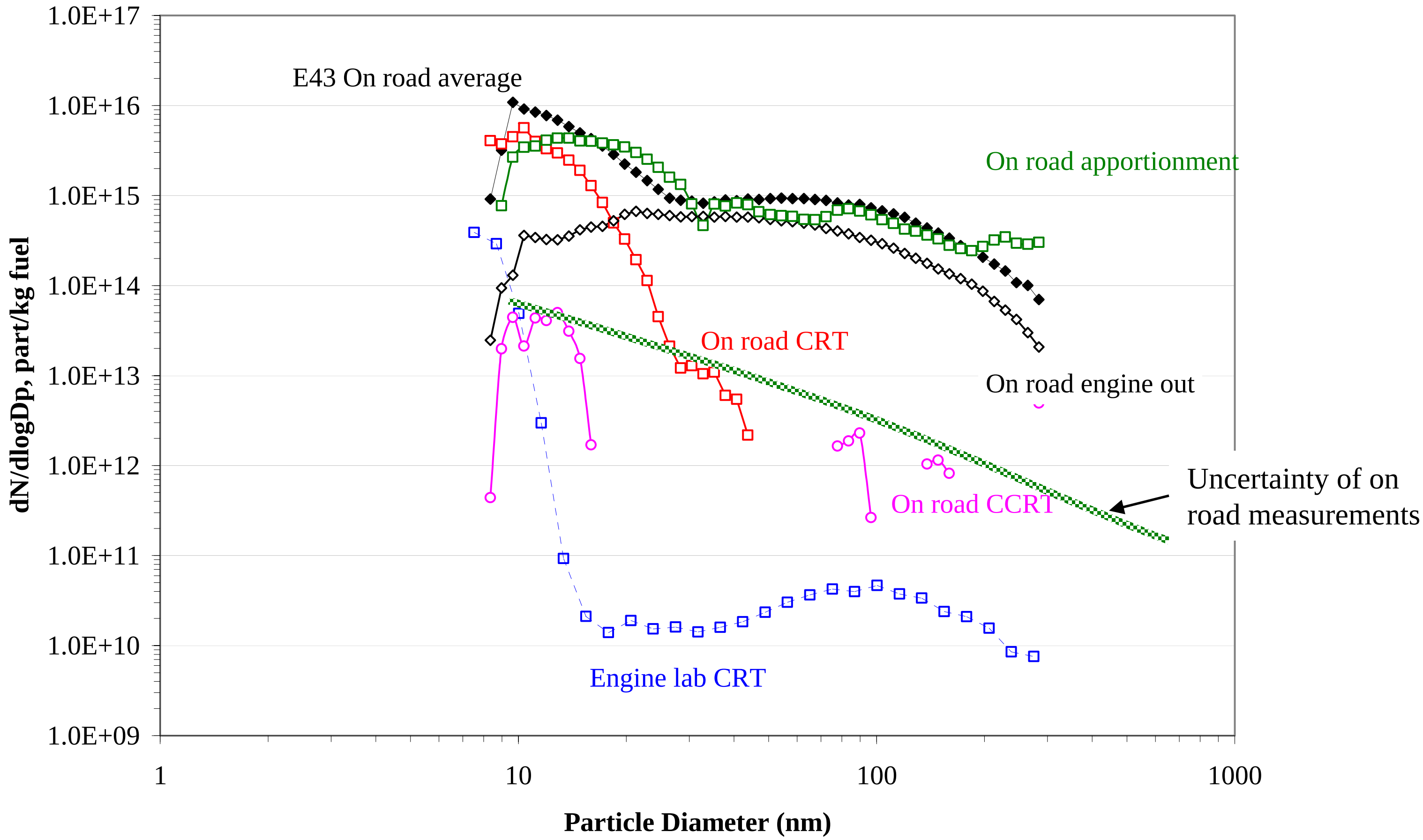


- Most PM filtration systems being considered for 2007 are the wall flow type shown on the left. Without regeneration to oxidize soot these devices quickly plug.
- Catalyzed filtration systems like the J-M CRT® shown on the right reduce regeneration temperature by producing NO_2 from exhaust NO in an 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

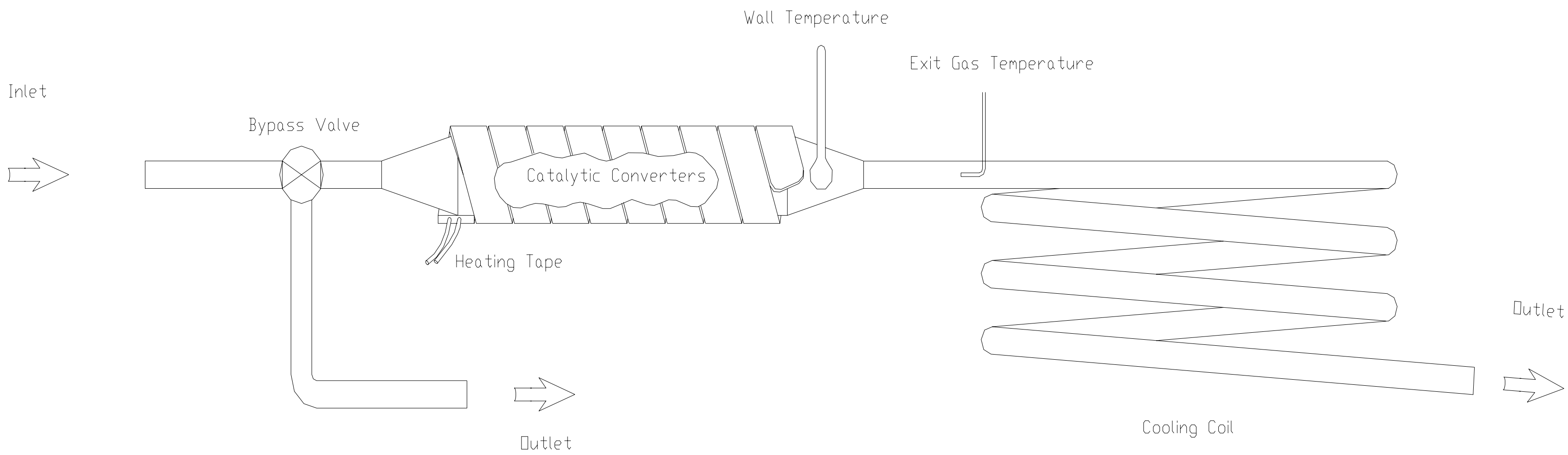
On-road evaluations of exhaust particle filters – plume sniffing of MEL with CRT, CCRT

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.

Fuel specific emissions, comparisons with other lab and on road studies



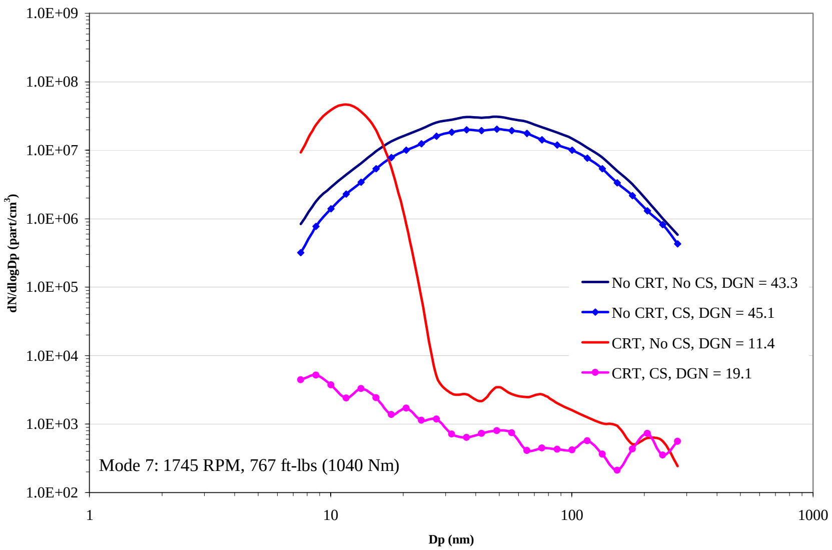
Lab tests of volatility of Diesel particles with and without aftertreatment

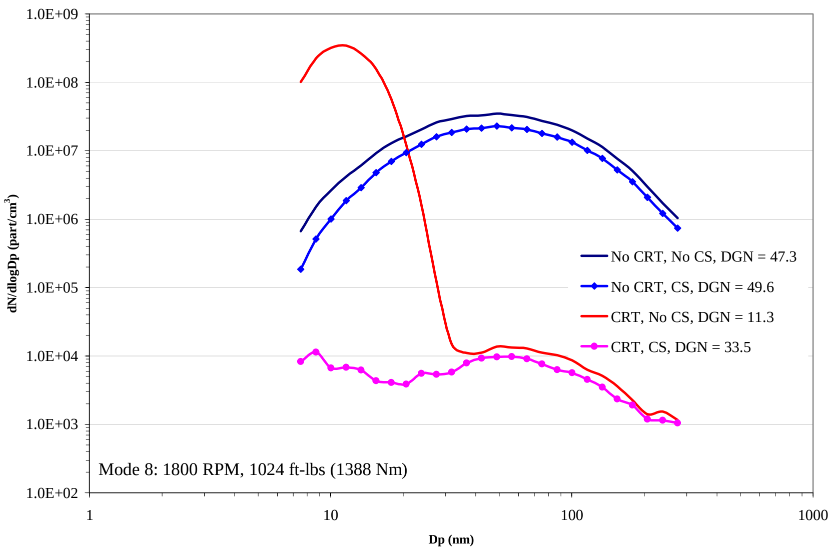


- U of M catalytic stripper to remove volatiles
  - Stripper consists of a 2 substrate catalyst* followed by a cooling coil
  - The first substrate removes sulfur compounds
  - The second substrate is an oxidizing catalyst
  - Diffusion and thermophoretic losses present but well defined

*Catalysts were provided by Johnson-Matthey

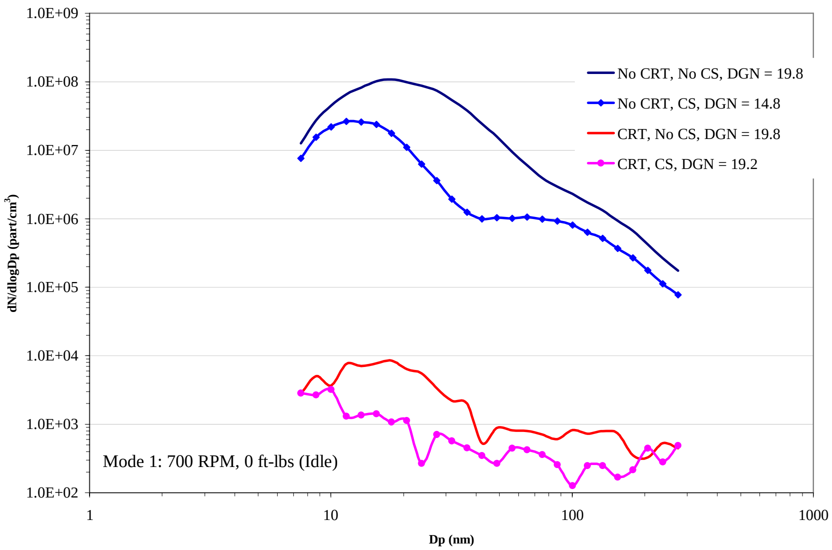
Size distributions of total and solid particles

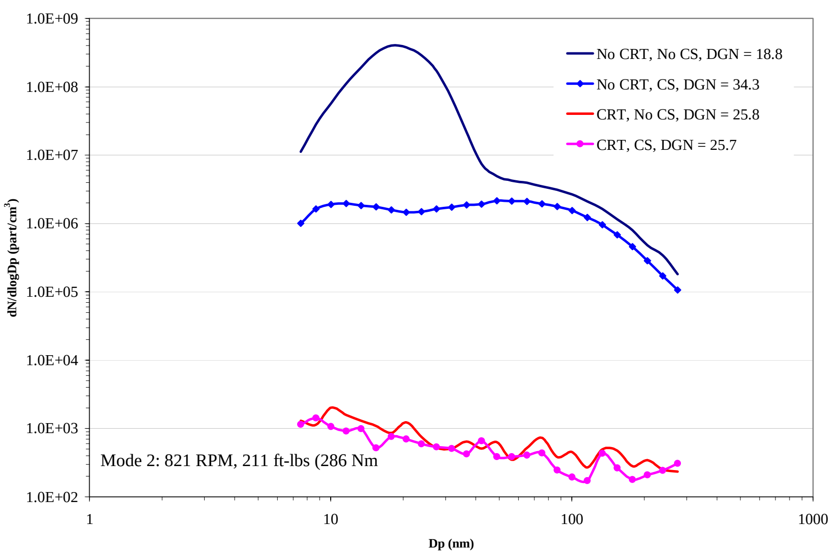




- Heavy-duty 2004 complaint engine running with catalyzed exhaust filtration AVL modes 7 and 8 – high load
- BP50 fuel
- Both of these modes form a nucleation mode downstream of the catalyzed exhaust filtration system
  - No nucleation mode without filtration
  - The nucleation mode with filtration is entirely volatile
- The exhaust filtration system reduces solid particle concentrations by 3 to 4 orders of magnitude

Size distributions of total and solid particles





- Mode 1 and 2 are cases that show a nucleation mode without filtration but none with
- Mode 1 shows a clear nucleation mode even after volatile materials are removed by the CS. This suggests that it consists of nonvolatile materials – lube oil ash, very heavy HCs??
- Mode 2 also shows a small nonvolatile nucleation mode
- We have seen this behavior at light load with many engines – solid nucleation mode particles that would be ignored by 20 nm PMP cutoff
- With filtration the solid particle concentrations are reduced 3 to 4 orders of magnitude

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SI Engine Particle Emissions - Influence of Load and Additives

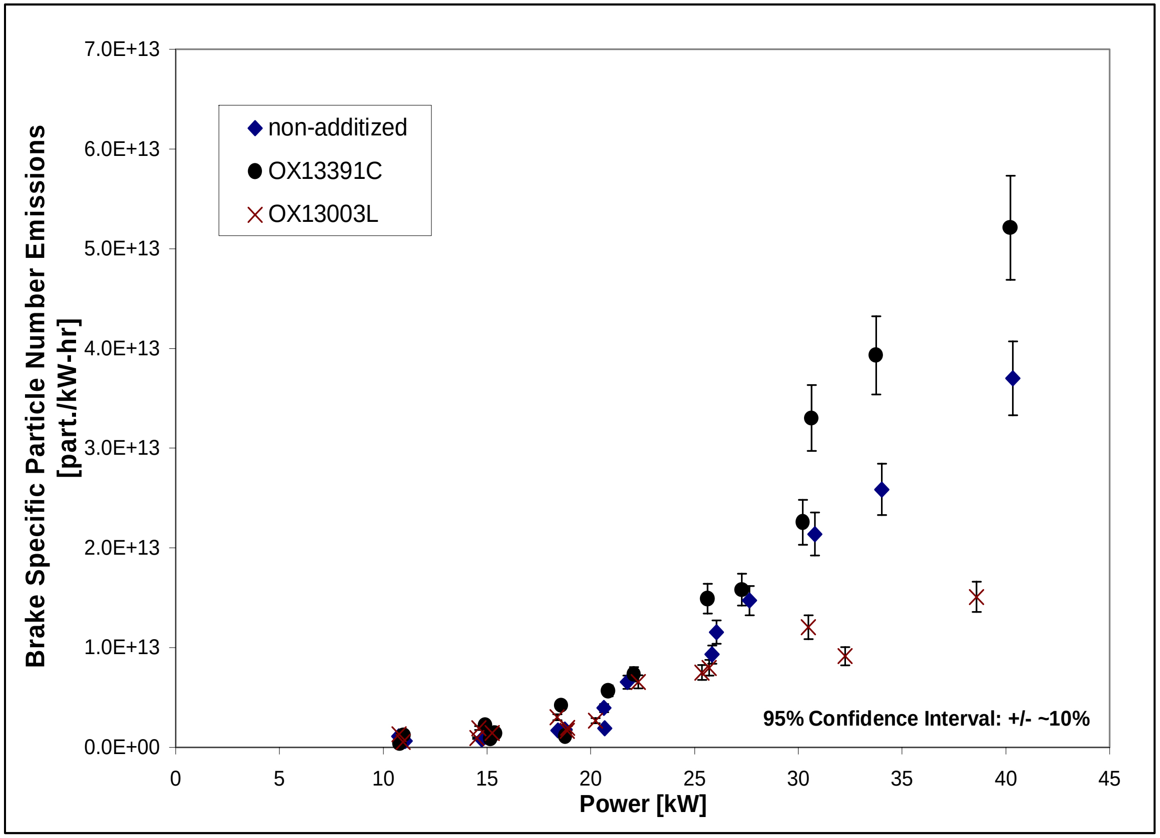


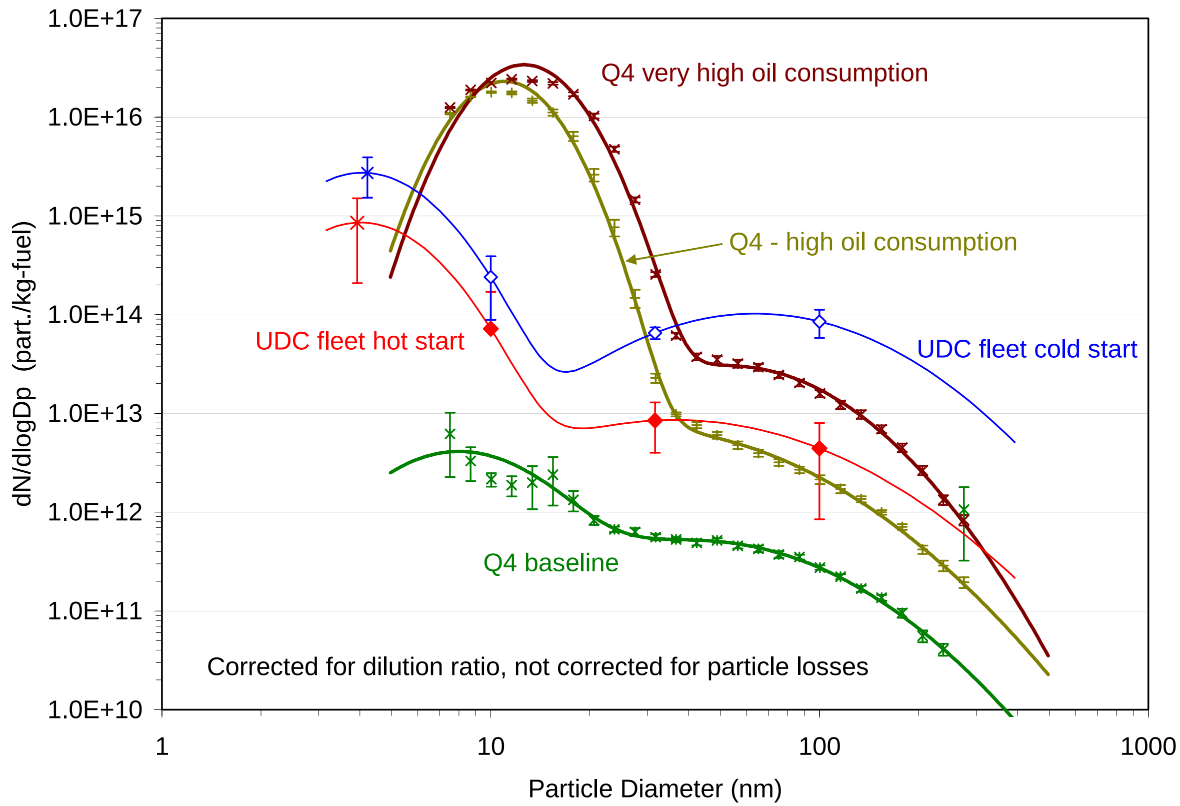
Figure 2. Brake Specific Particle Number Emissions as a Function of Power with 95% Confidence Intervals

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.

Ultrafine SI engine emissions are strongly influenced by cold starts and engine wear



Q4 - Quad 4 engine dyno tests with varied oil consumption, steady state cruise

UDC – Chassis dyno tests of small fleet on UDC cycle

Kittelson, D. B., W. F. Watts, J. P. Johnson, D. Zarling, A. Kasper, U. Baltensperger, H. Burtscher, J. J. Schauer, C. Christenson, and S. Schiller. 2003. Gasoline vehicle exhaust particle sampling study. Contract Final Report U. S. Department of Energy Cooperative Agreement DE-FC04-01AI66910.

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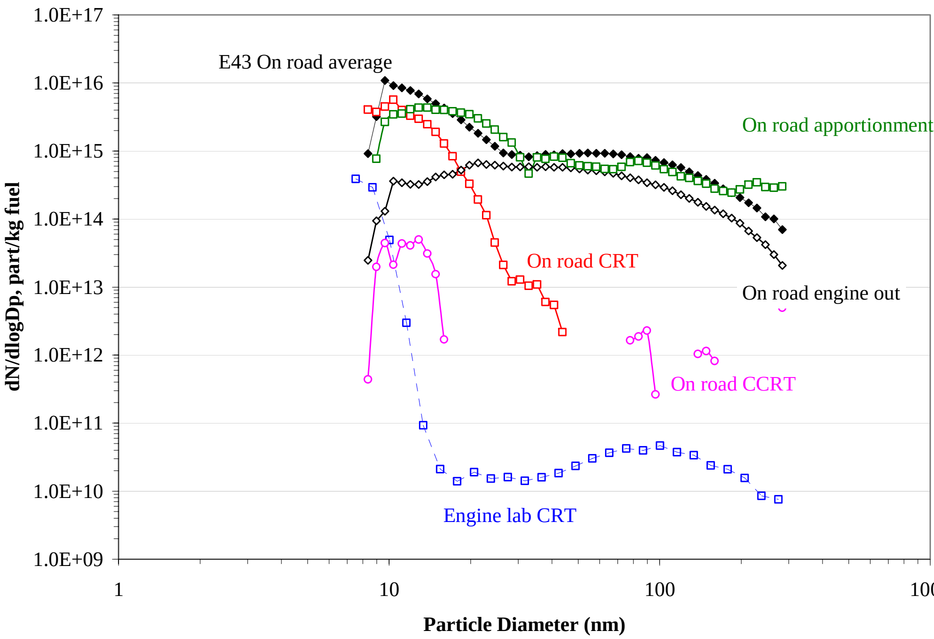
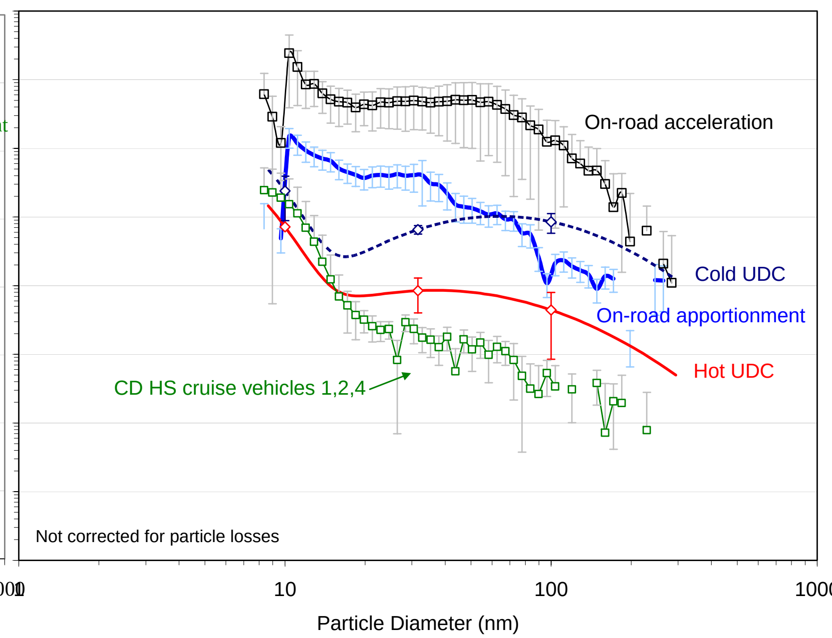
On-road and lab experiments – comparison of Diesel and gasoline SI emission





- 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.

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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

Acknowledgements

- I have had help from many collaborators
  - In the Center for Diesel Research
    - Feng Cao, Marcus Drayton, Jason Johnson, Hee Jung Jung, Duane Paulsen, Winthrop Watts, Robert Waytulonis, Qiang Wei, Darrick Zarling, Tom Jones, Jake Savstrom
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