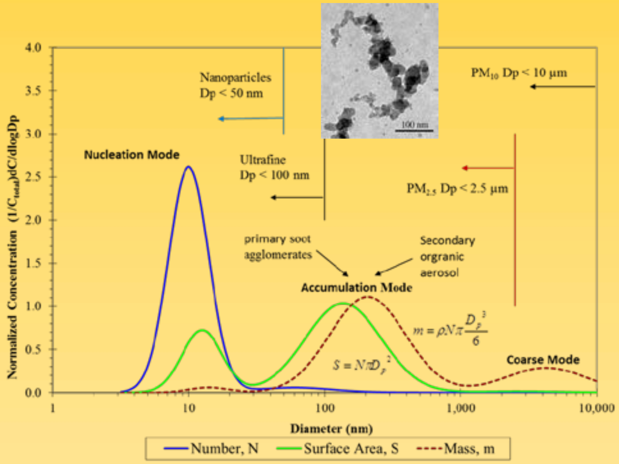
Particle Emissions of Internal Combustion Engines and Their Control

David Kittelson
TE Murphy Engine Research Laboratory
Department of Mechanical Engineering
University of Minnesota

4th International Workshop
Nanoparticle Emissions from Heavy-Duty Vehicles
Faculty of Mechanical Engineering, Technion,
Haifa, Israel
June 21, 2016



Engine-Generated Nanoparticles, Gaseous Emissions

Emissions

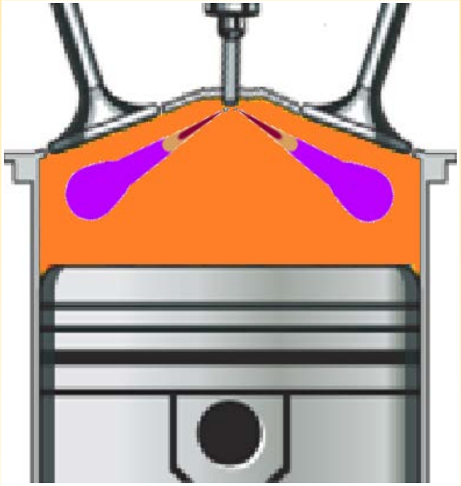
DME, Syngas, Hydrous EtOH, LPG, 2nd Gen Biofuels

Alt. Fuels

Combustion Systems

Low Temperature Combustion, Dual Fuel Modes, Reactivity Control

Energy

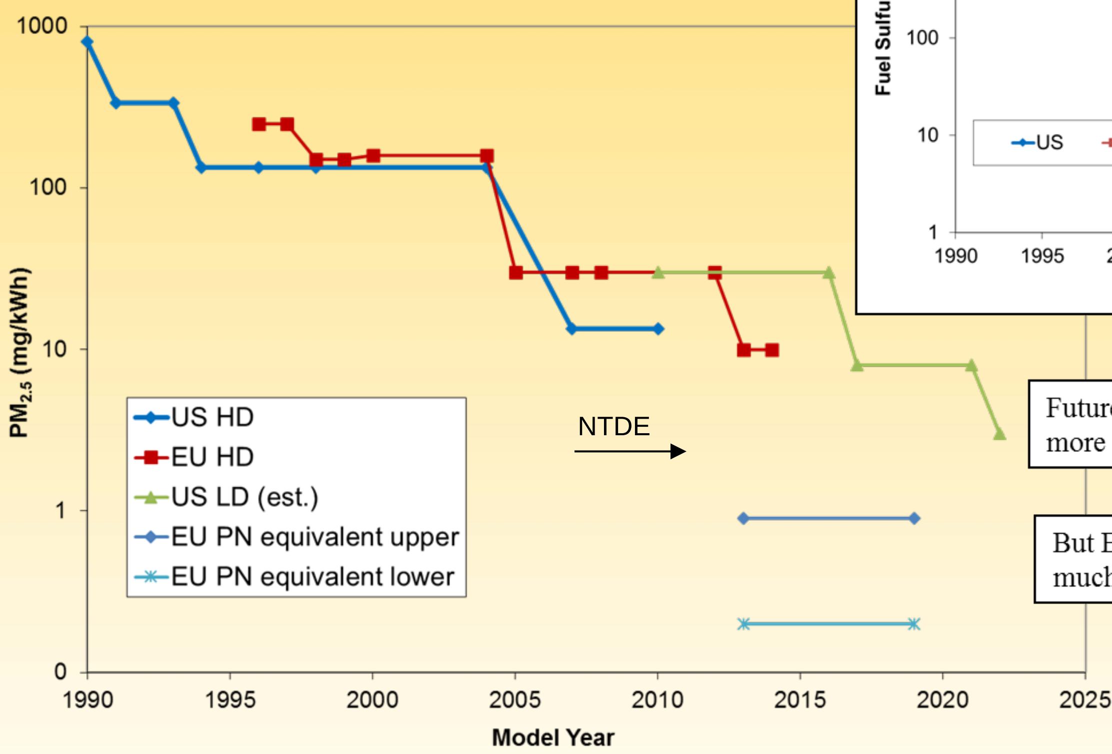


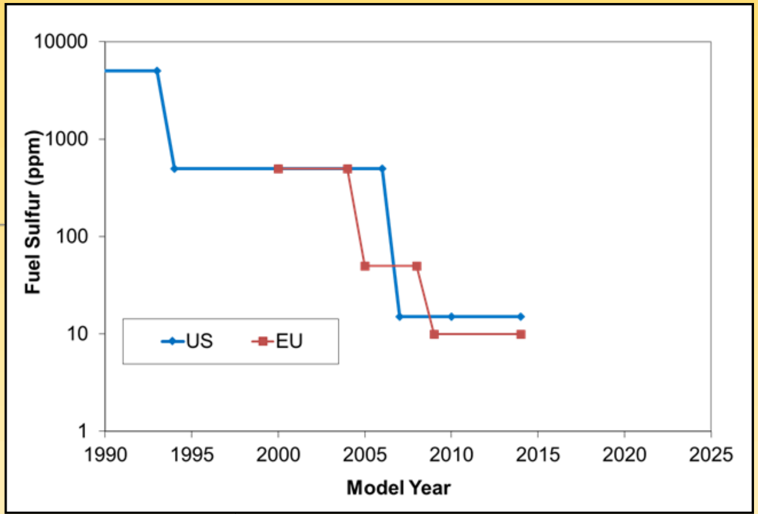
Real-world vehicle energy, CO_2 emissions and impacts

Outline

- Background
- Particle structure and size
- Diesel emission control
- NOx emissions
- Gasoline engine emissions

Dramatic reductions in PM standards have been facilitated by fuel sulfur reductions





Future LD standard 5 times more stringent than current HD

But EU PN standards are much, much more stringent

Mass and number emission standards

The EU has set a number based emission standards for light and heavy duty Diesel vehicles based on "solid" particles larger than 23 nm

- Light-duty, Euro 5b/6, September 2011/2014
  - The standard is 6×10^{11} particles/km
  - The mass emission standard is 4.5 mg/km, but the number standard corresponds to about 0.15 to 0.7 mg/km, depending on DGN – a much tighter standard!
  - An interim standard of 6×10^{12} has been set for gasoline vehicles, through 2017, after that they must meet diesel standard
  - US/CARB standards are still mass based – 2017: 1.8 mg/km, 2025: 0.6 mg/km
- Heavy-duty, Euro VI, January 2013
  - The standards are 6×10^{11} and 8×10^{11} particles/kWh on the WHTC and the WHSC, respectively
  - The mass emission standard is 10 mg/kWh, but the number standard corresponds to about 0.2 to 0.9 mg/kWh, depending on DGN – again a much tighter standard!
- Meaningful filter mass measurements are very difficult at levels corresponding to these number standards
- CARB 2025 light-duty standard of 0.6 mg/km may be difficult to measure by traditional filter sampling but corresponds to 5×10^{11} to 3×10^{12} particles/km, easily measured

Some history

Association between roadway traffic and ultrafine and nanoparticles is nothing new

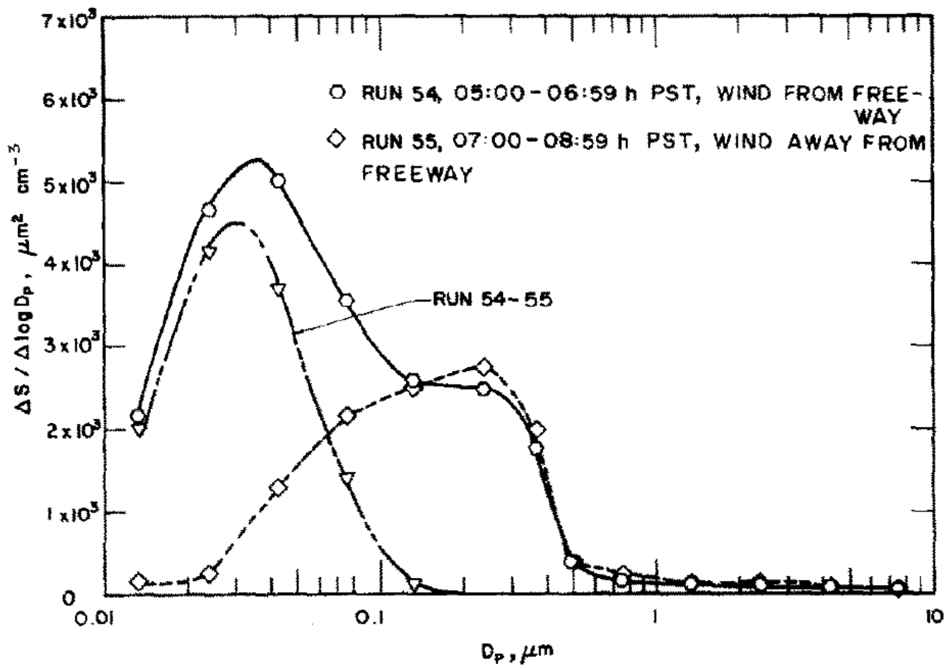


Fig. 7. Plot of the surface size distributions, $\Delta S/\Delta \log D_p$ for Run 54 when the wind was from the freeway, Run 55 when the wind was blowing toward the freeway, and the difference distribution, Run 54 minus Run 55 for D_p less than 0.15 µm.

ME Department of Mechanical Engineering

From: Characterization Of California Aerosols-i. Size Distributions Of Freeway Aerosol, K. T. Whitby, W. E. Clark.,V. A. Marple, G. M. Sverdrup, G. J. Sem, K. Willeke, B. Y. H. LIU And D. Y. H. Pui, Atmospheric Environment Vol. 9. pp. 463-482. Pergamon Press 1975.

Those old particles might not have been very healthy, mostly lead

Figure 1. 1967 Chrysler 300 test vehicle

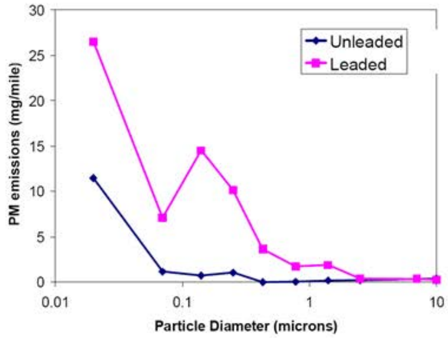


Figure 4. MOUDI PM size fractionation results

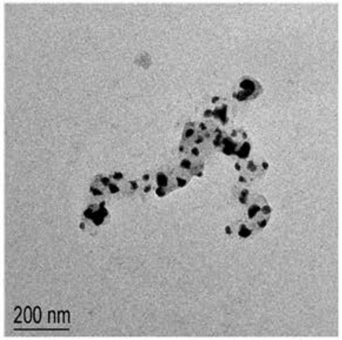


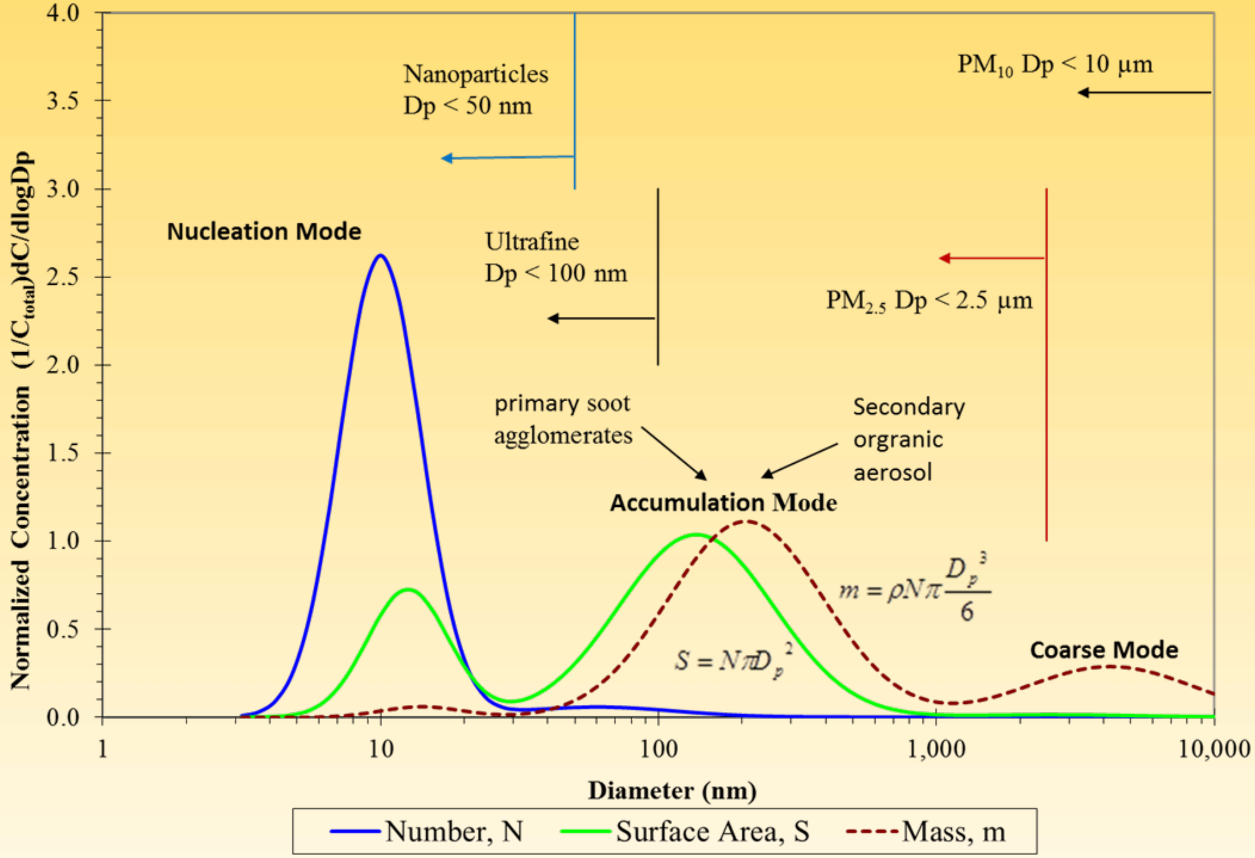
Figure 7. Micrograph of a typical particle emitted by the vehicle using leaded fuel.

Vehicle or standard	PM emission (mg/km)	Comments
Well maintained 1967 Chrysler[1]	240	Mainly lead compounds
Federal Tier 2 bin 5	6	Not usually measured for gasoline vehicles
Current well maintained gasoline[2]	<1	
Post 2000 typical gasoline[3]	<5	
EU Euro 5	4.5	Often <1 Diesel and gasoline
High emitters[2]	7 - 1700	Mainly EC, OC

[1]John M. E. Storey, C. Scott Sluder, Douglas A. Blom, Erin Higinbotham, (2000). Particulate Emissions from a Pre-Emissions Control Era Spark-Ignition Vehicle: A Historical Benchmark, SAE paper #2000-01-2213.
[2]Wei Li, (CE-CERT), Evaluation of Particulate Matter Emissions of Light-Duty Gasoline Vehicles Operating in California, Asian-American Environmental Symposium, UCLA, November 4, 2006
[3]Edward Nam, James Warila, Harvey Michaels, Carl Fulper, Richard Rykowski, and Carl Scarbro, An Analysis of the Particulate Matter Deterioration Rates from Gasoline Light Duty Vehicles Based on Kansas City and Other Studies

Particle structure and size

Engine PM found mainly in three size modes **but modes may shift** and overlap

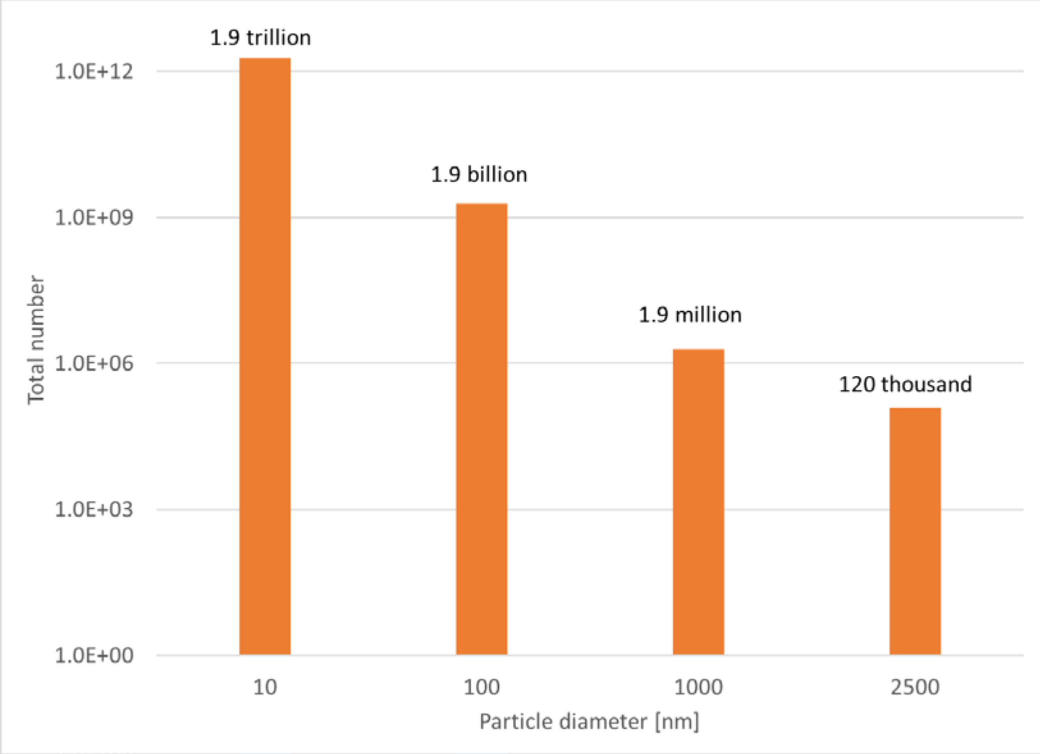


Concentration proportional to area under curve in each size range

Why do we care about size?

- Health effects
- More surface area and number per unit mass
- Behavior in atmospheric
  - Visibility
  - Residence time
  - Surface reactions
- Performance of aftertreatment devices - filters

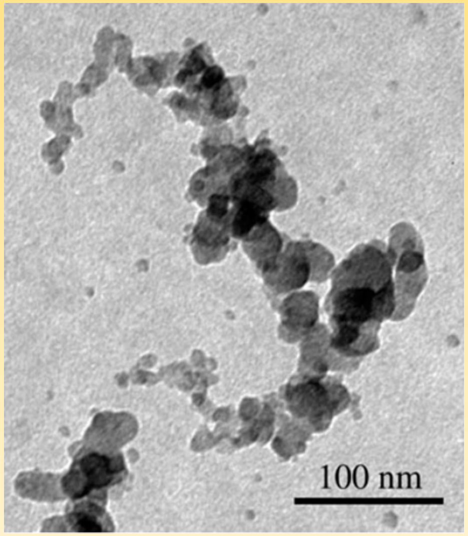
Number of particles in 1 microgram PM



Sources of particulate matter emissions from engines – primary and secondary

Primary Particles

- Particles formed in the engine itself
  - Elemental carbon
  - Lube oil ash and wear metals
  - Time scale: milliseconds to seconds
- Particles that form as the exhaust dilutes and cools in the atmosphere
  - Heavy, partially oxidized hydrocarbons from fuel and lubricating oil
  - Sulfates from sulfur in fuel and lubricating oil
  - ***Most of the nanoparticles emitted are formed in this manner***
  - Time scale: seconds to minutes
- Mechanically generated particles
  - Re-suspended soot
  - Crankcase fumes



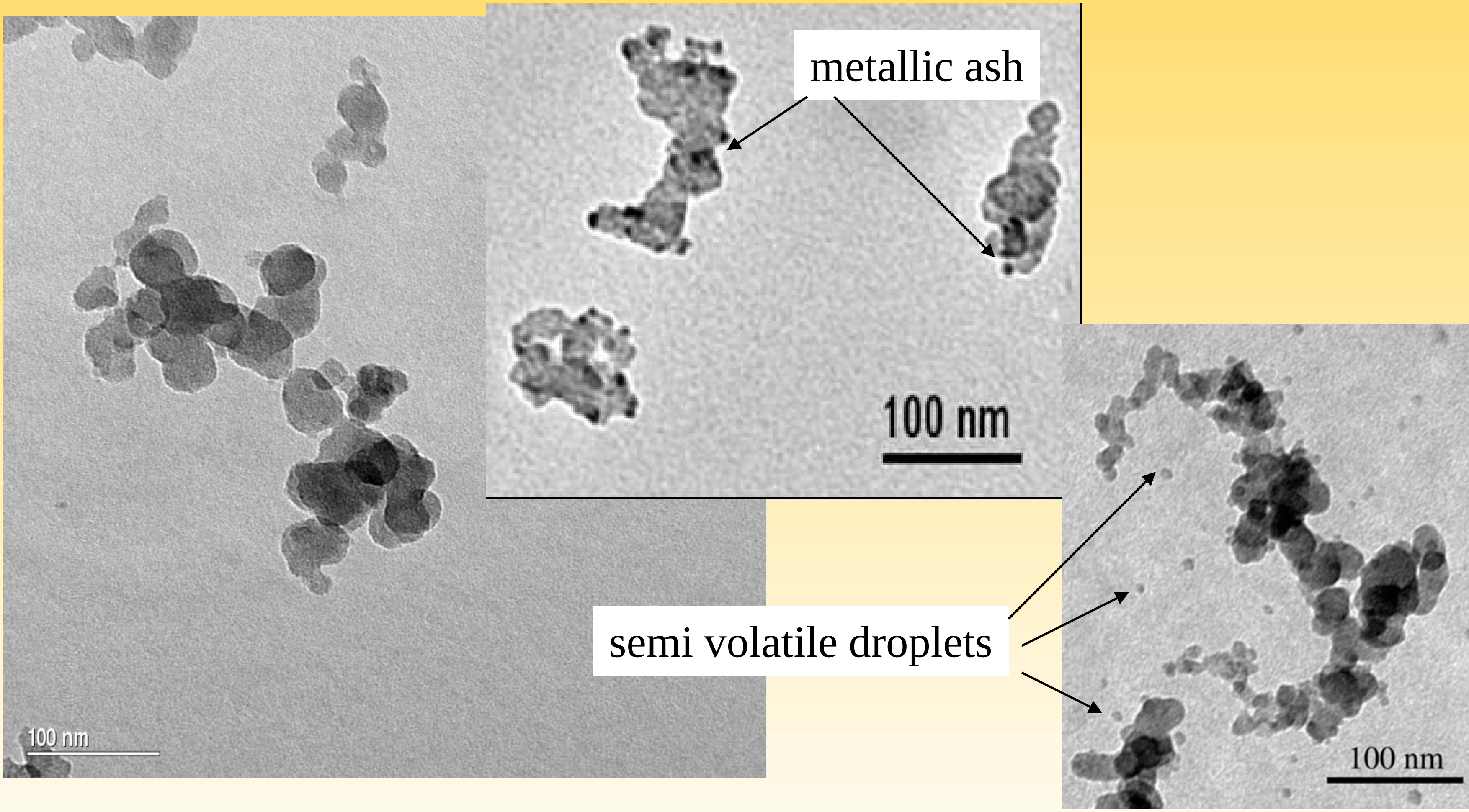
Secondary particles – not new but new concerns

- Particles that form from mainly gaseous emissions by photochemical reactions
  - Oxides of nitrogen and volatile organic carbon primary precursors
  - Secondary organic aerosol, sulfates, nitrates, haze, $PM_{2.5}$, O_3
  - Time scale: hours to days

Emissions of semi-volatile and solid nanoparticles from engines

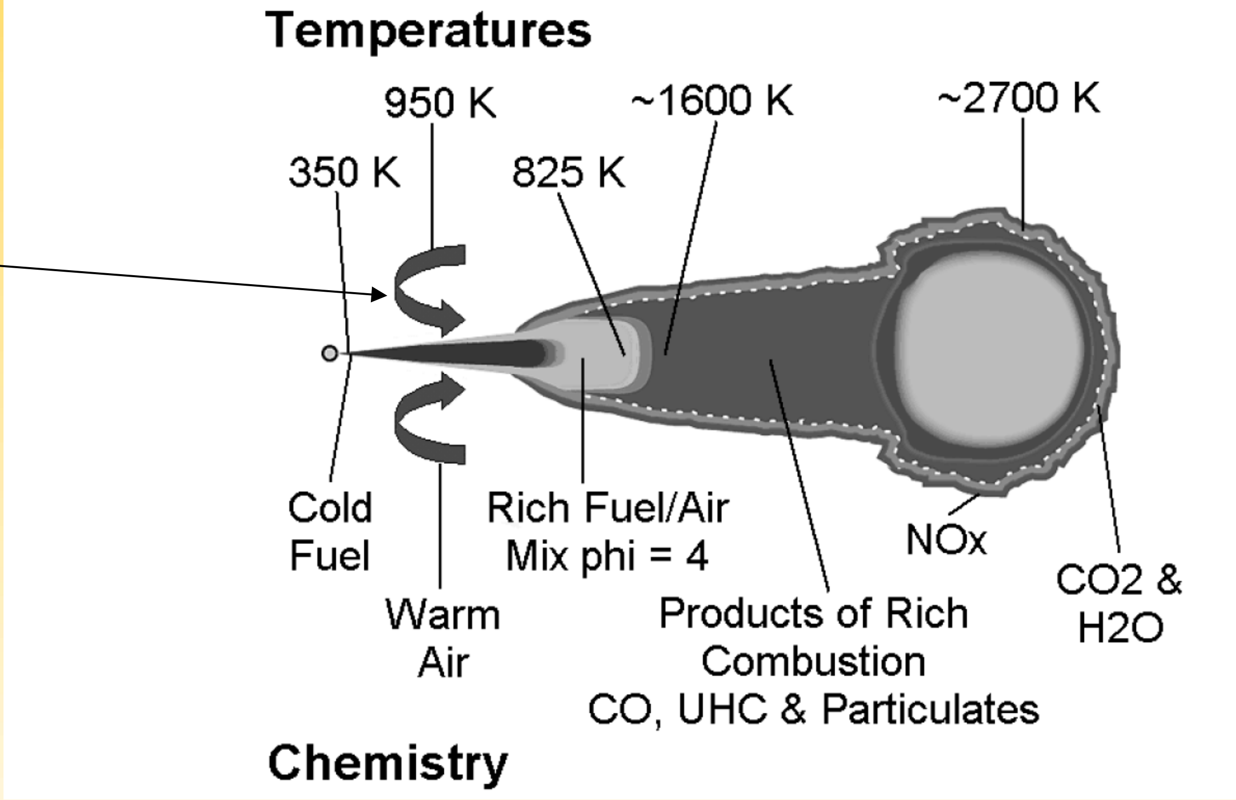
- Semi-volatile particle formation during sampling and dilution is highly nonlinear and extremely sensitive to conditions
- Semi-volatile nanoparticles consist mainly of heavy hydrocarbons and derivatives, and sulfates
  - For engines without aftertreatment, typically more than 90% of particle number and more than 30% of particle mass are formed from semi-volatile precursors during exhaust dilution.
  - Emissions from engines with catalyzed DPF systems are nearly all semi-volatile nanoparticles!
  - Emissions from SI engines
    - PFI high semi-volatile fraction (cruise)
    - GDI low semi-volatile fraction
  - Emissions from soot free combustion are nearly all semi-volatile nanoparticles
- "Solid" nanoparticles consist of carbon and ash
  - Solid nanoparticles larger than 23 nm currently regulated in EU
  - The definition of solid nanoparticles is an operational one
  - Diffusion losses are an issue for the smallest particles
  - The role of ash or carbon nucleation sites is unclear

Carbon agglomerates comprise most mass from current Diesel engines, different structures evident



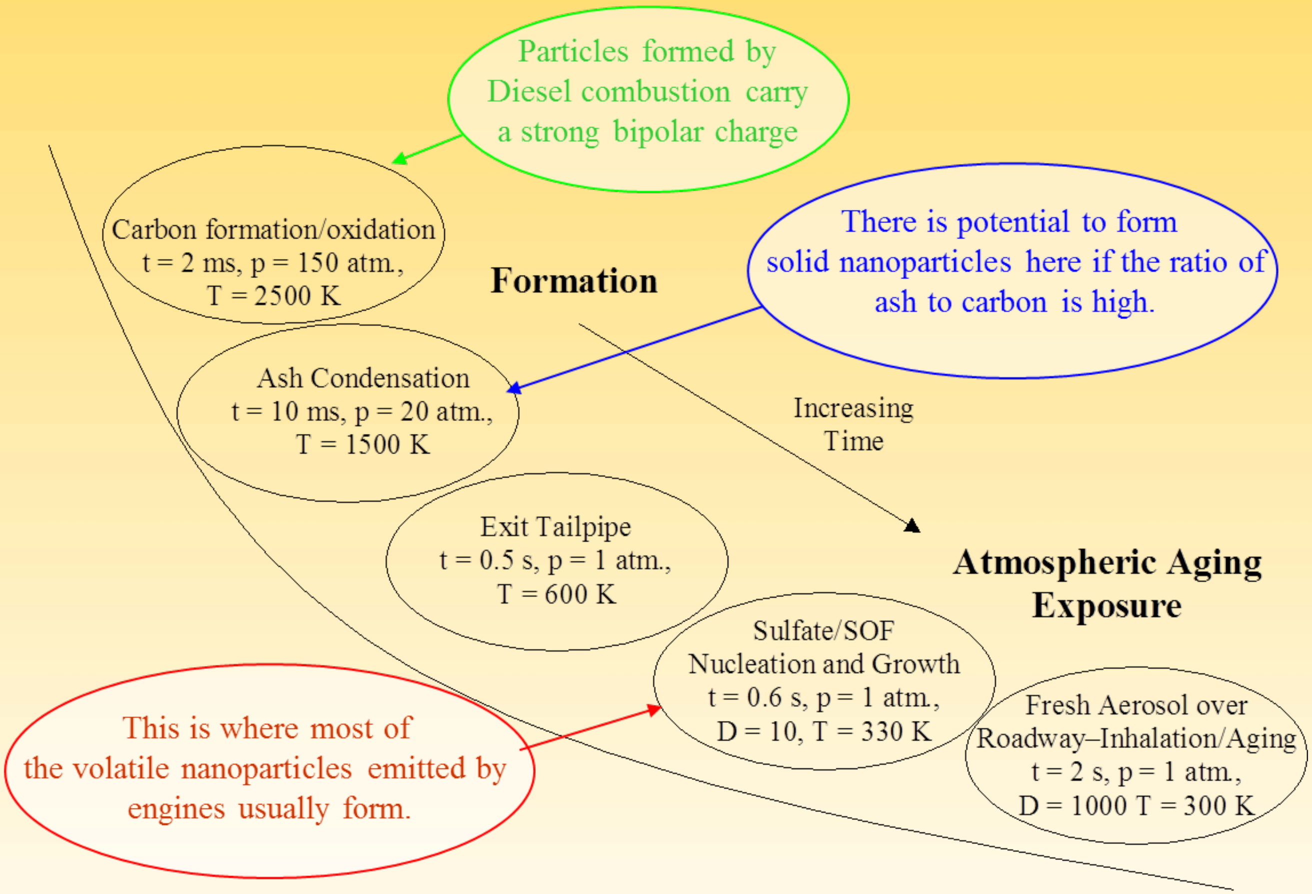
Diesel combustion – fuel jet entrains oil carrying oil and ash metals, sulfur

- The burning fuel jet entrains atomized and evaporated oil
- Oil contains metals from additives and engine wear leading to ash emissions
- Oil sulfur content much higher than in fuel, significant fraction of sulfur emissions



Patrick F. Flynn, et al. Diesel Combustion: an Integrated View Combining Laser Diagnostics, Chemical Kinetics, and Empirical Validation, SAE paper number 1999-01-0509

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

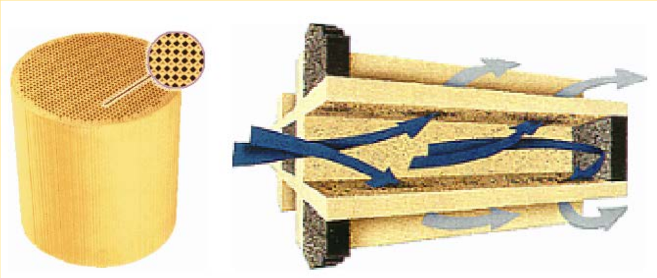


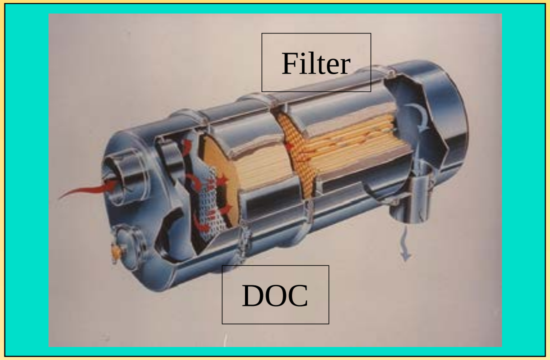
Kittelson, D. B., W. F. Watts, and J. P. Johnson 2006. “On-road and Laboratory Evaluation of Combustion Aerosols Part 1: Summary of Diesel Engine Results,” Journal of Aerosol Science 37, 913–930.

Diesel engine emission controls

- Diesel engines produce very low CO, HC, and evaporative emissions – NOx and particulate matter (PM) are the main problems
- Engine out controls – managing the mixture composition mixing history
  - Advanced fuel injection systems
  - Air management
  - Cooled EGR
- Aftertreatment
  - For PM control
    - Diesel oxidation catalyst – removes much of organic carbon fraction, also reduces CO and HC (already low)
    - Particle filters
  - For NOx control
    - SCR
    - Lean NOx trap
    - Combined systems

Filtration systems for removing particulate matter (PM) from Diesel exhaust

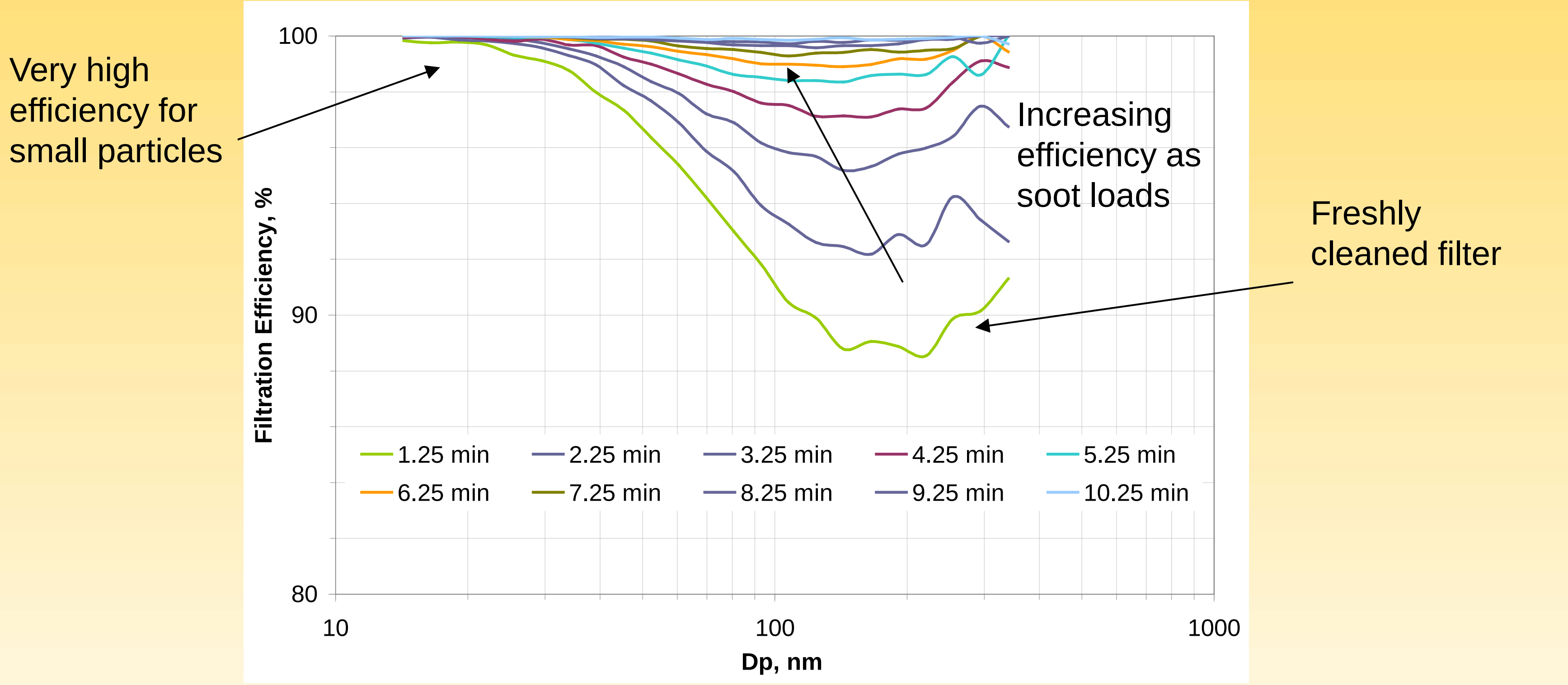




Figures courtesy Corning and Johnson-Matthey

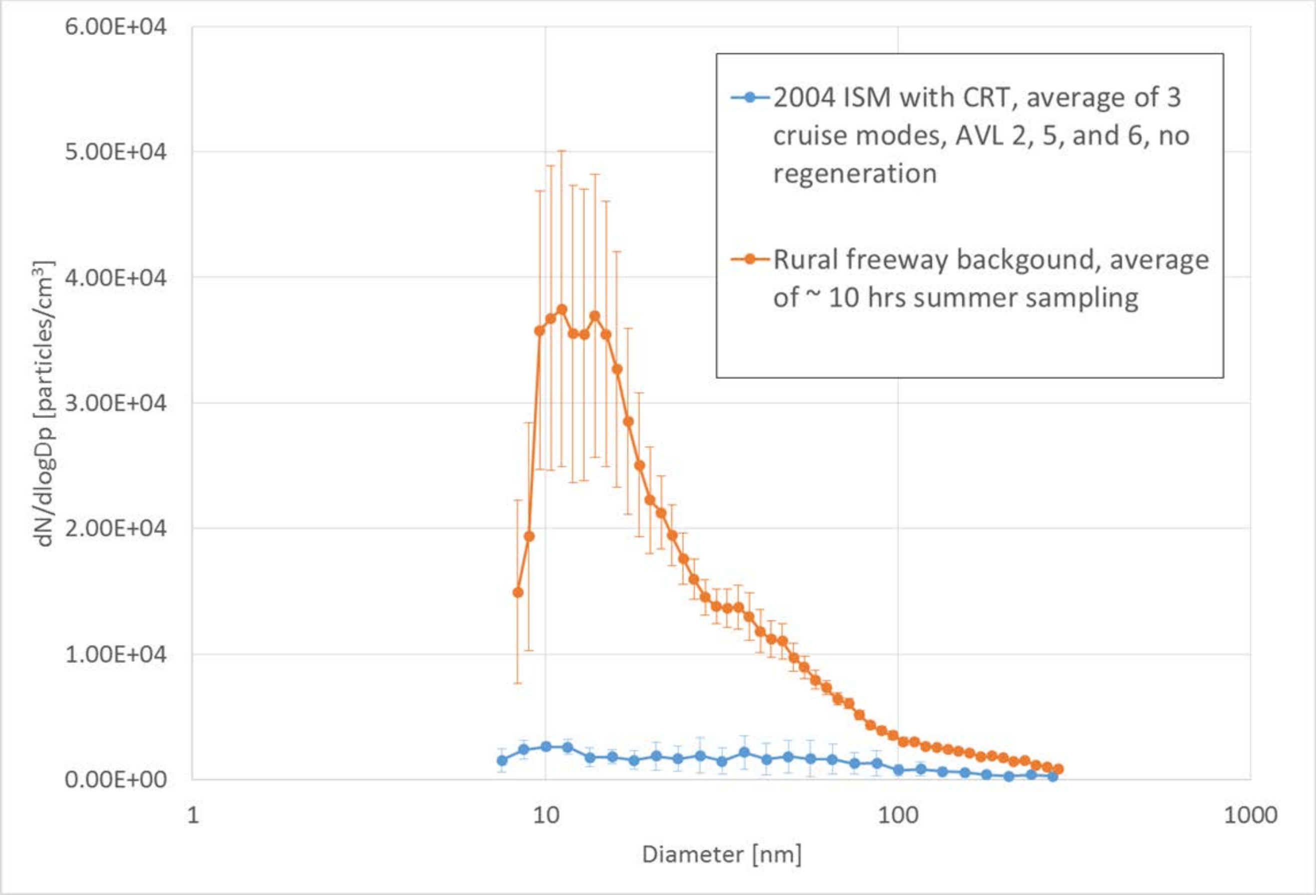
- Most filters are wall flow type shown
- Without regeneration to oxidize soot these devices quickly plug.
- Regeneration schemes
  - Passive - catalyzed systems like the J-M CRT® shown on the right reduce regeneration temperature by producing NO_2 from exhaust NO in an oxidizing catalyst (DOC) upstream of filter
    - NO_2 emissions a concern
    - The catalyst also converts SO_2 to SO_3 at higher temperatures
  - Active – fuel injected ahead of the DOC
  - Fuel borne catalyst may be used to assist regeneration, less active DOC, less NO_2
  - Offline – remove and bake or heat electrically

DPF are very efficient, aided by soot layer.

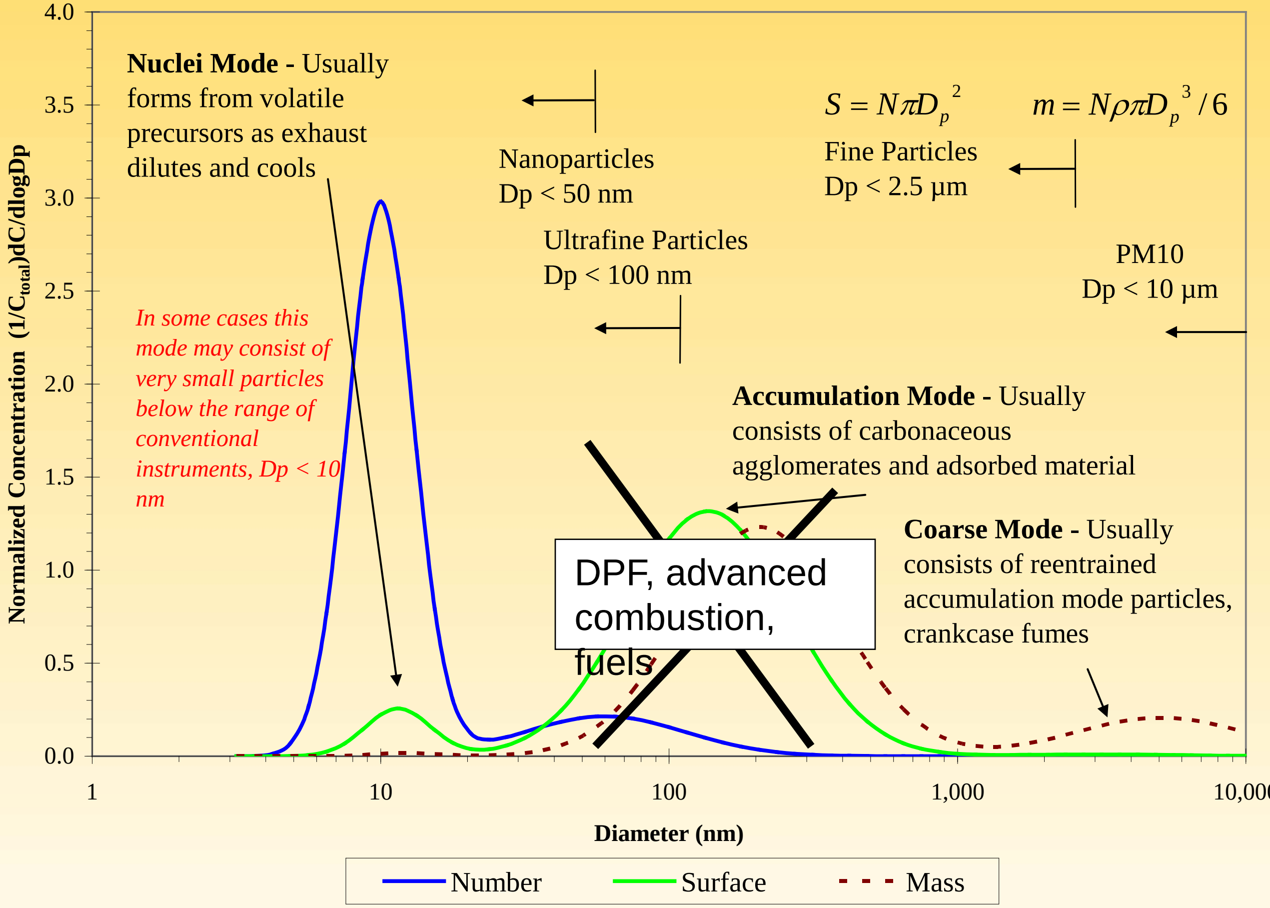


Swanson, J. J.; W. F.; Watts, W. F.; Kittelson, D. B.; Newman, R. A.; Ziebarth, R. R. Filtration efficiency and pressure drop of miniature diesel particulate filters. Aerosol Science and Technology. 2013, 47, 452–461.

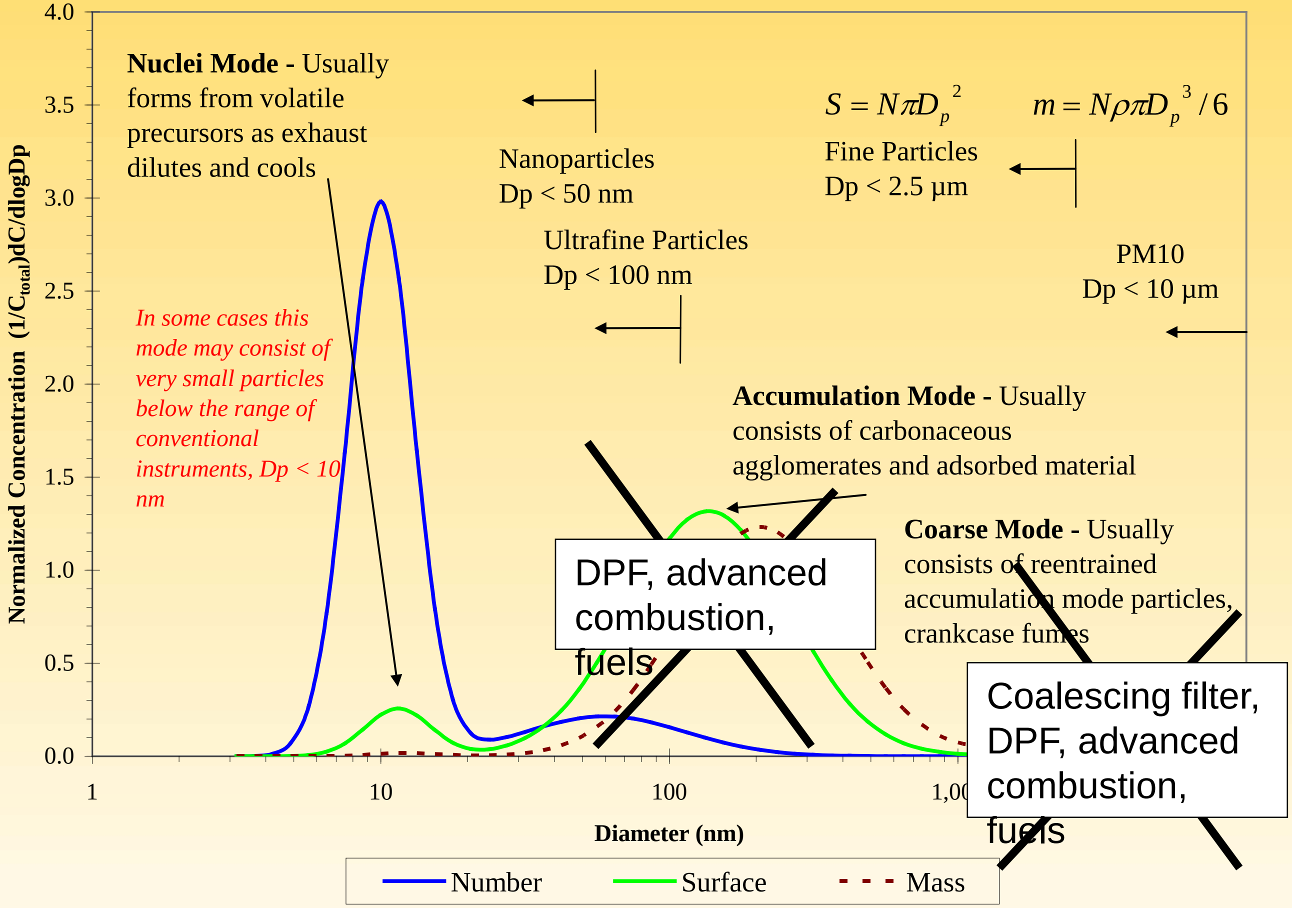
Engines with modern particle filters may be air cleaners, exhaust cleaner than rural background



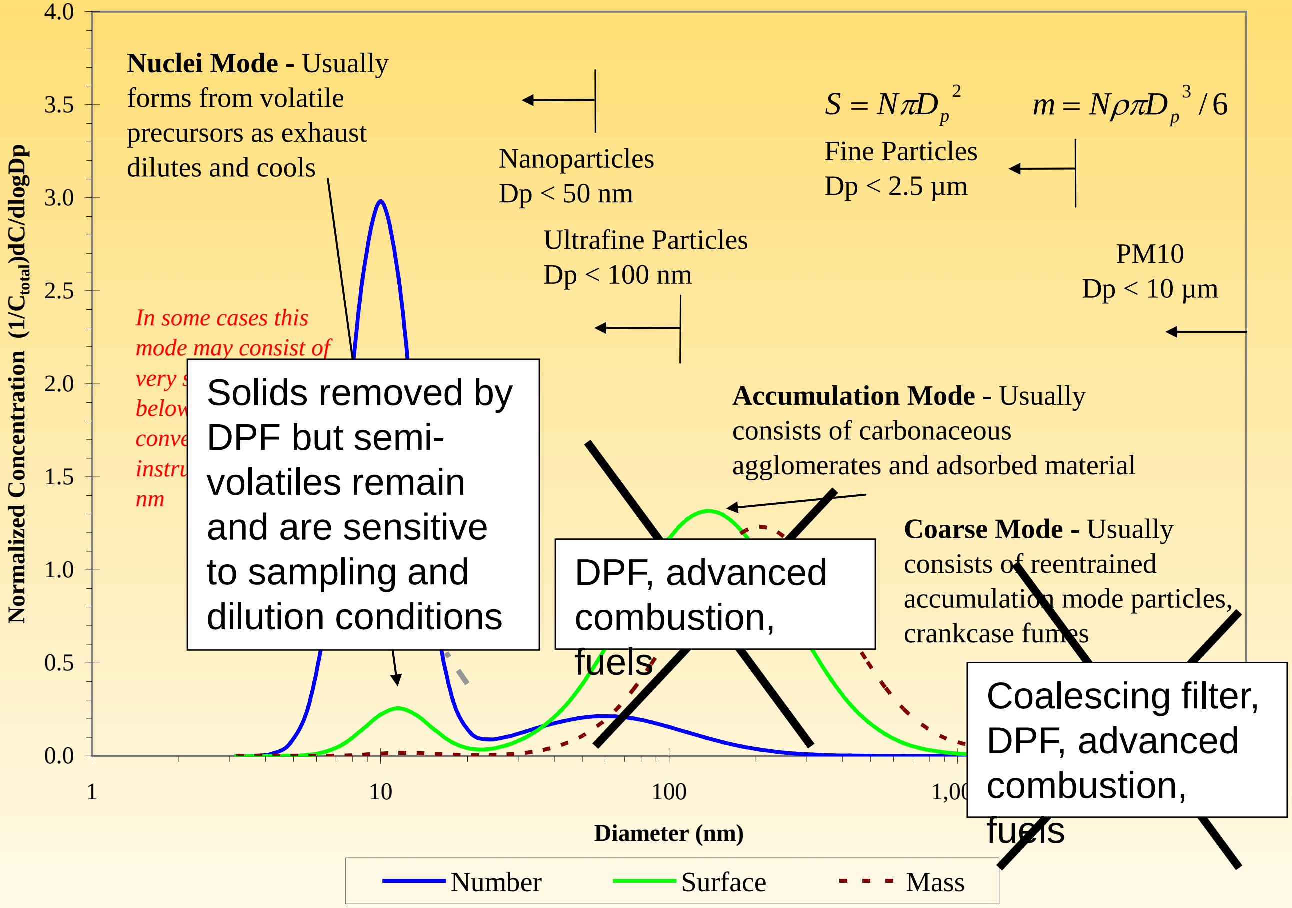
Diesel emission control – influence on size modes. Soot nearly eliminated by DPF, LTC, or low soot fuels



Diesel emission control – Coarse PM nearly eliminated by closed crankcase, coalescing filter



Diesel emission control – DPF eliminates solid nucleation mode but some semi-volatiles remain



Health concerns about diesel exhaust – who is right?

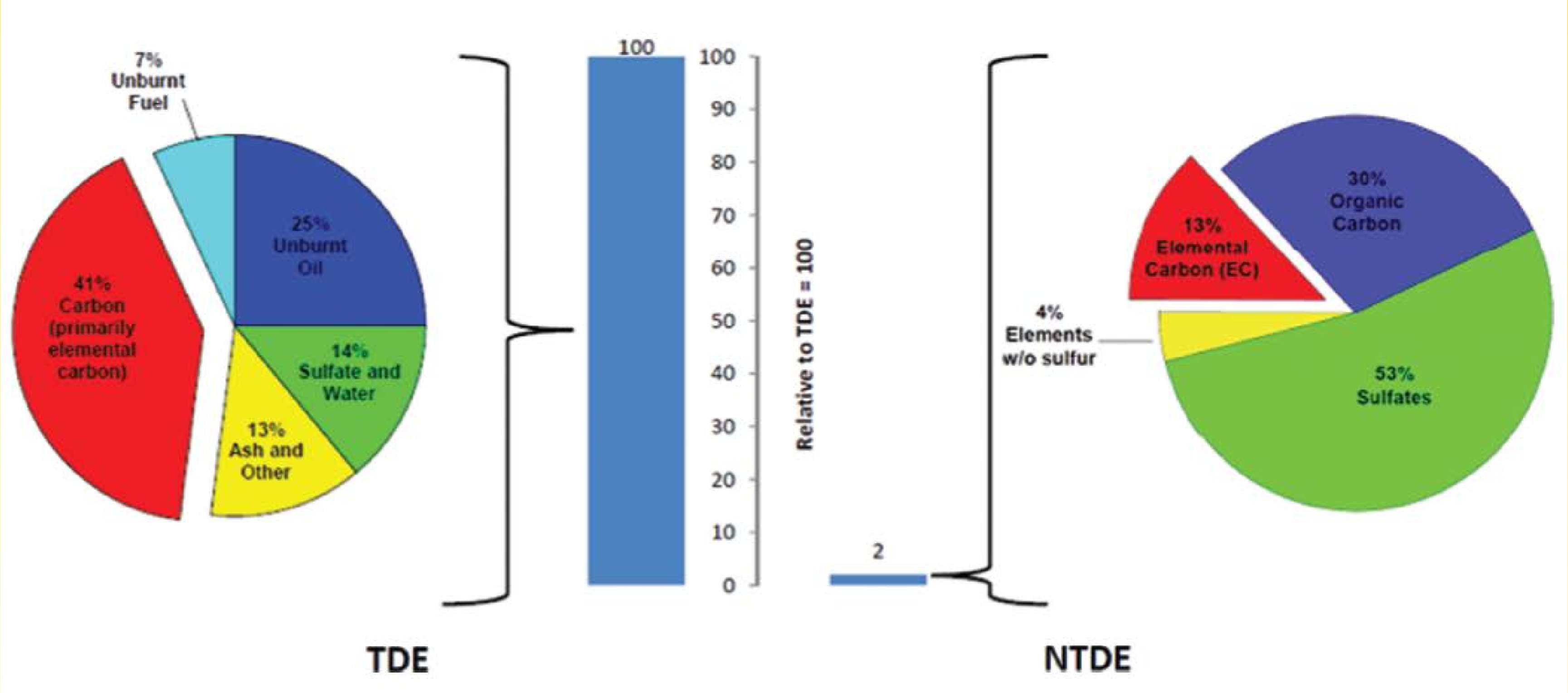
Lyon, France, June 12, 2012

After a week long meeting of international experts, the International Agency for Research on Cancer (IA RC), which is part of the World Health Organization (WHO), today classified **diesel engine exhaust as carcinogenic to humans** (Group1), based on sufficient evidence that exposure is associated with an increased risk for lung cancer.

Boston, April 12, 2012

STUDY FINDS FEW HEALTH EFFECTS FROM NEW TECHNOLOGY DIESEL ENGINES: The first results of the most comprehensive study ever undertaken of the health effects of exposure to **new technology diesel engines** has found **no evidence of gene damaging effects** in the animals studied, and only a few mild effects on the lungs, according to a report issued today by the Health Effects Institute (HEI) 1 . The study – the Advanced Collaborative Engine Study (ACES) – is exposing rats and mice for 16 hours a day to emissions from a heavy duty diesel engine meeting stringent 2007 US EPA standards that reduce emissions of fine particles and other pollutants by over 90% from levels emitted by older engines.

The IARC work based on tests old TDE, very different from modern NTDE used by ACES



Traditional Diesel Emissions New Technology Diesel Emissions

Hesterberg, Thomas W.; Long, Christopher M.; Sax, Sonja N.; Lapin, Charles A.; Mcclellan, Roger O.; Bunn, William B.; Valberg, Peter A., 2011. Particulate matter in new technology diesel exhaust (NTDE) is quantitatively and qualitatively very different from that found in traditional diesel exhaust (TDE), Journal of the Air and Waste Management Association, v 61, n 9, p 894-913.

Diesel PM emission control, traditional combustion

- Engine with DPFs
  - US post 2010 heavy-duty engines rely heavily on passive regeneration, little CO2 penalty
  - Proposed 10x reduction in NOx standard would require tuning for lower engine out NOx and higher PM – more active regeneration and associated CO2 penalty
  - Ash accumulation
    - Lube oil and wear metals
    - Fuel borne catalyst (light-duty)
  - Sulfur storage and release
    - Engines relying on passive regeneration may store a large fraction of the sulfur compounds associated with combustion of fuel and lube oil sulfur[1]
    - Release may occur under high load conditions leading to emission hotspots[2]

[1] CRC Report: ACES Phase 2, Phase 2 of the Advanced Collaborative Emissions Study, November 2013

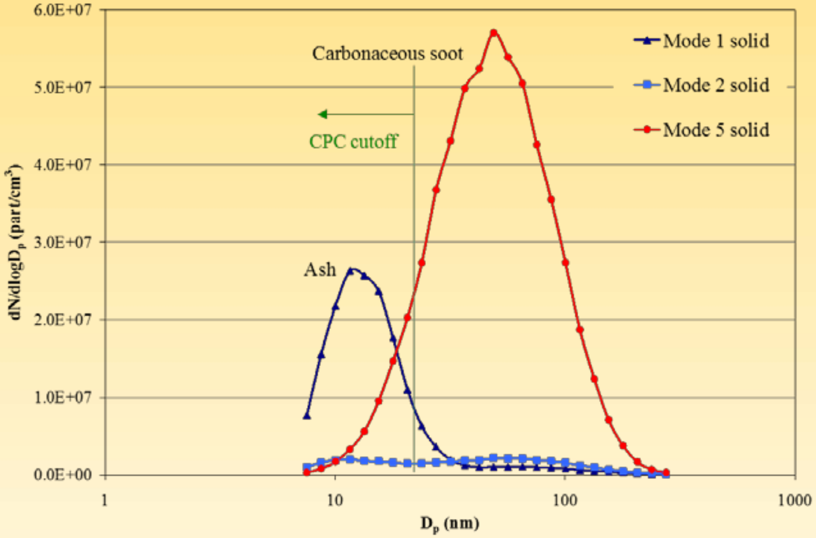
[2] Swanson, J. J., D. B. Kittelson, W. F. Watts, D. D. Gladis, and M. V. Twigg, 2009. Influence of Storage and Release on Particle Emissions from New and Used CRTs, Atmospheric Environment, Volume 43, Issue 26, August 2009, Pages 3998-4004.

Diesel PM emission control, traditional combustion

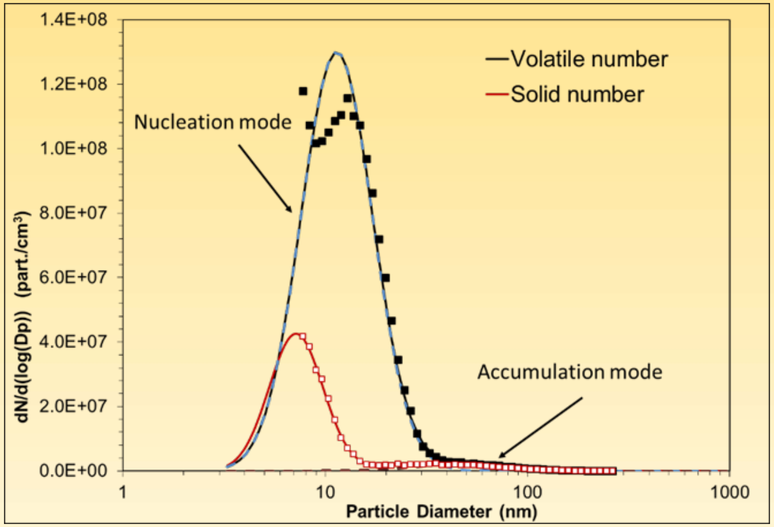
- Engines without DPFs
  - Some engines are meeting Tier 4 off-road standards with SCR only and no DPF
  - Ash emissions in nucleation mode
  - Would not meet EU number emission standard
  - Emission signature unlike NTDE

Low soot concentration ash may form solid nucleation mode

On-road HD engine 2004 MY



Off- road Tier 4 engine



Engines with emissions similar to this are being certified (off-road) without DPF, wouldn't pass number standard

Lucachick, Glenn, Aaron Avenido, Winthrop Watts, David Kittelson, and William Northrop, 2014. Efficacy of In-Cylinder Control of Particulate Emissions to Meet Current and Future Regulatory Standards, SAE paper number 2014-01-1597.

NOx emissions from buses in real-world operation

Diesel NO_x aftertreatment

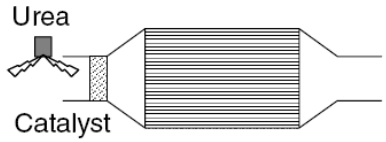
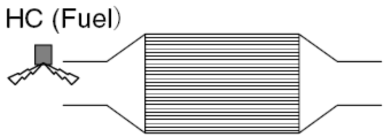
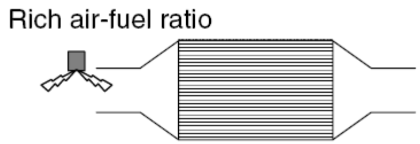
	System configuration	Issues
Urea-SCR	 $4NO + 4NH_3 + O_2 \rightarrow 4N_2 + 6H_2O$ $6NO_2 + 8NH_3 \rightarrow 7N_2 + 12H_2O$ $4NH_3 + 2NO + 2NO_2 \rightarrow 4N_2 + 6H_2O$	· Establishment of new infrastructure · Equipping · Freezing of urea-water
HC-SCR	 $4NO + C_3H_8 + 2O_2$ $\rightarrow 2N_2 + 3CO_2 + 4H_2O$	· Restricted temperature range where high NO_x reduction efficiency can be achieved
NO_x Storage-reduction	 Lean: $NO + 1/2O_2 + MO \rightarrow MNO_3$ Rich: $MNO_3 + 2CO \rightarrow MO + 2CO_2 + 1/2N_2$ $MNO_3 + 2H_2 \rightarrow MO + 2H_2O + 1/2N_2$ $9/2MNO_3 + C_3H_6$ $\rightarrow 3CO_2 + 3H_2O + 9/2MO + 9/4N_2$	· NO_x reduction efficiency at low temperatures · Technology ensuring rich mixture · Fuel penalty

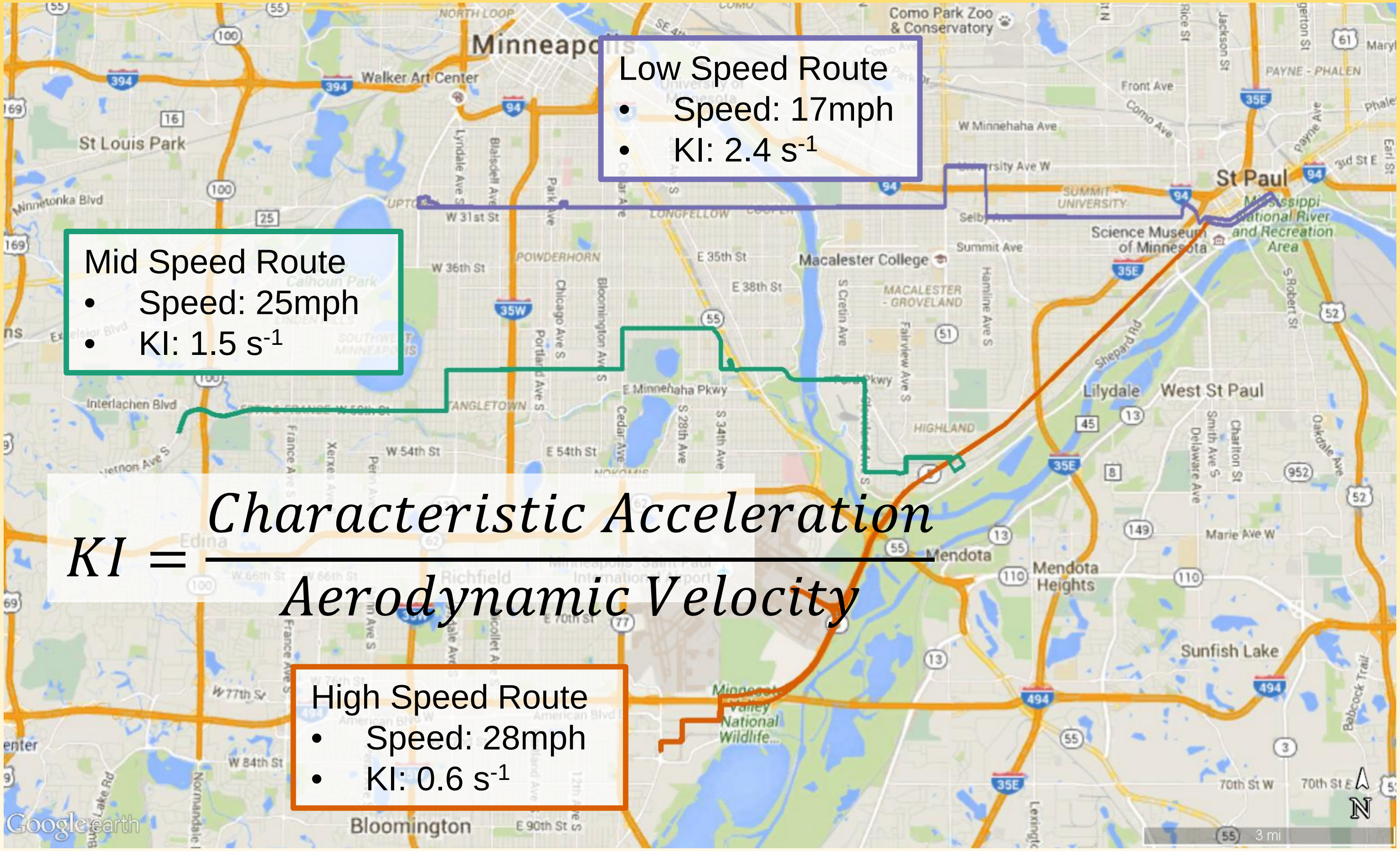
Figure 1 Conventional NO_x reduction technology[1], [2], [3]

From: "Study on Low NOx Emission Control Using Newly Developed Lean NOx Catalyst for Diesel Engines," Tomoko Morita, Norio Suzuki, Naohiro Satoh, Katsuji Wada and Hiroshi Ohno, SAE paper 2007-01-0239

Test buses

	2013 MY 1503 - Standard Diesel	2013 MY 7290 - Series Hybrid	2013 MY 7327 - Parallel Hybrid	2015 MY 1713 - Standard Diesel
Bus Manufacturer Layout	GILLIG Low Floor	New Flyer Xcelsior™	GILLIG Hybrid	GILLIG Low Floor
Engine	Cummins ISL 8.9L	Cummins ISB 6.7L	Cummins ISB 6.7L	Cummins ISL 8.9L
Transmission	ZF-Ecolife™	BAE HybriDrive™	Allison Electric Drives™	ZF-Ecolife™
Emissions	2013 Certified SCR and DPF			2015 Certified SCR and DPF
AC Compressor	Thermoking Belt Driven	Thermoking 3-Phase Electric	Thermoking Belt Driven	Thermoking Belt Driven
Power Steering	Mechanical Engine Coupled	230VAC 3-Phase Electric	Mechanical Engine Coupled	Mechanical Engine Coupled
Engine Fans	EMP - 28VDC Electric 8 or 9 Fan			
Air Compressor	Mechanical Engine Coupled	230VAC 3-Phase Electric	Mechanical Engine Coupled	Mechanical Engine Coupled

Test routes selected – normal passenger service



Low Speed Route

- Speed: 17mph
- KI: 2.4 s^{-1}

Mid Speed Route

- Speed: 25mph
- KI: 1.5 s^{-1}

$$KI = \frac{Characteristic\ Acceleration}{Aerodynamic\ Velocity}$$

High Speed Route

- Speed: 28mph
- KI: 0.6 s^{-1}

Test Matrix – wide range of conditions

	2013-14 test program testing 1503, 7290, 7337: conventional, series hybrid , parallel hybrid				2015-16 test program testing 1503 and 1713	
	Summer 13	**Winter 14**	**Spring 14**	**Summer 14**	**Summer 15**	**Winter 16**
Min. Temperature	58 ºF	-17 ºF	39 ºF	42 ºF	58 ºF	6 ºF
Max. Temperature	90 ºF	38 ºF	78 ºF	91 ºF	90 ºF	46 ºF
Avg. Temperature	71 ºF	10 ºF	56 ºF	71 ºF	77 ºF	26 ºF
Good Test Days	9	19	13	16	9	9
Start Date	8/5/2013	1/13/2014	5/5/2014	7/14/2014	8/9/2015	2/8/2016
End Date	8/20/2013	2/13/2014	5/20/2014	8/14/2014	9/5/2015	2/20/2016

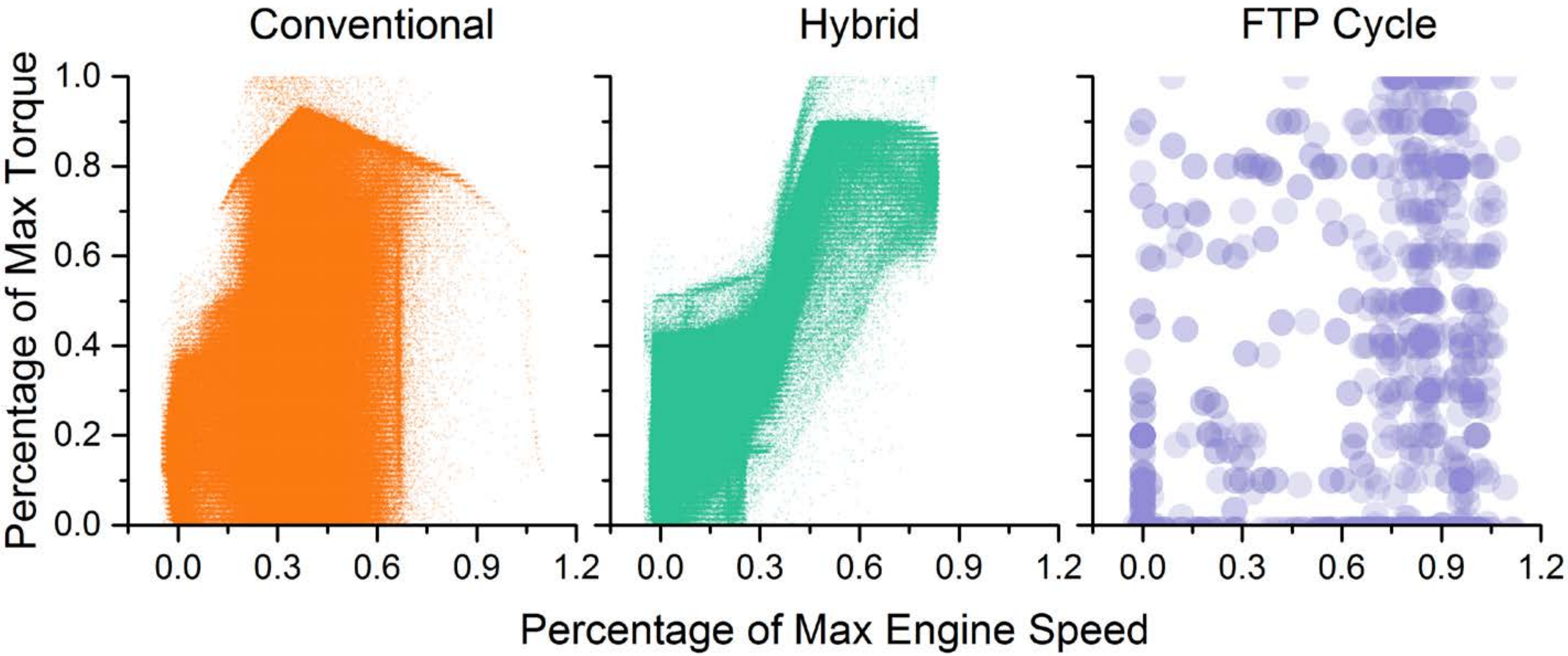
Very low real-world NO_X emissions from 2013 retro and 2015 buses

- New study operation over 10 days:
  - 2013 MY – 258 Hours
  - 2015 MY – 260 Hours
  - $1.8*10^6$ Data Entries

MY	Bus #	Type	Test Year	Model Year	gNO_X/kW-hr	SCR Conversion
2013	7290	Hybrid	2014	2013 ISB 6.7L	0.852	77.9%
2013	1503	Conventional	2014	2013 ISL 8.9L	1.360	79.6%
2013	1503	Conventional	Summer 15	2013 ISL 8.9L	1.053	80.0%
2015	1713	Conventional	Summer 15	2015 ISL 8.9L	**0.208**	92.7%
2013 Retro	1503	Conventional	Winter 16	2013 ISL 8.9L	**0.258**	93.4%
2015	1713	Conventional	Winter 16	2013 ISL 8.9L	**0.418**	91.8%
				2010 FTP NO_X Standard =	*0.267 g/kW-hr*	
				2010 NTE NO_X Standard =	*0.401 g/kW-hr*	

Real-world operating conditions compared to FTP

FTP certification cycle far from bus operating conditions



*Kotz, A. J.; Kittelson, D. B.; Northrop, W. F. Lagrangian Hotspots of In-Use NOx Emissions from Transit Buses. Environ. Sci. Technol. **2016** DOI: 10.1021/acs.est.6b00550.*

Particle Emissions from Gasoline Spark Ignition Engines (SI)

- Why do gasoline engines produce less PM that diesel? Simply stated combustion is much more premixed
- Two major classes of gasoline SI engines
  - Port fuel injection, PFI
    - Until recently the most common design
    - Stoichiometric operation, 3-way catalyst
    - Low particle emissions except during cold start and high load
    - Small, semi-volatile particles under cruise conditions
  - Gasoline direct injection GDI, DISI
    - Better fuel economy than PFI
    - Mainly stoichiometric operation, 3-way catalyst
    - Particle emissions intermediate between PFI and Diesel
    - Low semi-volatile fraction
    - Lean burn, better fuel economy but higher PM and PN emissions
    - Likely to need filters to meet PN

Particles from PFI engines highest for cold start, hard acceleration, fuel rich

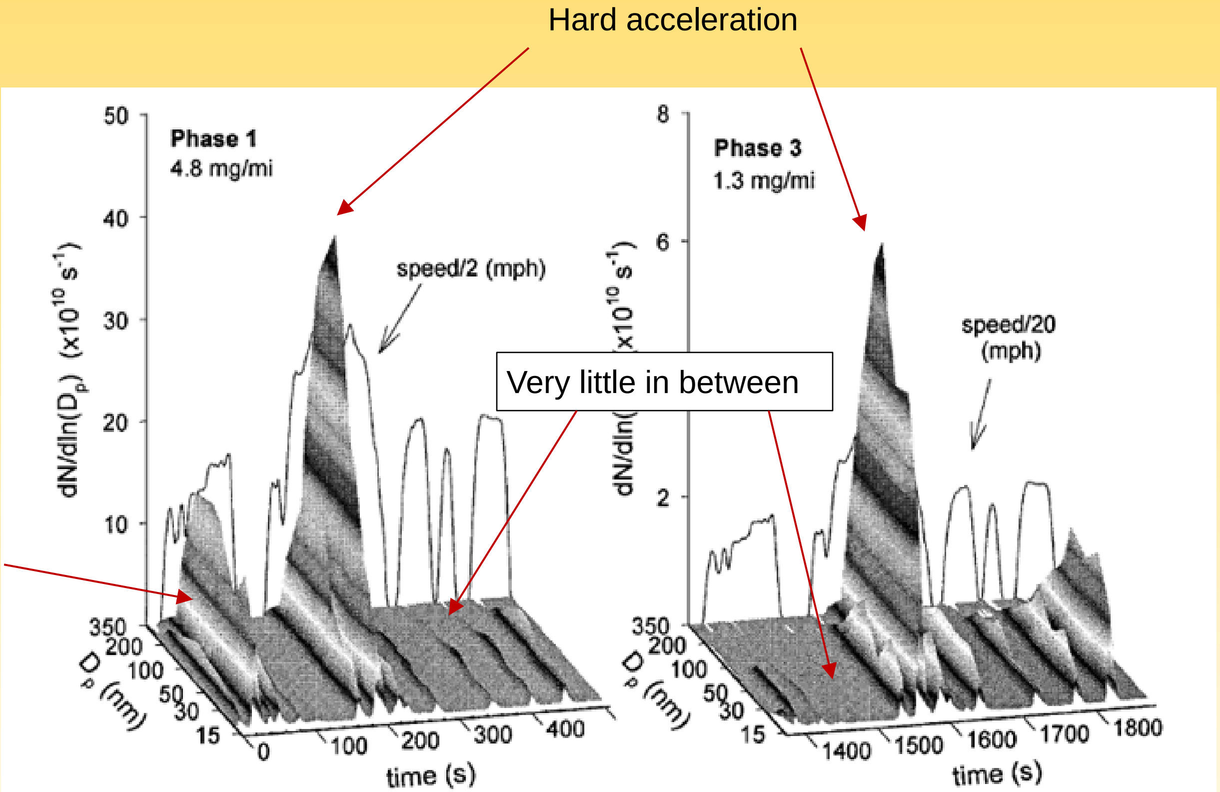


FIGURE 3. Comparison of size-resolved particle emissions from a gasoline light-duty truck (T5) during the cold start (phase 1) versus the hot start (phase 3) of the FTP. Note the change in vertical scale from phase 1 to phase 3. Vehicle speed is shown by the traces along the rear walls of the plots.

Highest numbers from GDI also cold start, high load but doesn't drop off as much in between

Cold start and run

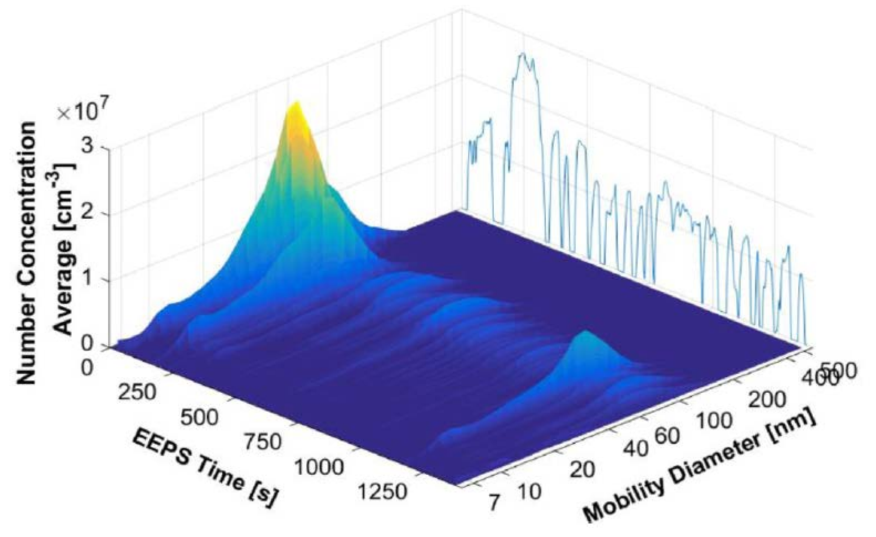


Figure 2. The PSD for phases 1 and 2 of the FTP cycle. The drive trace is included for visual reference.

Warm start

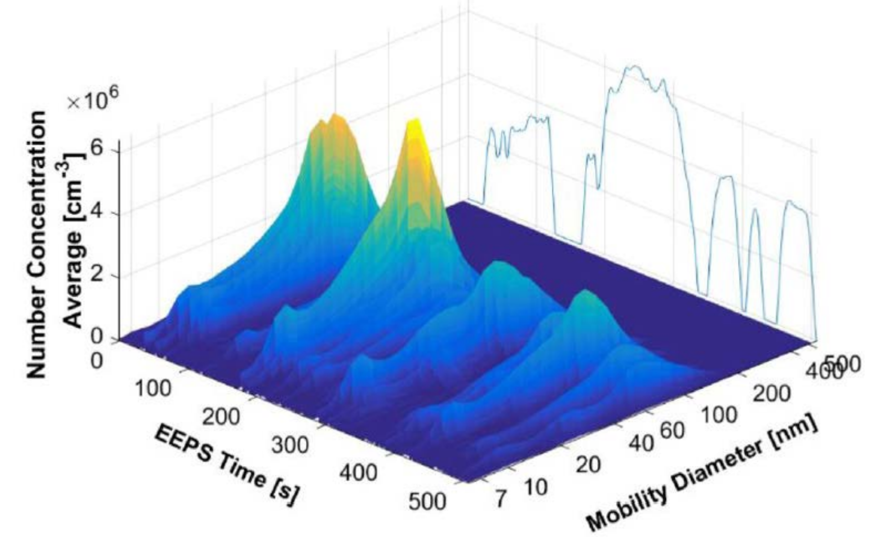
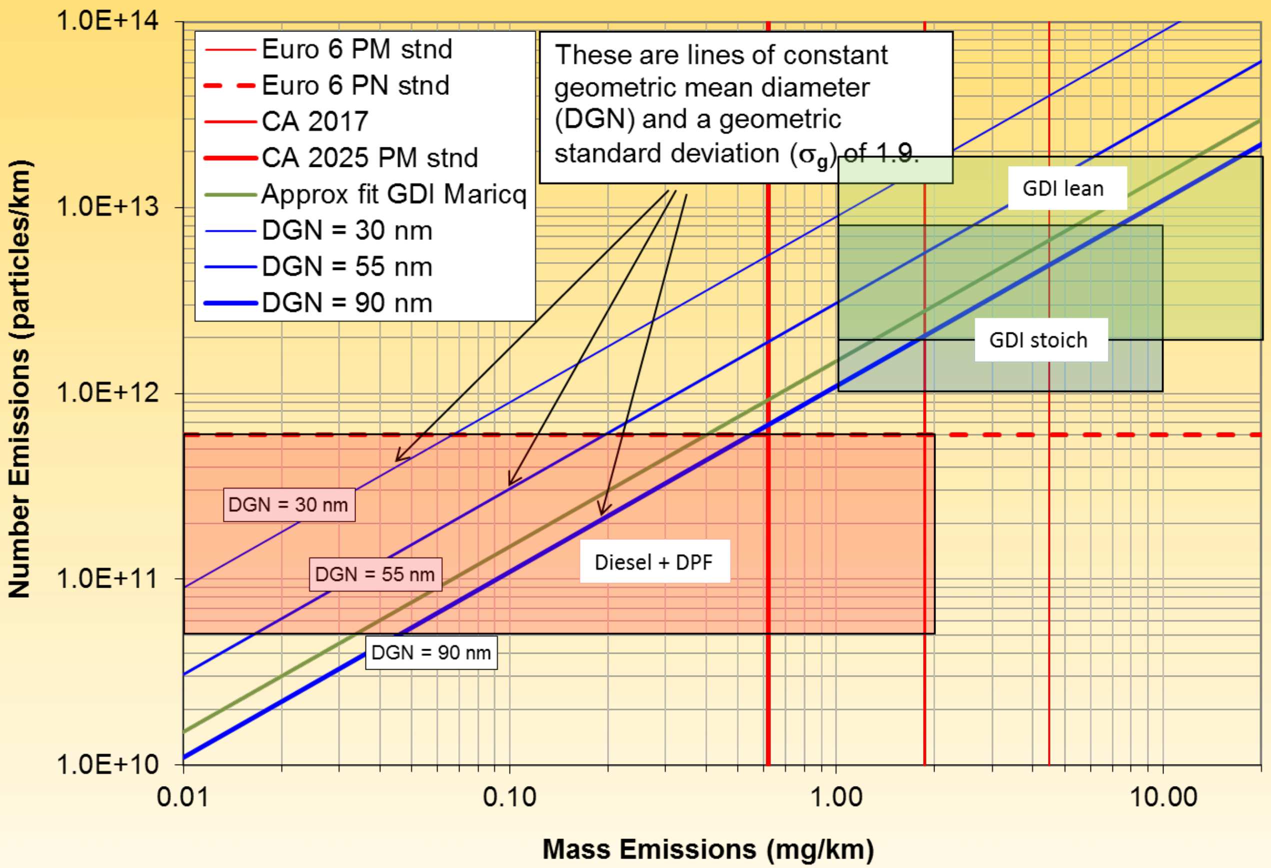


Figure 3. The PSD for phase 3 of the FTP cycle. The drive trace is included for visual reference.

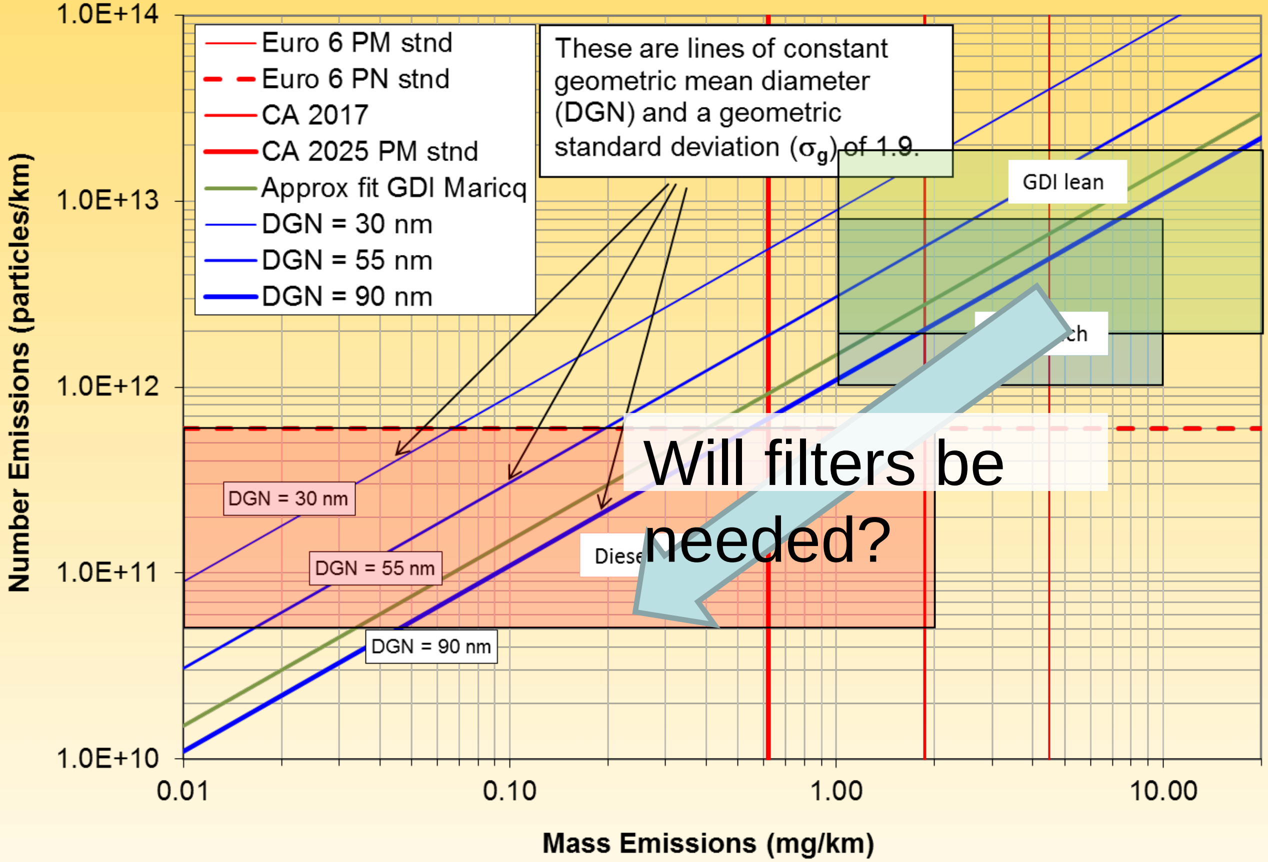
Koczak, J., Boehman, A., and Brusstar, M., "Particulate Emissions in GDI Vehicle Transients: An Examination of FTP, HWFET, and US06 Measurements," SAE Technical Paper 2016-01-0992, 2016, doi:10.4271/2016-01-0992.

Passenger car particle standards, mass, number, size



Trend line based on Maricq, 2010, shaded areas based on data from Giechaskiel, et al., 2012

Passenger car particle standards, mass, number, size



Trend line based on Maricq, 2010, shaded areas based on data from Giechaskiel, et al., 2012

Thank you, questions?