

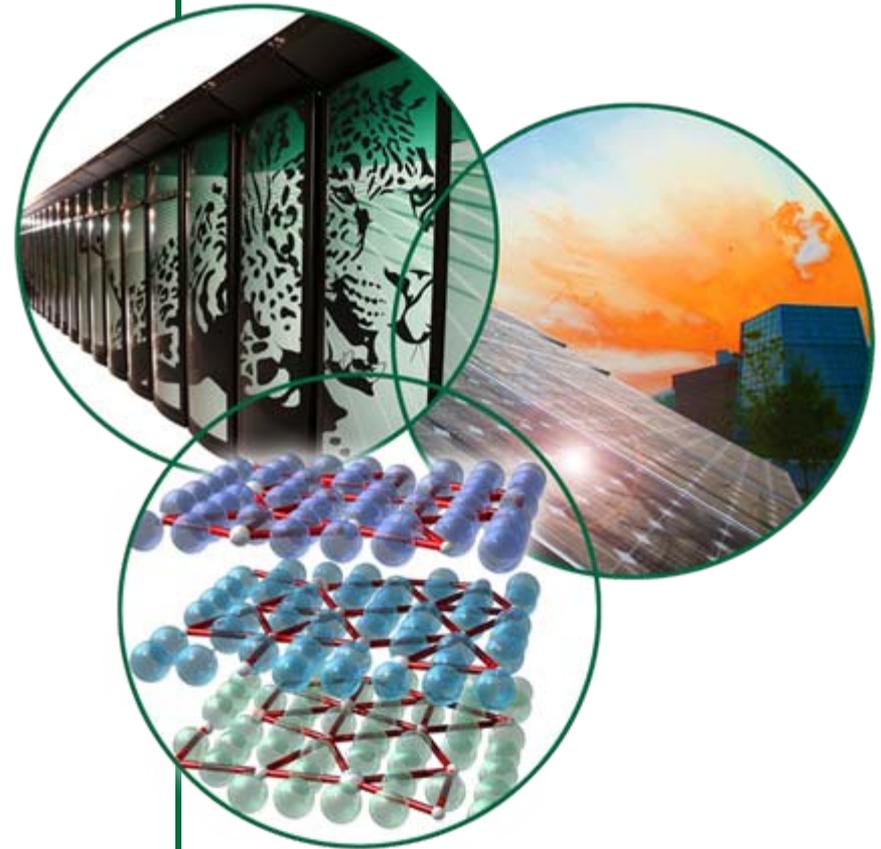
An Analysis of DISI Particle Morphology

Teresa Barone, John Storey,
Jim Szybist, Adam Youngquist

Fuels, Engines, and Emissions
Research Center

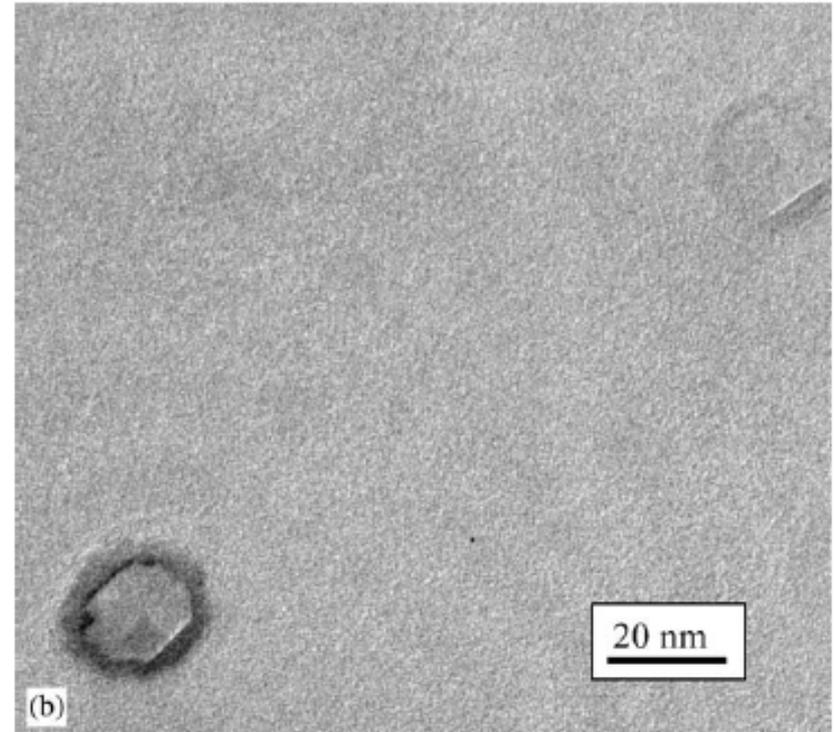
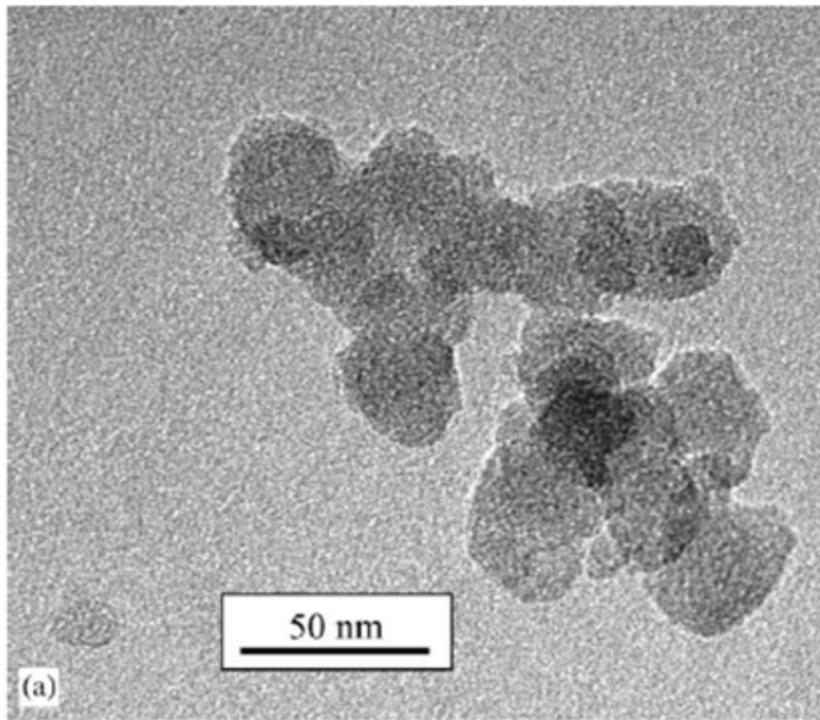
Acknowledgement
Dr. James Eberhardt, U.S. DOE, VT

May 1, 2012



DISI Vehicle Particle Emissions

DISI particle number concentration emissions greater than that for PFI and CI-DPF vehicles (Mathis et al., 2005)

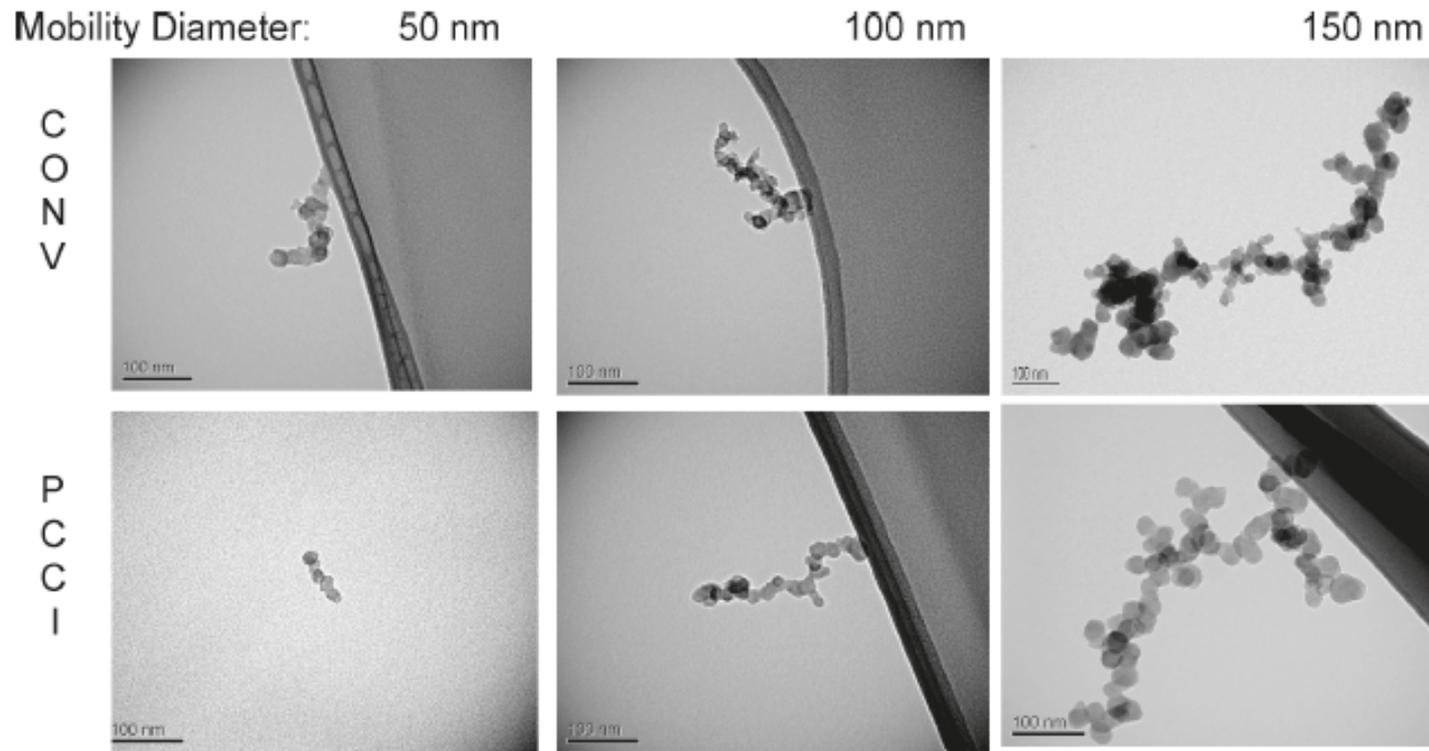


Soot and volatile nanoparticles present in DISI exhaust (Mathis et al., 2004)

Background: Conventional Diesel & PCCI

- Primary particle diameter range: 20 – 25 nm

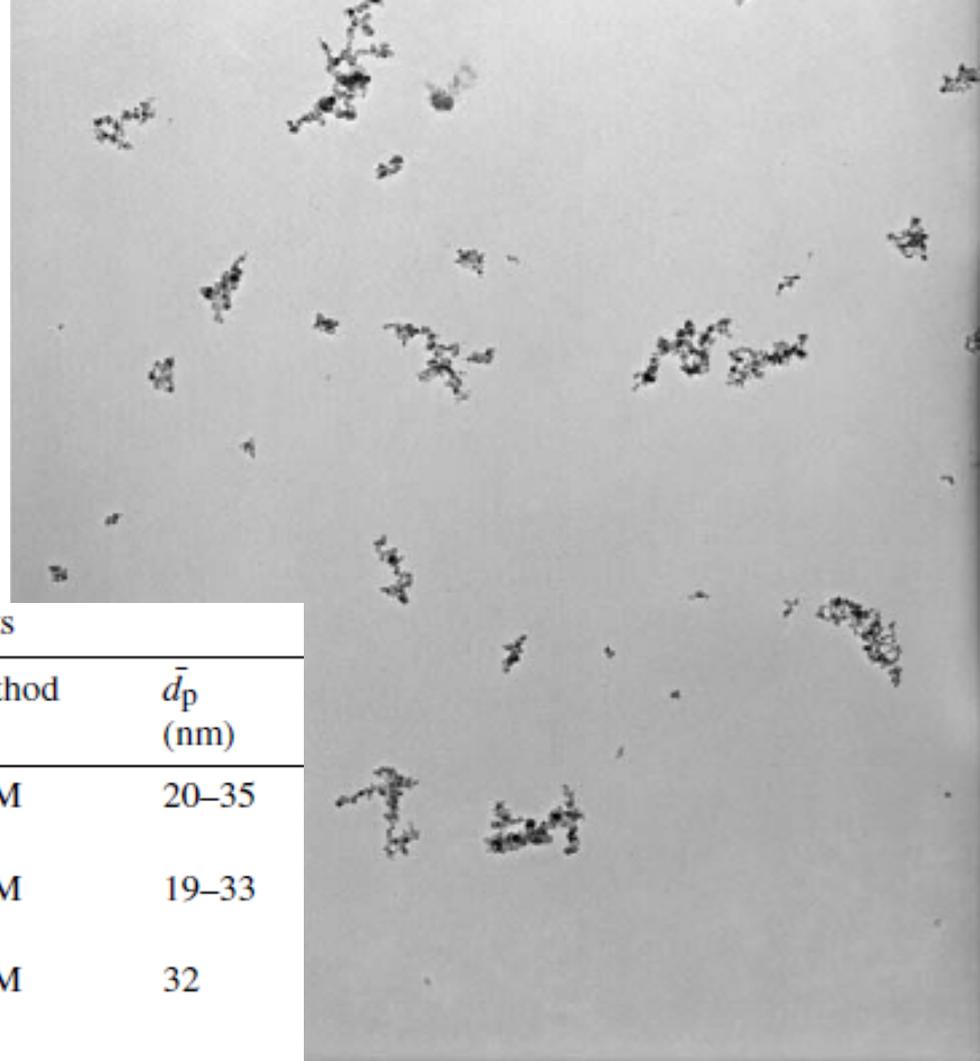
mode	mobility diameter (nm)	d_{PP} (nm)
conventional	50	24 ± 3
	100	22 ± 4
	150	25 ± 4
PCCI	50	23 ± 4
	100	20 ± 2
	150	21 ± 3



Energy & Fuels
Barone et al. (2011)

1500 rpm, 2.6 bar

Comparison of Conventional Diesel Particle Studies



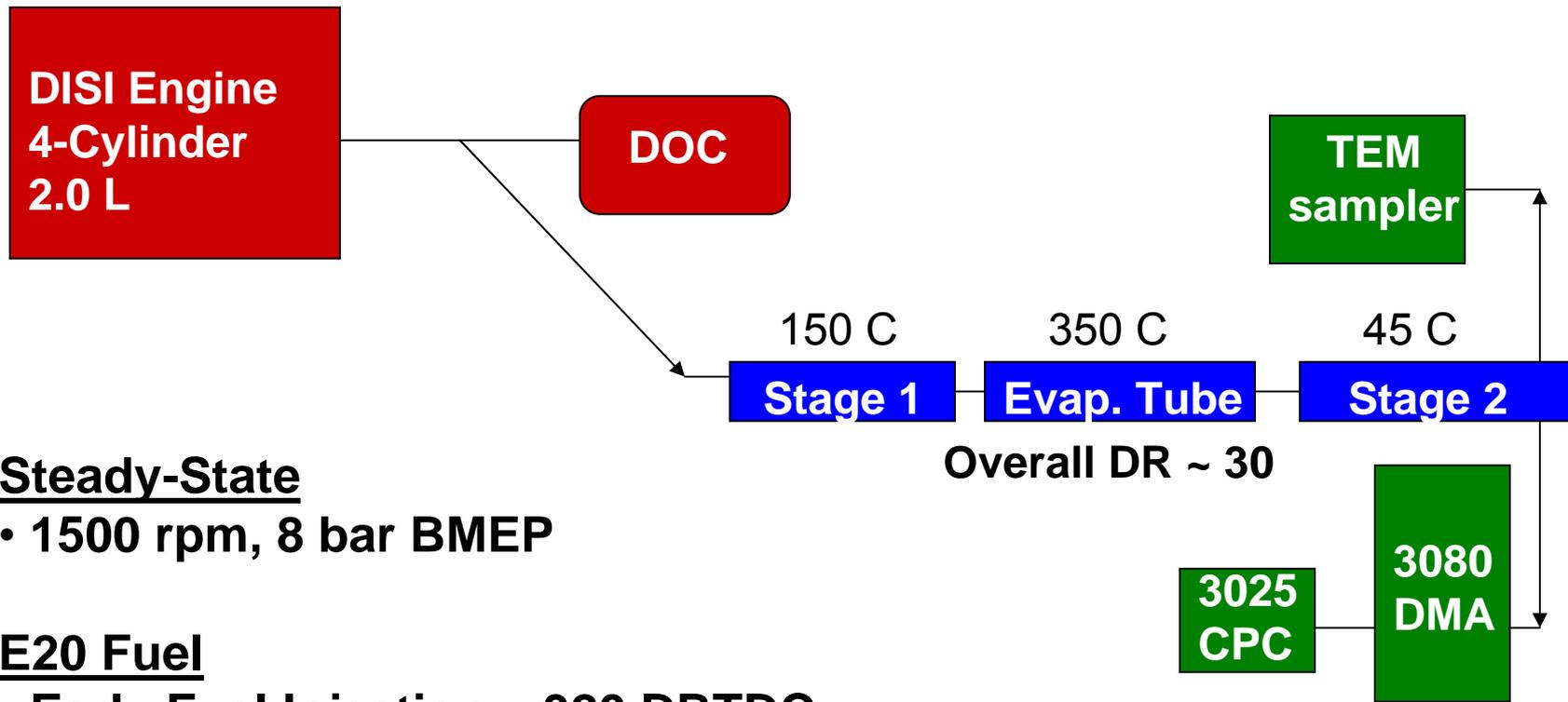
- Neer and Koylu (2006)

Comparison of diesel soot properties from TEM measurements

Study	Diesel engine type	Method	\bar{d}_p (nm)
Present study	6-cylinder engine, various loads and speeds	TEM	20–35
Zhu et al. [13]	Light-duty engine, various loads and speeds	TEM	19–33
Park et al. [11] ^a	4-cylinder engine, single operating condition	TEM	32
Wentzel et al. [8] ^b	Unknown engine, single operating condition	TEM	23
Lee et al. [12]	Heavy-duty engine, four operating conditions	TEM	28–34

Primary size range over
several studies:
19 – 35 nm

Sampling and Analysis Methods



Steady-State

- 1500 rpm, 8 bar BMEP

E20 Fuel

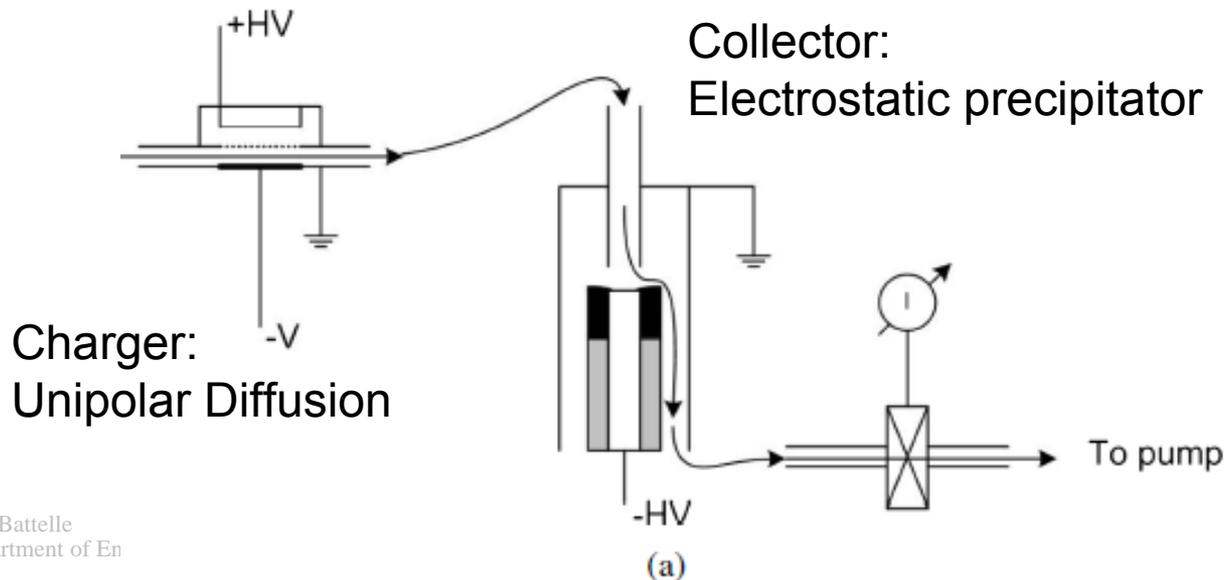
- Early Fuel Injection – 320 DBTDC
- Fuel Injection for Low PN – 280 DBTDC

Particle Collection for TEM Analysis



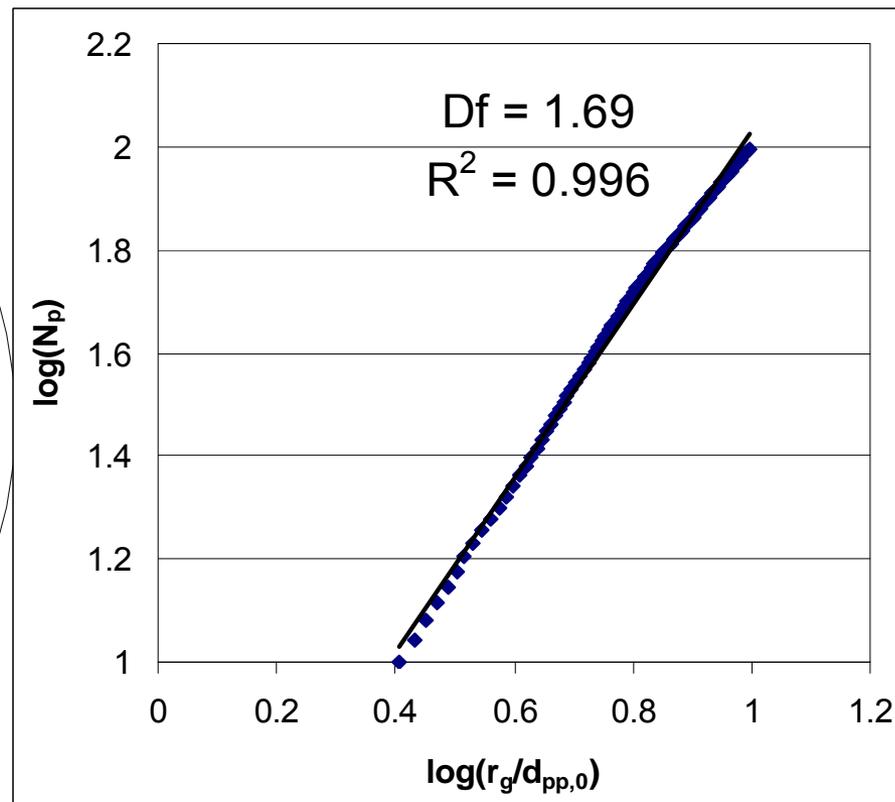
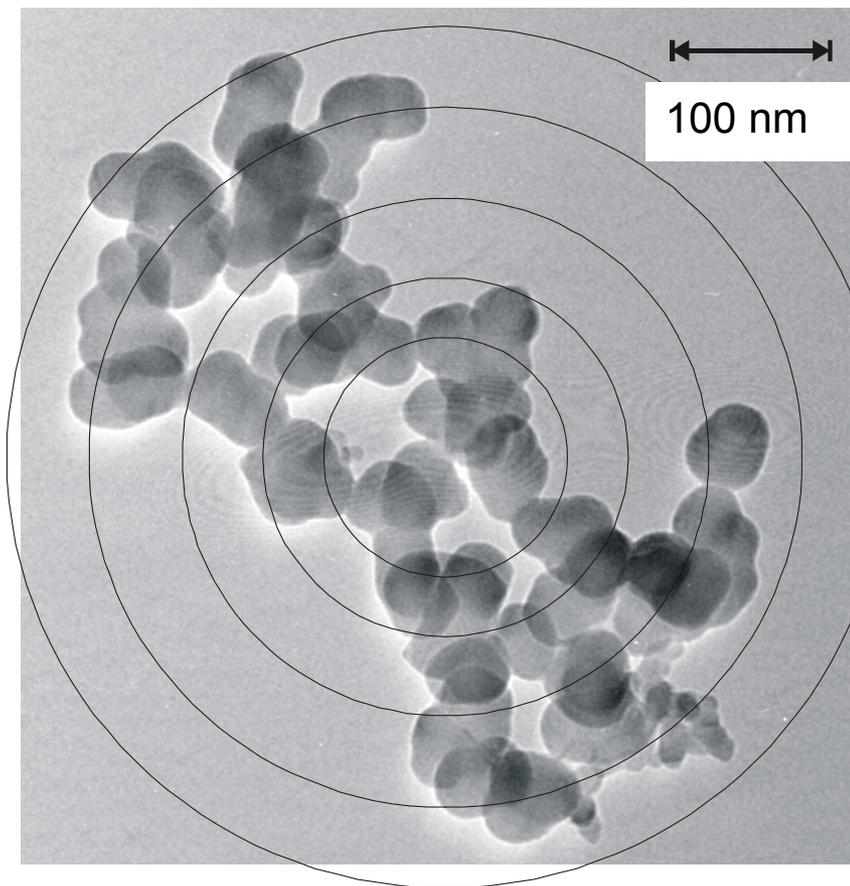
Fierz, Kaegi and Burtcher (2007)
University of Applied
Sciences Northwestern
Switzerland

Uniform collection across substrate
Optimized sampling time
Sampling efficiency vs. particle size



Aggregate Image Analysis

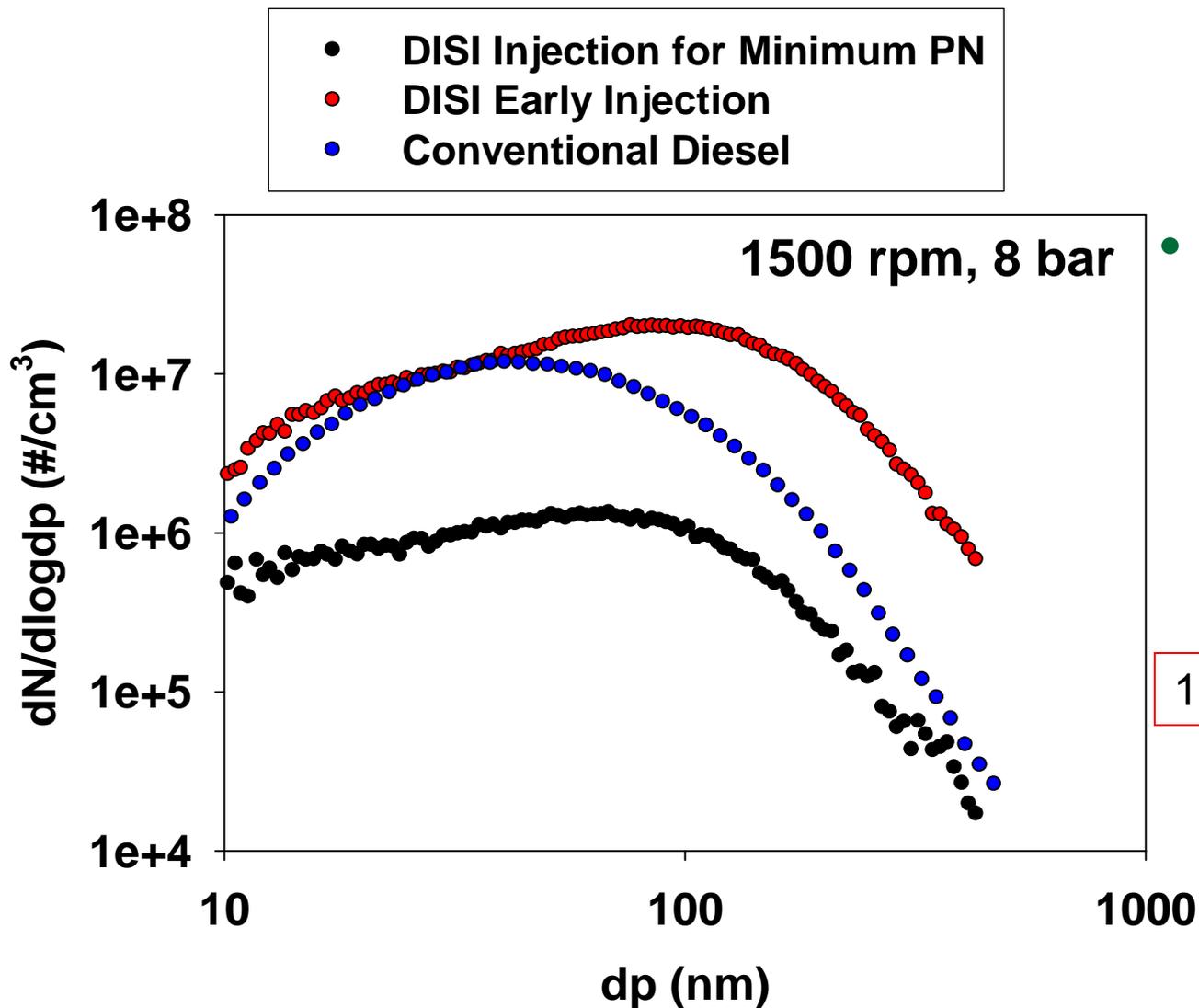
- Xiong and Friedlander (2001)



Atmospheric, 2006, *J. Nanoparticle Research*
Diesel & PCCI, 2011, *Energy and Fuels*

$$N_p = A_s \left(\frac{r_g}{d_{pp,0}} \right)^{D_f}$$

DISI and Conventional Diesel Size Distributions

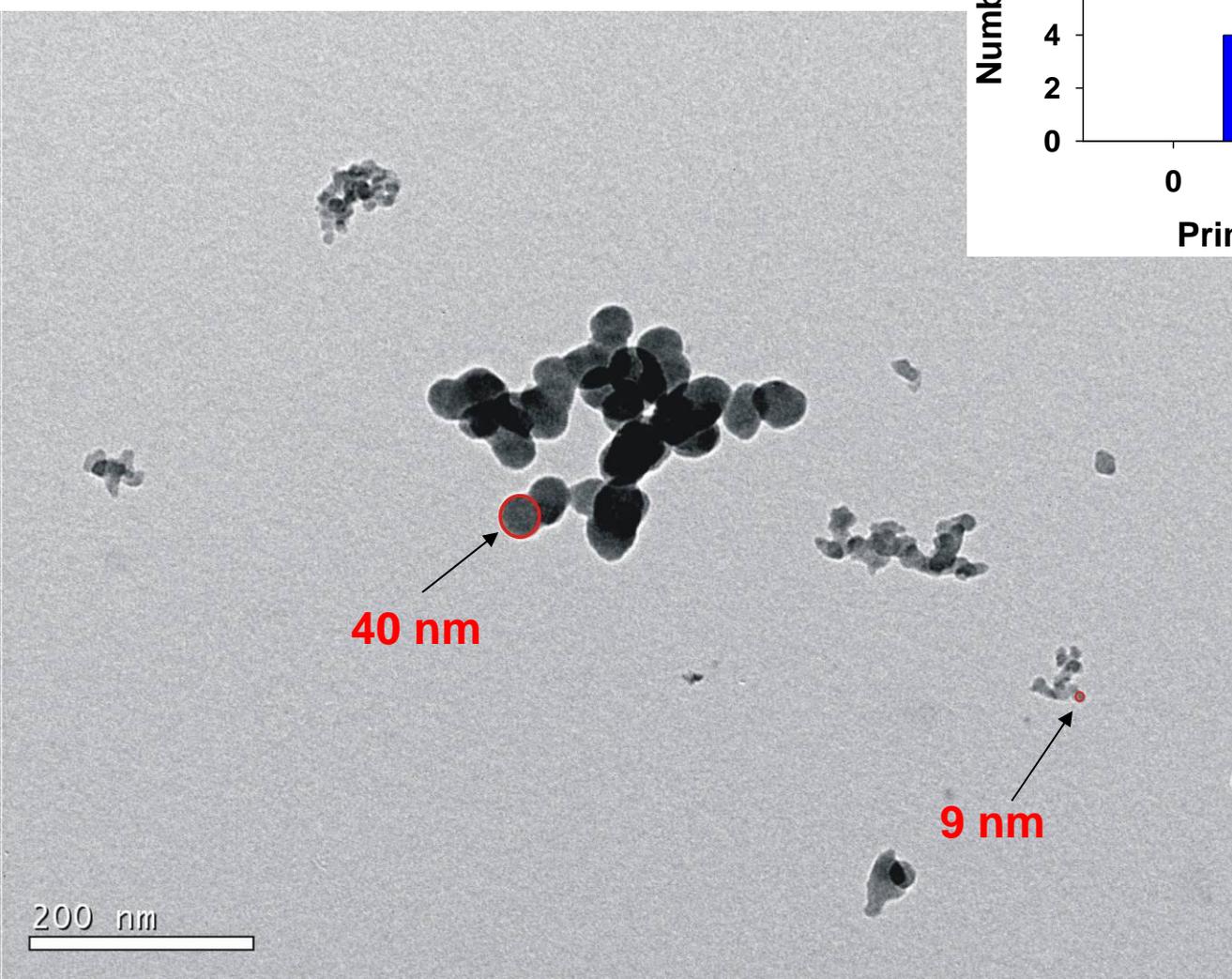
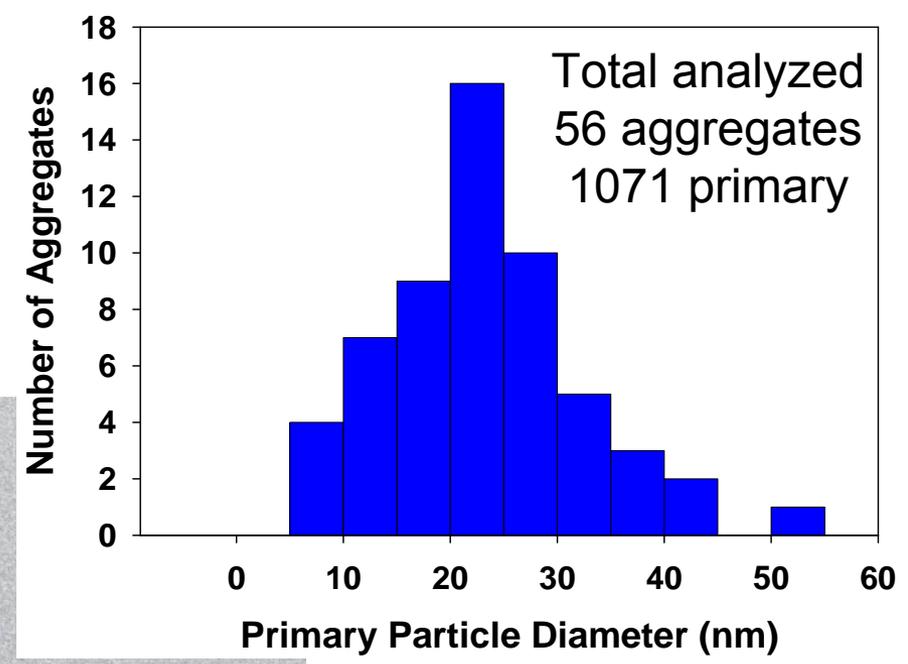


- Difference between peak and 10 nm particle concentration greater for diesel

10 nm range solid or volatile?

Early Injection Particle Morphology

- E20, DI320 BTDC, 1500 rpm/8 bar, Engine-out
- 2-stage dilution with evaporator tube, DR=30



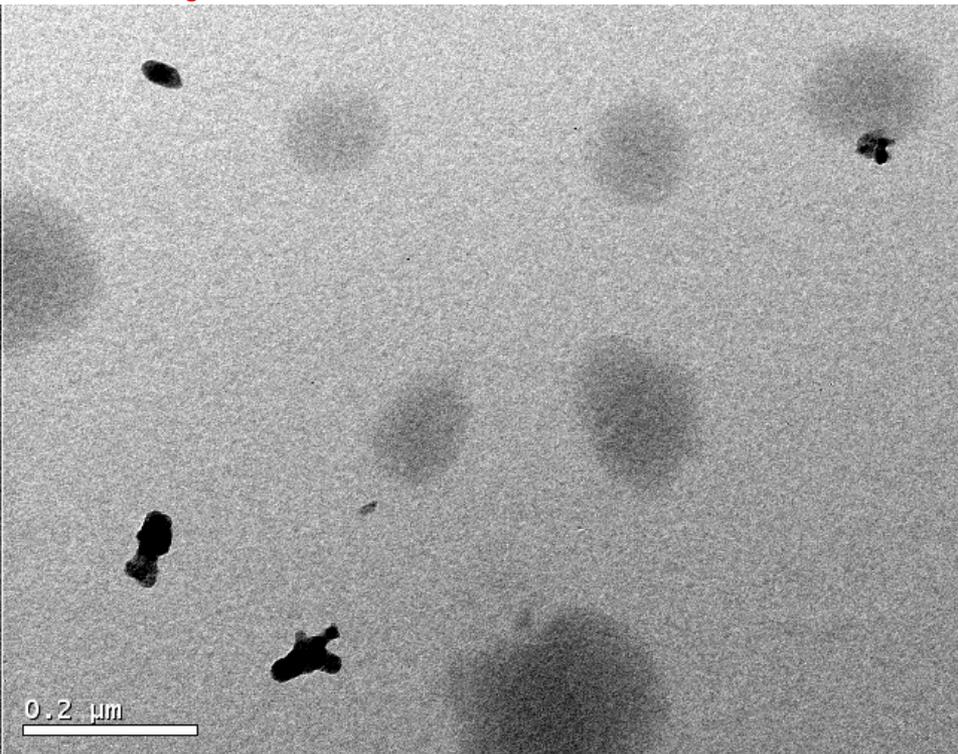
Large variation primary particle diameter

- Greater range than for diesel aggregates

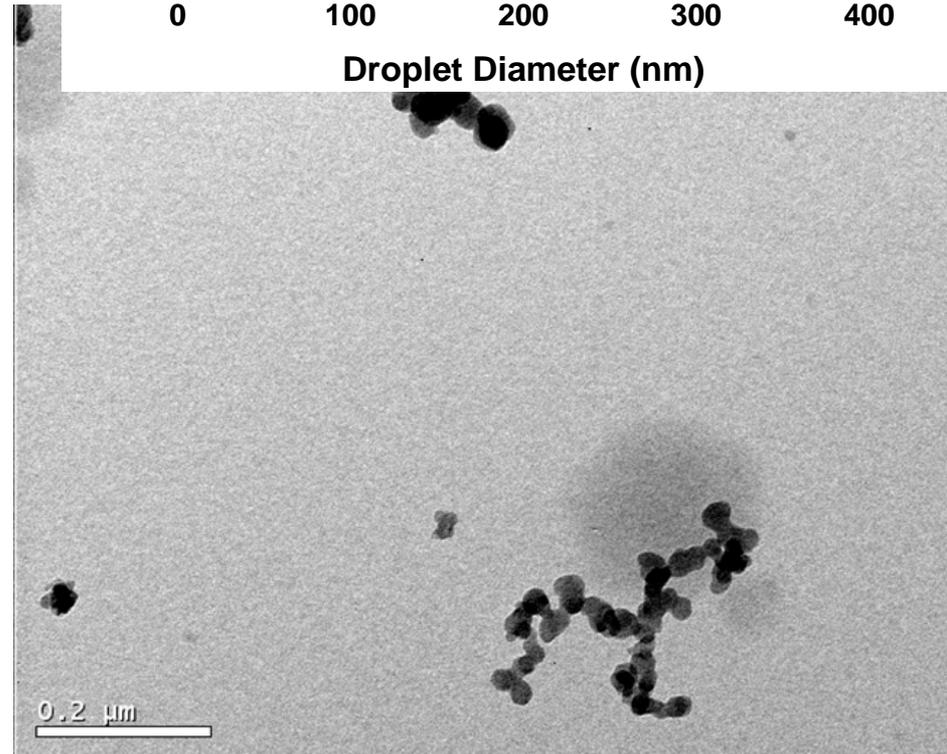
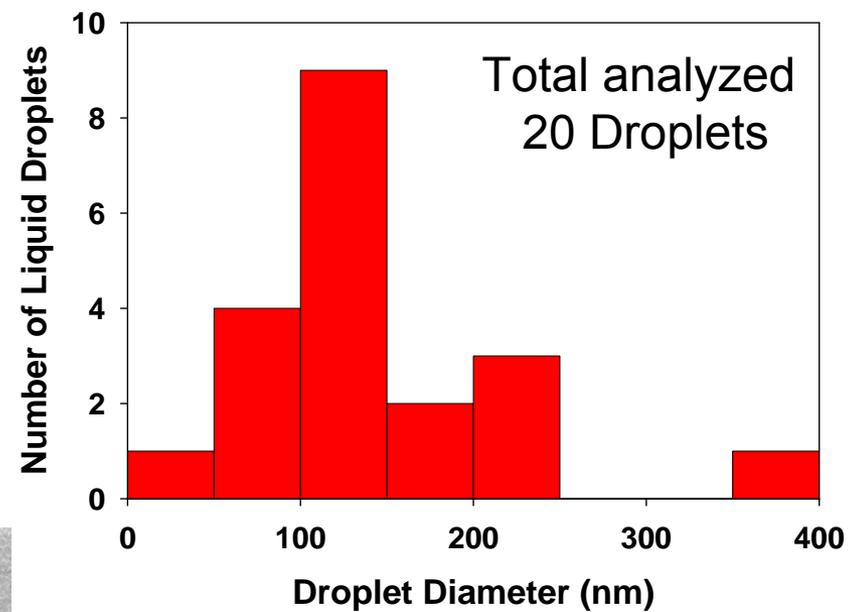
- **Heterogeneous fuel/air mixing**

Early Injection Particle Morphology

- Liquid droplets abundant
 - Condensation of unburned fuel and lube
 - Possible fuel impingement from early injection



10 Scale bar 200 nm



E20, DI320 BTDC, 1500 rpm/8 bar, Engine-out 2-stage dilution with evaporator tube, DR=30

Fuel Injection for Minimum PN

- Peak primary diameters smaller than early injection but still wide range
- Fewer unburned fuel/oil droplets
 - Less impingement on cylinder since later injection

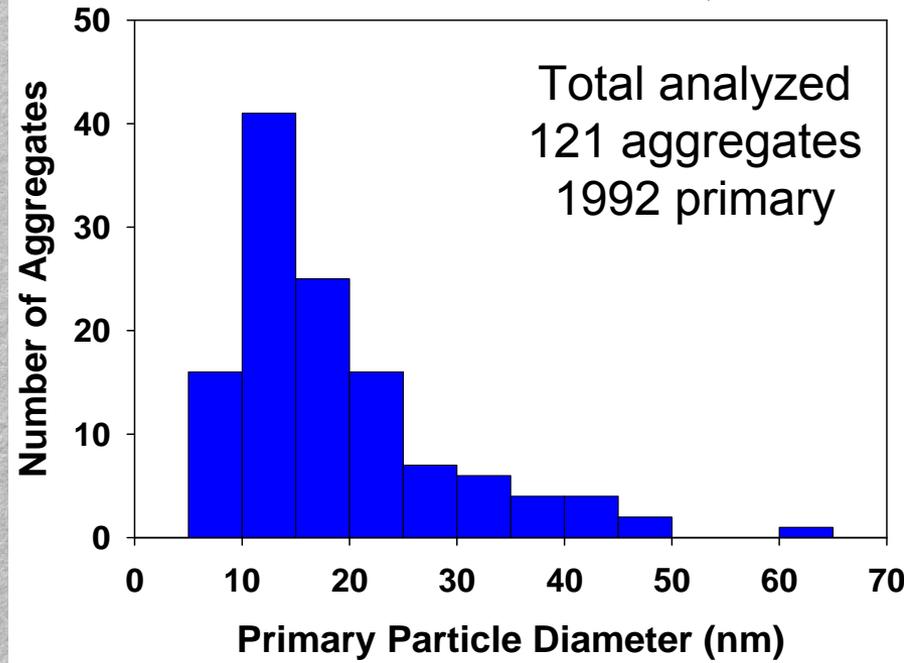
E20, DI280
BTDC 1500
rpm/8 bar
Engine-out

2-stage
dilution with
evaporator
tube, DR=30

35 nm

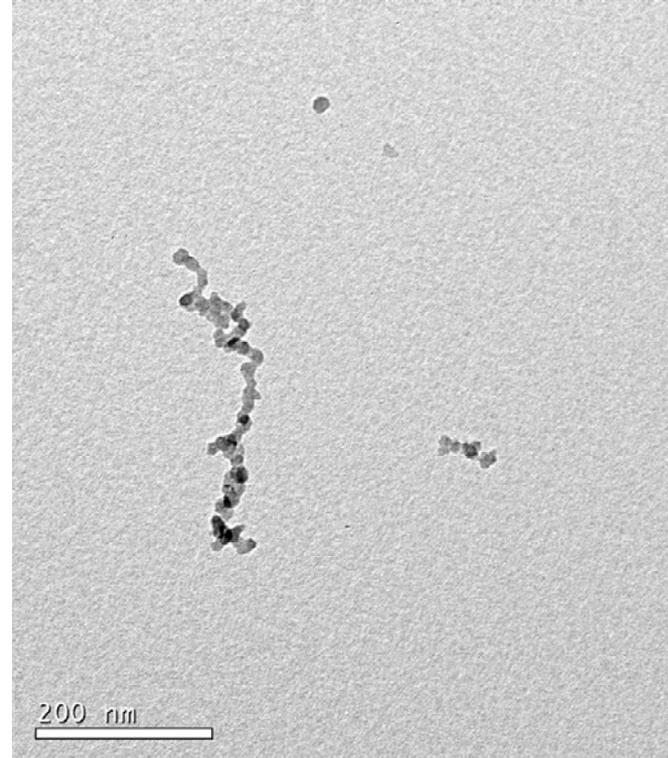
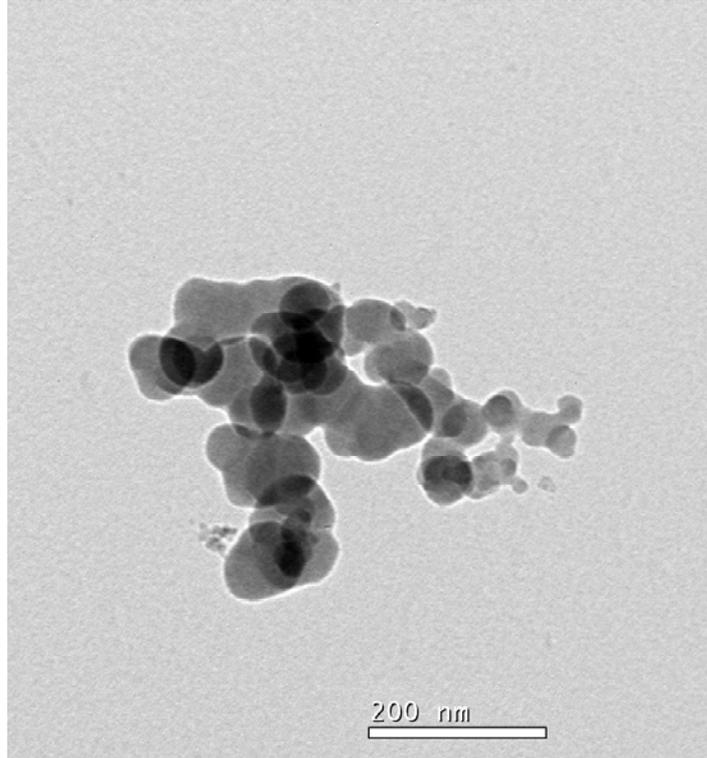
15 nm

200 nm



Fuel Injection for Minimum PN

- Presence of large and small primary particles indicates heterogeneous mixing

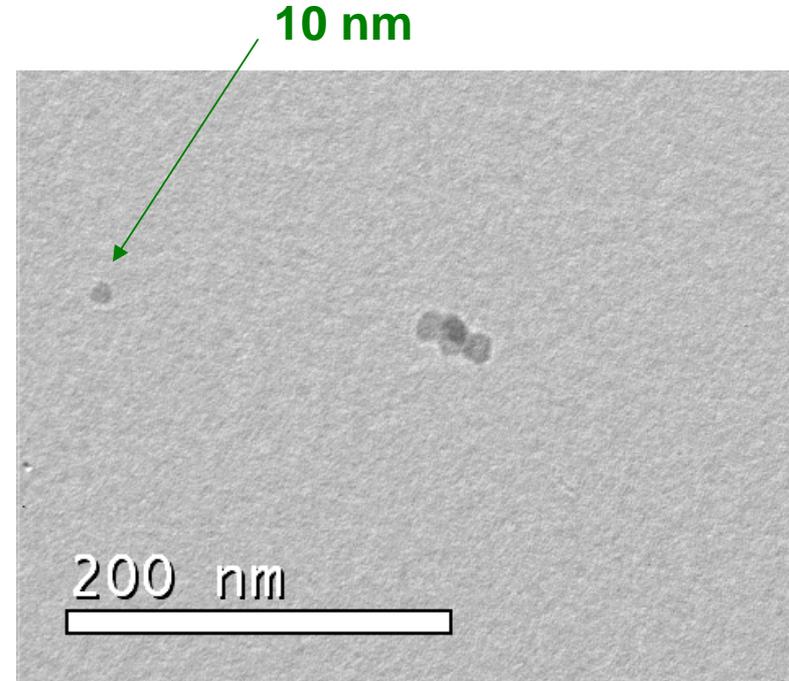
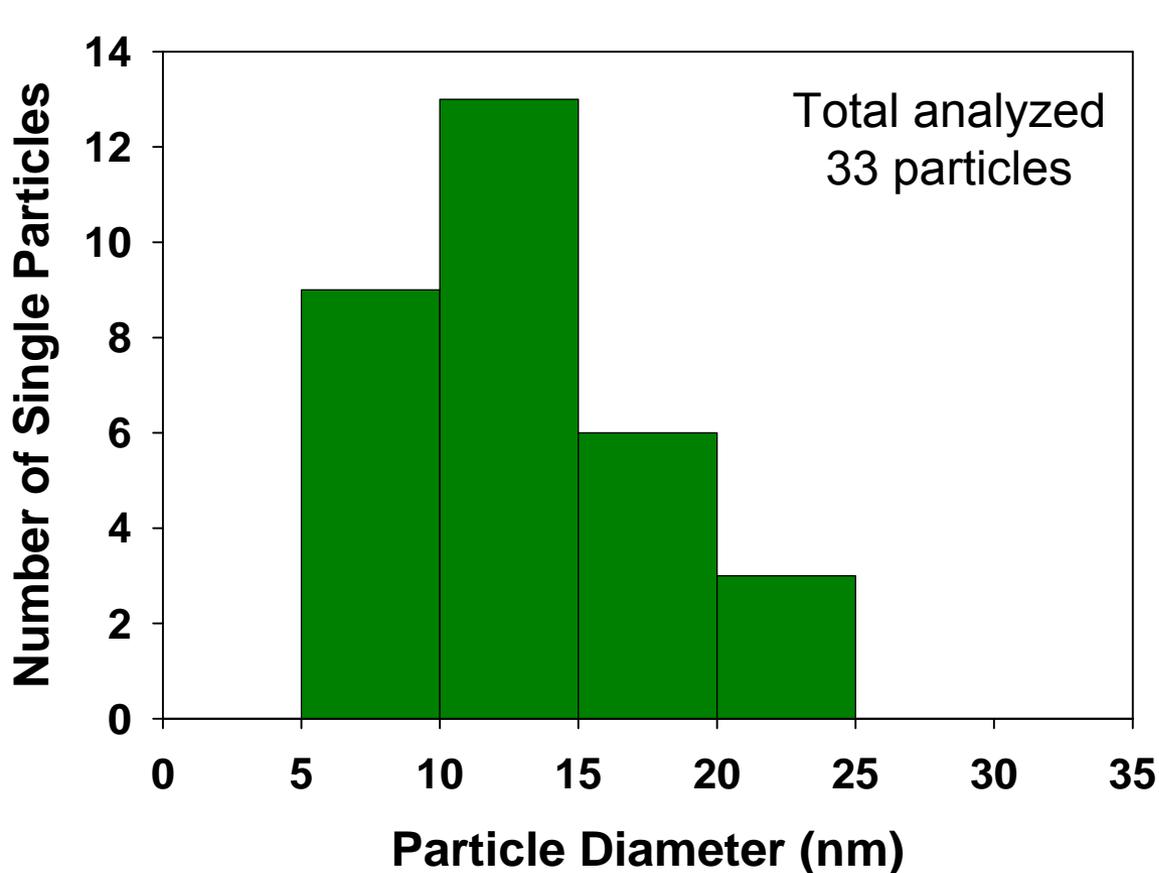


Both images have same magnification

E20, DI280 BTDC, 1500 rpm/8 bar, Engine-out
2-stage dilution with evaporator tube, DR=30

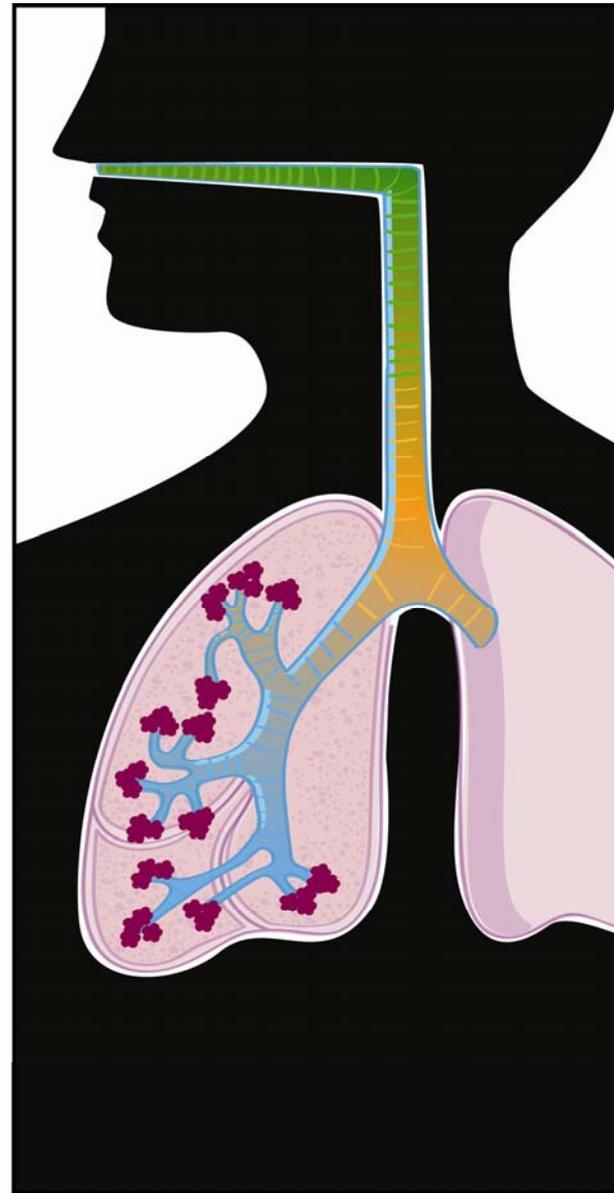
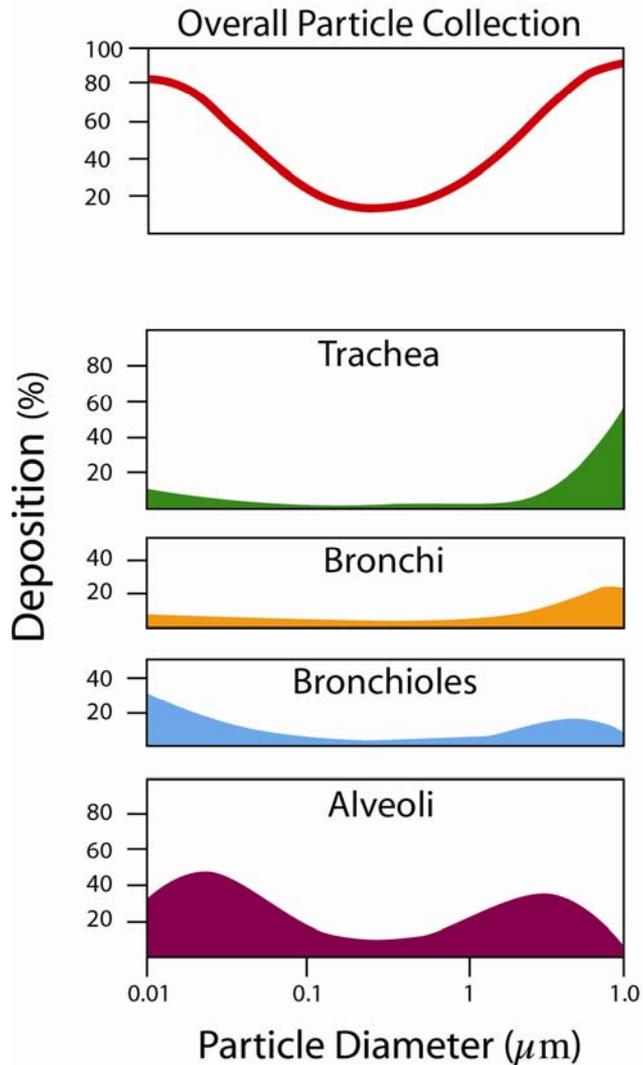
Fuel Injection for Minimum PN

- Single solid nanoparticles (~10 nm) smaller than E.U. particle number regulation limit (23 nm)



E20, DI280 BTDC, 1500 rpm/8 bar, Engine-out
2-stage dilution with evaporator tube, DR=30

Nanoparticles Can Penetrate to Alveolar Region



Adapted
from
Heyder
(2004)

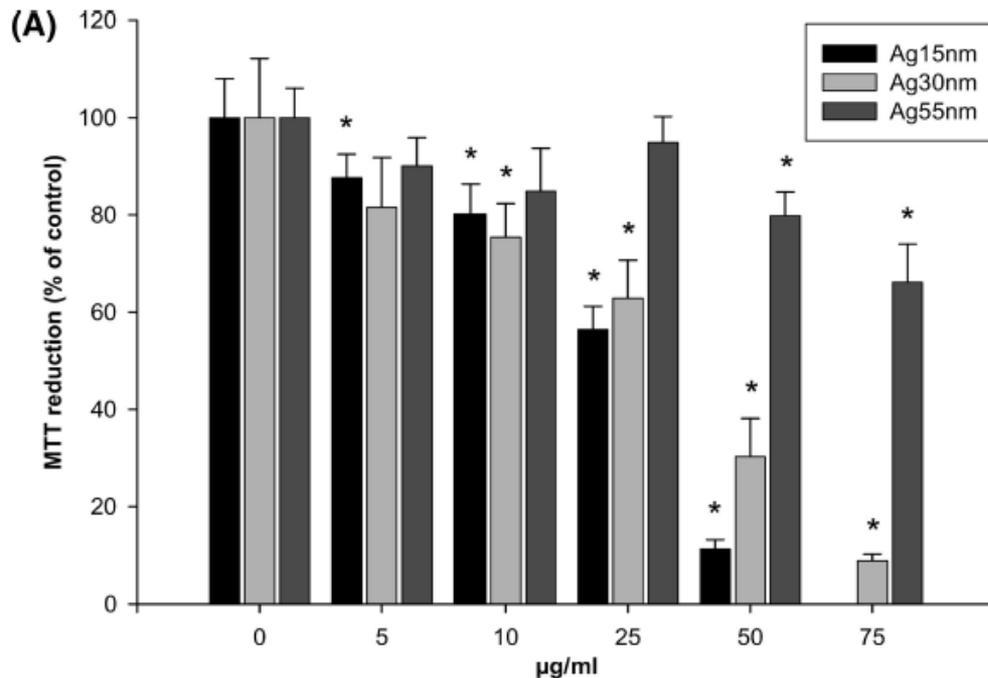
International
Commission
on Radiological
Protection
Model

Toxicity of 15, 30 & 55 nm Silver Particles

- Rat alveolar macrophages exposed for 24 hr to agglomerates

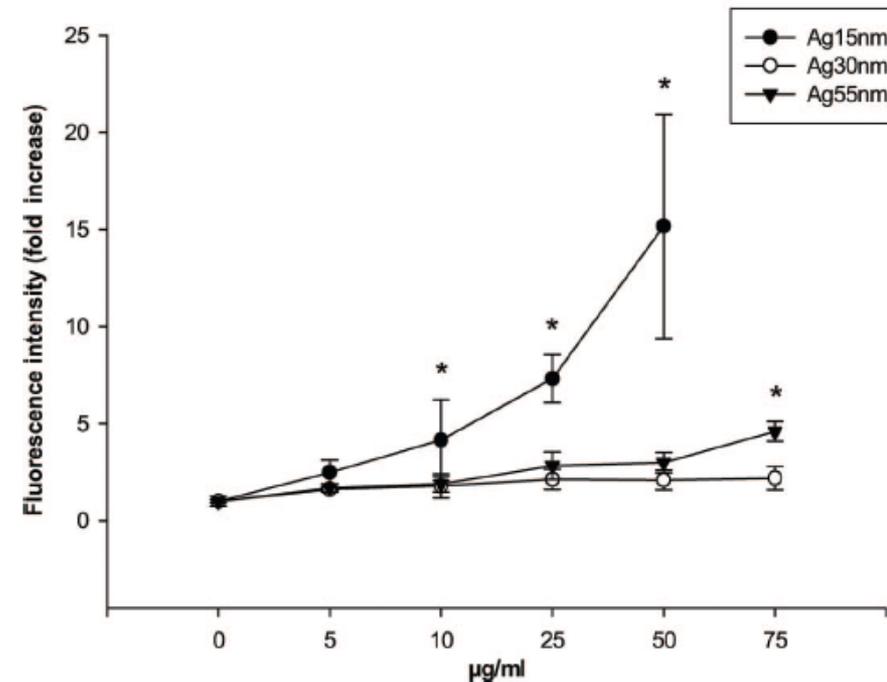
Carlson et al. (2008)

Mitochondrial Function



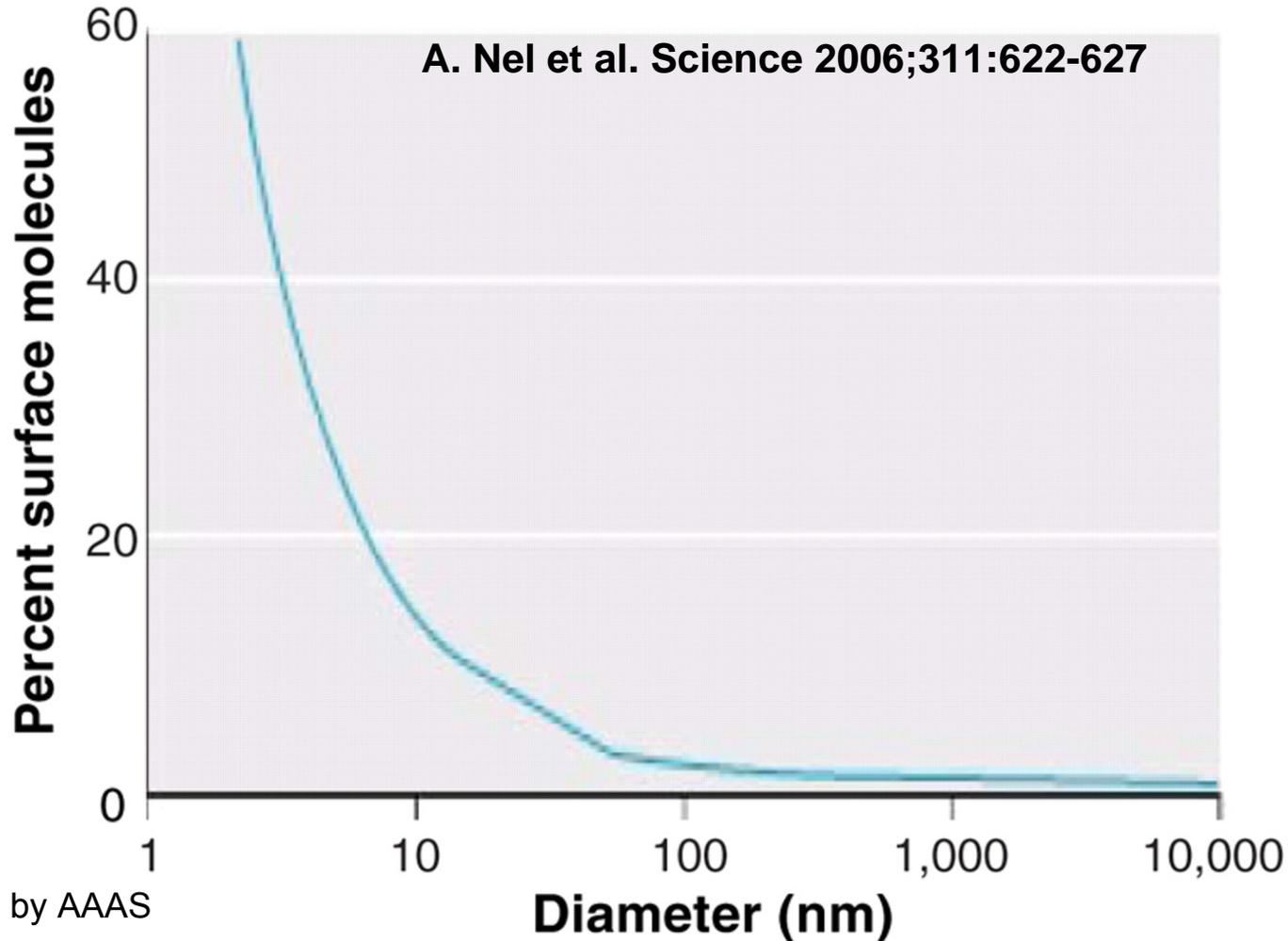
Inner membrane damage,* permeability transition (PT) pore opening,* energy failure,* apoptosis,* apo-necrosis, cytotoxicity

Reactive Oxygen Species



Phase II enzyme induction, inflammation, † mitochondrial perturbation*

Relative Number of Surface Molecules Inversely Related to Particle Size



Published by AAAS

Morphology Comparison for Injection Strategies

	Early – DI 320	Minimum PN – DI 280
Single Spheres	8%	21%
Aggregates	67%	78%
Droplets	25%	1%
Irregular	1%	-

- Injection for minimum PN generated fewer droplets and more single solid spheres than early injection
- Dependence of collection efficiency on particle size not reflected in this data

Idealized Aggregate Theory

- Derived by equating migration velocity of an aggregate and sphere
- Relates primary particle diameter (d_{pp}) and number of primary particles (N_p) to mobility diameter (d_m)
 - Lall and Friedlander (2006)

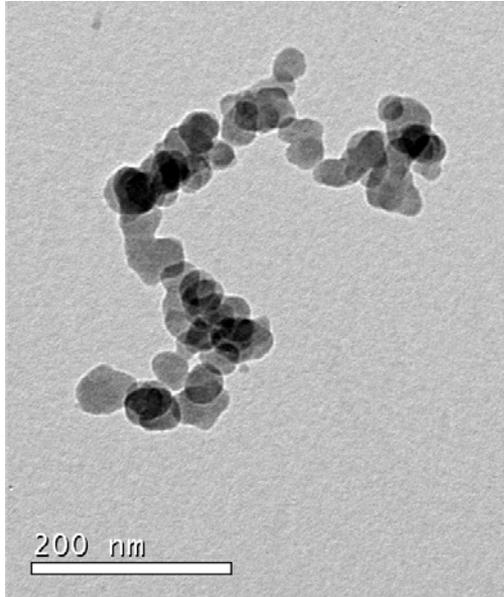
$$\frac{d_m}{C(d_m)} = \frac{c^* N_p d_{pp}^2}{12 \pi \lambda}$$

- d_m = Mobility diameter
- d_{pp} = Primary particle diameter
- N_p = Number of primary particles
- λ = Gas mean free path
- $C(d_m)$ = Slip correction factor
- c^* = Dimensionless drag force that depends on aggregate orientation

- Assumes most primary particles exposed to collisions with surrounding gas molecules ($D_f < \sim 2$)

Projected Area Equivalent Diameter

Direct-injection spark-ignition

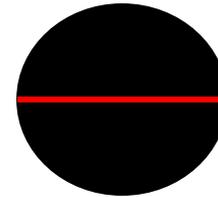


4-cylinder, 1.9 L engine
E20 fuel
280 DBTDC injection

Projected area



**Rogak, Flagan & Nguyen
(1993)**



$$d_m = \sqrt{\frac{4PA}{\pi}}$$

Other supporting studies

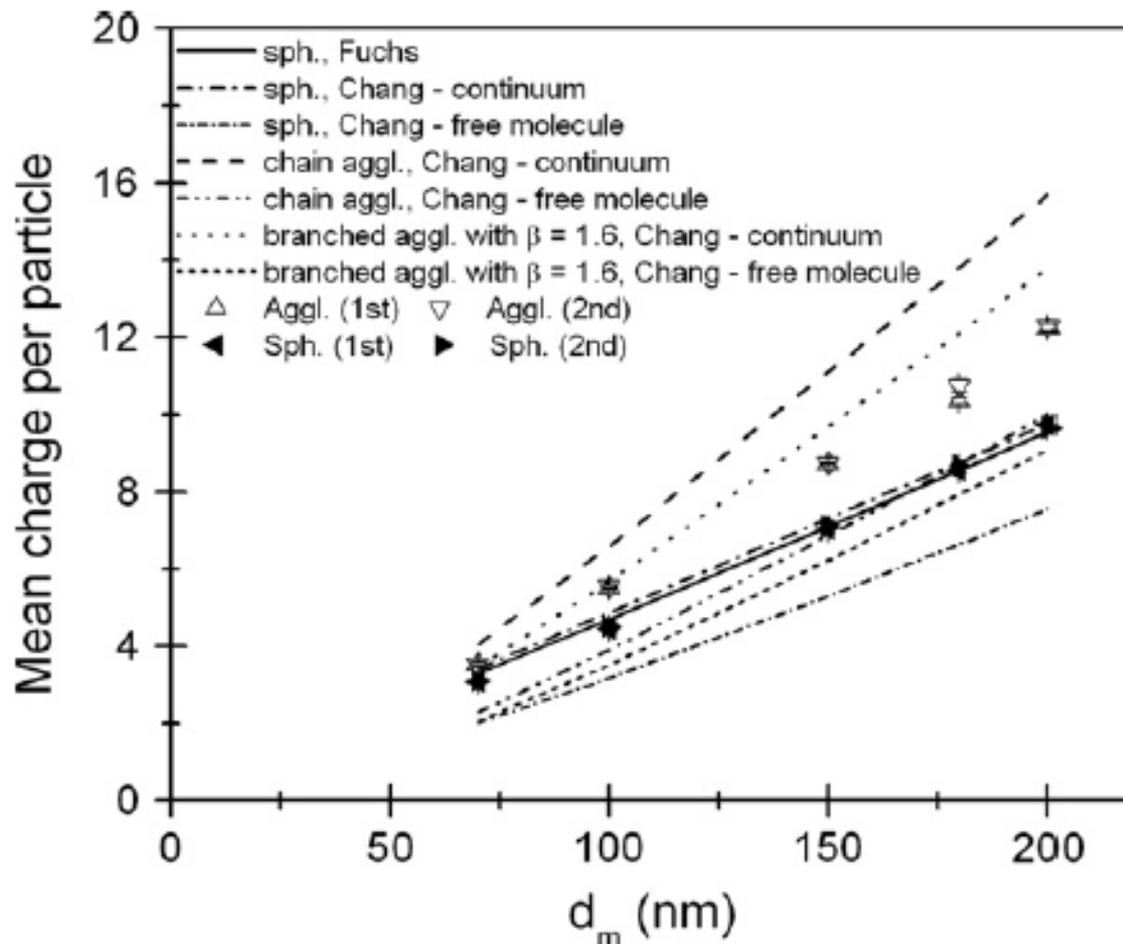
Park et al. (2004)

Ku & Maynard (2005)

Chakrabarty et al. (2007)

Charging Efficiency for Aggregates and Spheres

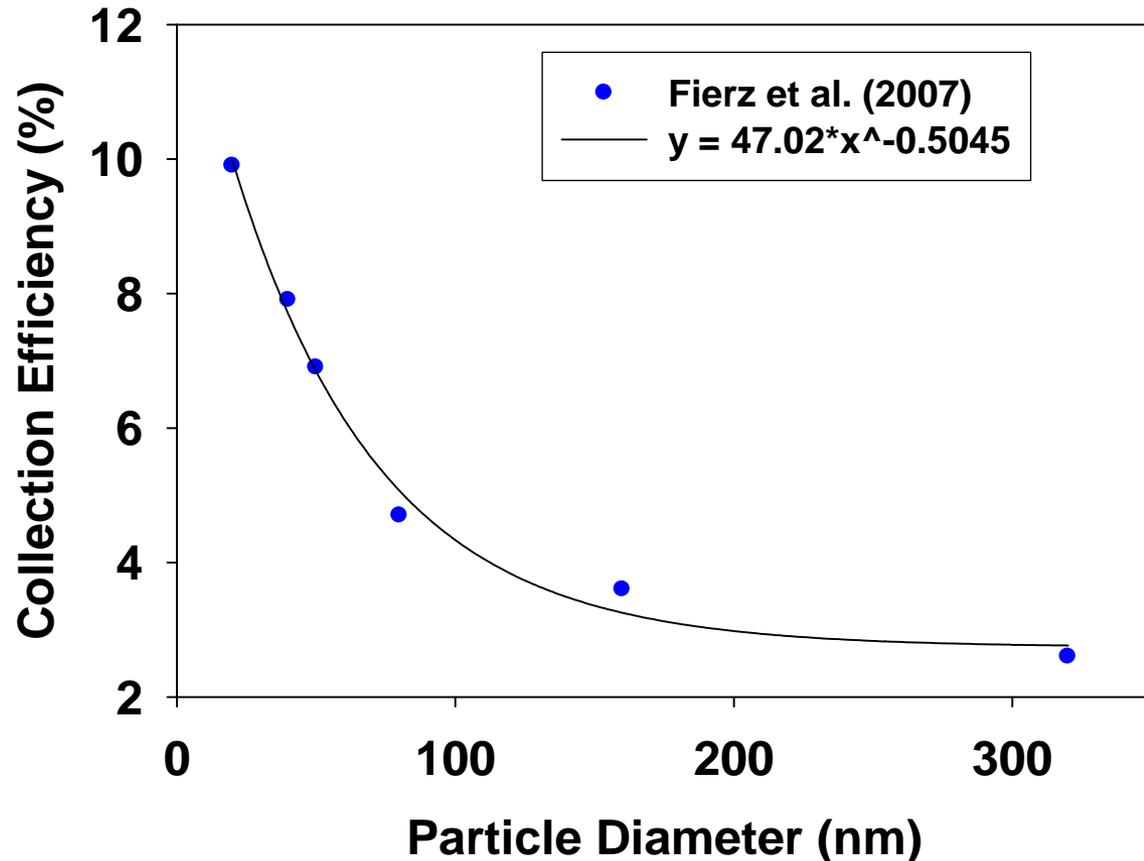
- Unipolar diffusion charger (Shin et al., 2010)
 - Difference between aggregate and sphere charging efficiency increases with increasing electrical mobility diameter.



Particle Collection Efficiency

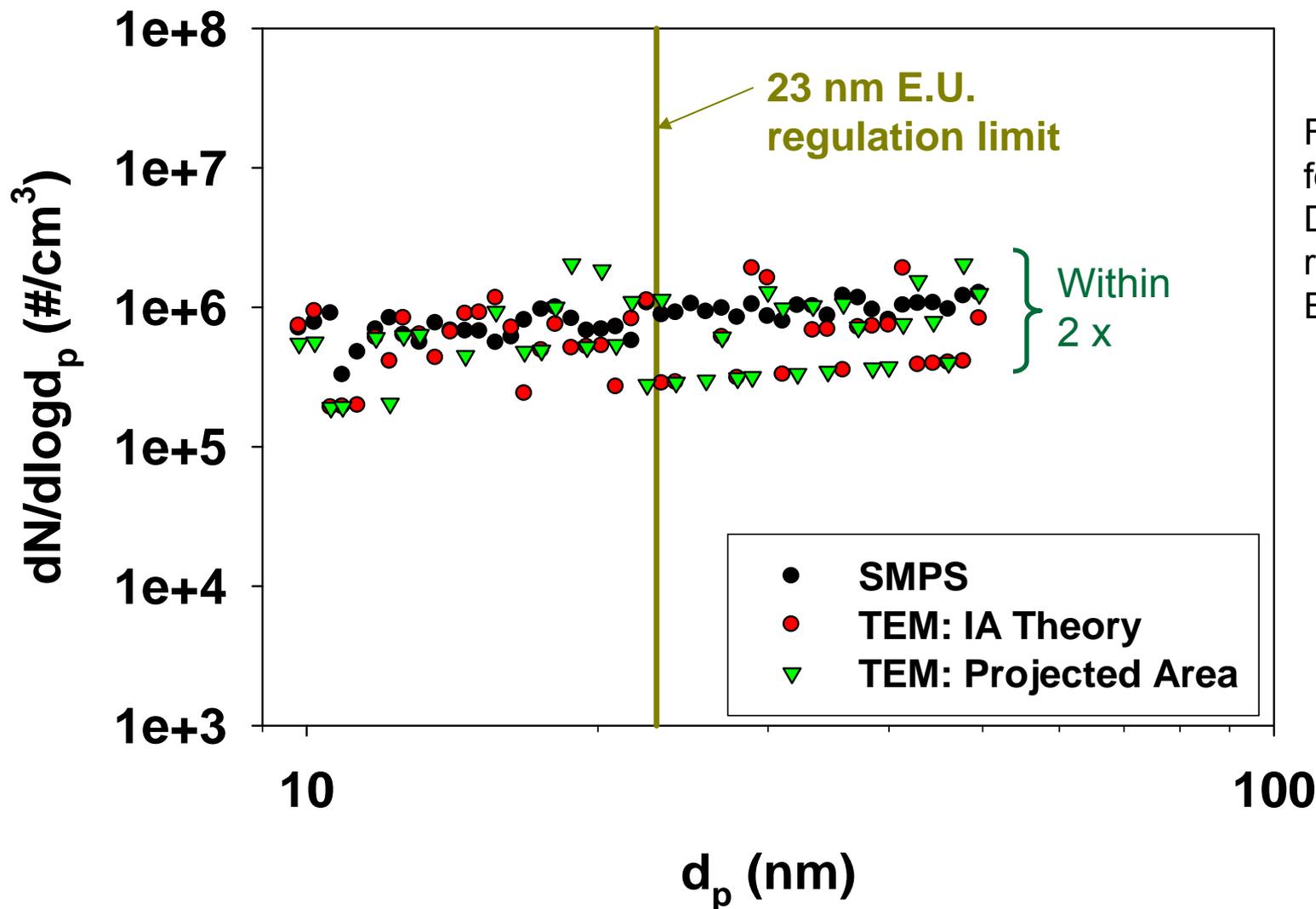
- Aerosol concentration calculation

- Analyzed 112 particles at 81K magnification
- Estimated aggregate mobility diameter using IA theory and projected area
- Extrapolated to area of TEM grid (3.05 mm diameter)
- Calculated collection efficiency from power law calibration curve



SMPS & TEM Size Distributions: 10 - 50nm

For < 23 nm solid number measured by TEM consistent with total number measured by SMPS



Fuel injection for low PN, 280 DBTDC, 1500 rpm/ 8 bar, Engine-out

2-stage dilution with evaporator tube, DR = 30

Conclusions

- Wide primary particle diameter range
 - 7 to 60 nm
 - Indicative of heterogeneous fuel and air mixing
 - Other speed and load points should be examined
- Small primary size relative to diesel for minimum PN injection point
 - 10 to 15 nm
 - Fuel and air mixing enhanced in some zones
- Presence of single solid particles smaller than 23 nm
 - TEM number concentration data consistent with SMPS for this size range
 - May be of health concern since can deposit in alveolar region and have greater percent surface area