Ultrafine Particles: How should they be defined and measured (cheaply)

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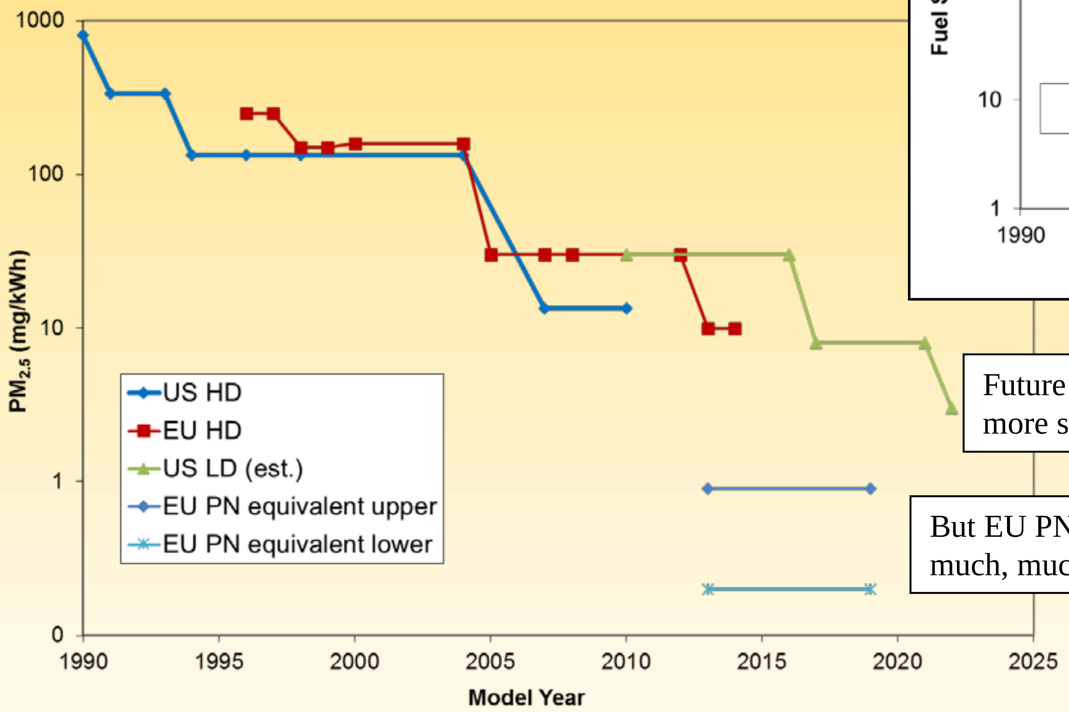
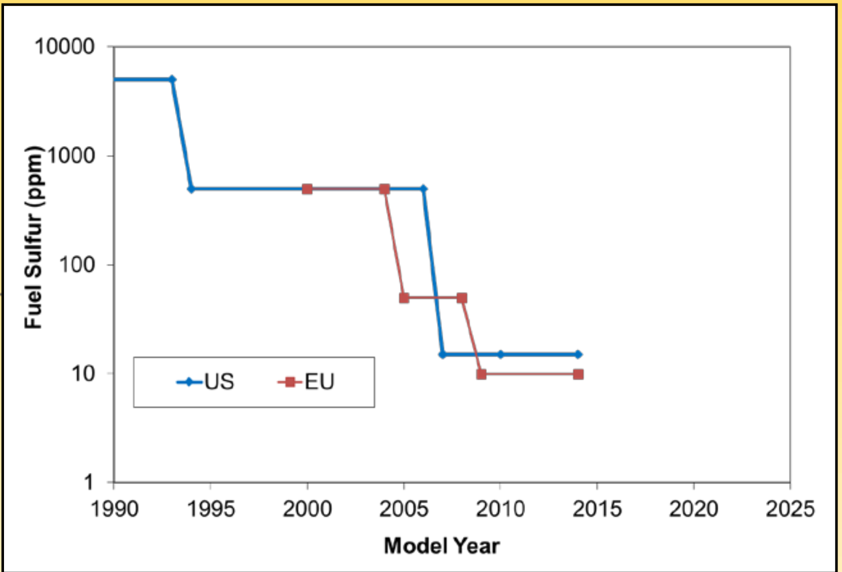
What are some physical metrics?

- Number
- Surface area
  - BET (Brunauer–Emmett–Teller)
  - Projected area (TEM)
  - External envelop, “active surface,” “lung deposited surface area, LDSA”
- Volume
- Mass
- Size
  - Mobility size
  - Aerodynamic size
  - Size measured with TEM
  - Fractal descriptions
- Volatile or non-volatile?
- Internal and external mixing
- Mass and number regulations

Dramatic reductions in PM standards facilitated by fuel sulfur reductions

At present emission regulations are based on gravimetric filter PM2.5. In the EU “non-volatile” particle number > 23 nm diameter is also regulated





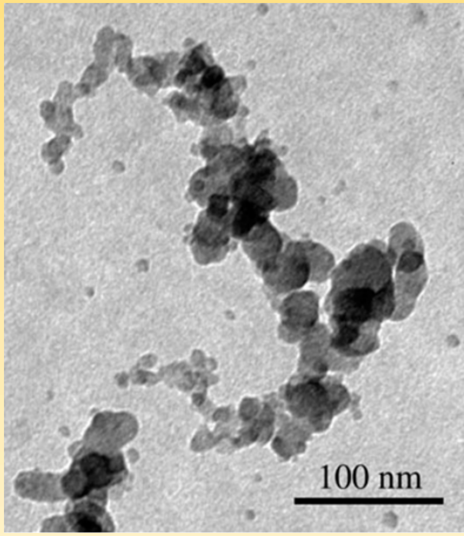
Future LD standard 5 times more stringent than current HD

But EU PN standards are much, much more stringent

Sources of particulate matter emissions from engine – primary and secondary

Primary particles

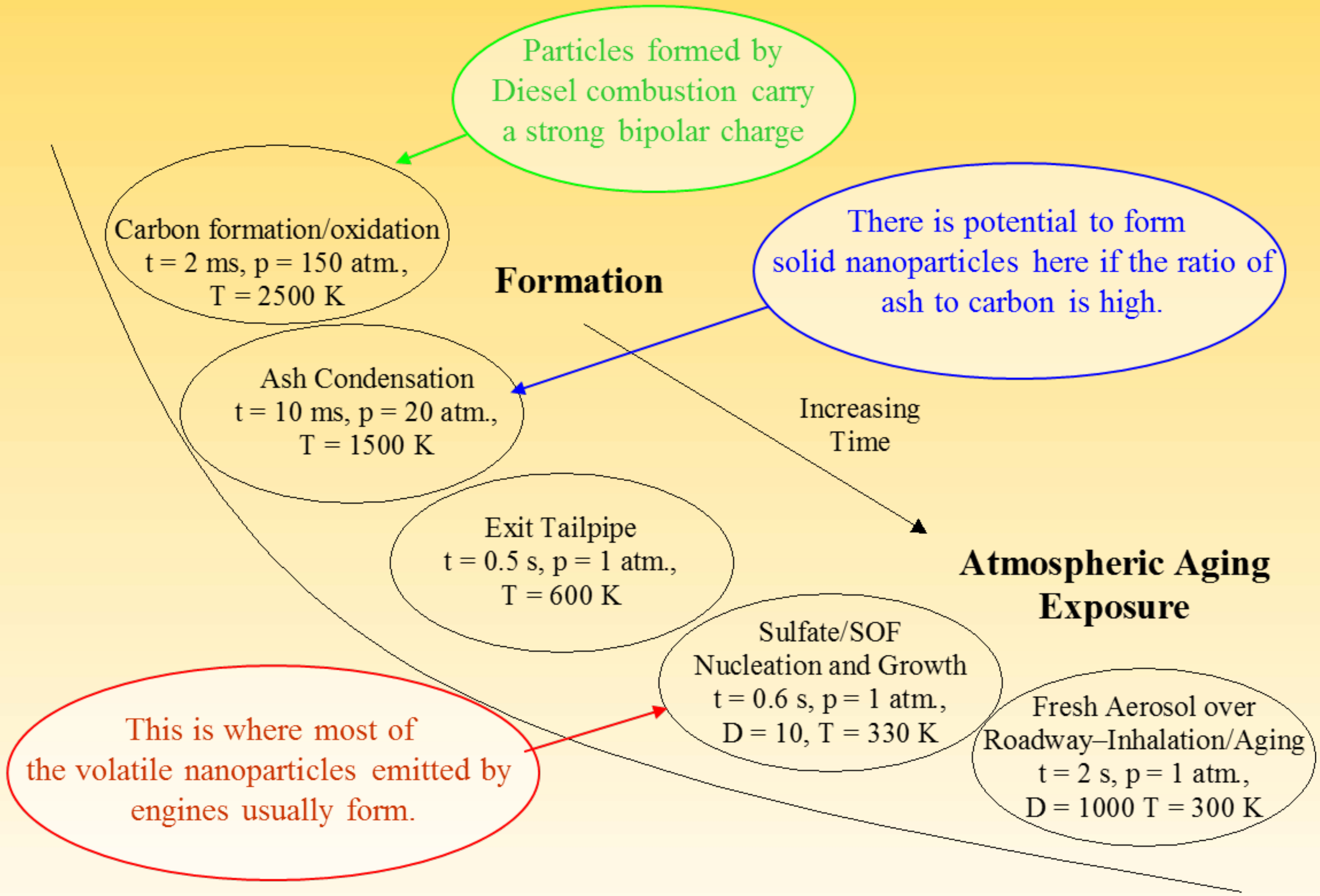
- Particles formed in the engine itself
  - Elemental carbon
  - Lube oil ash and wear metals
  - Time scale: milliseconds to seconds
- Particles that form as the exhaust dilutes and cools in the atmosphere
  - Heavy, partially oxidized hydrocarbons from fuel and lubricating oil
  - Sulfates from sulfur 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 – new concerns

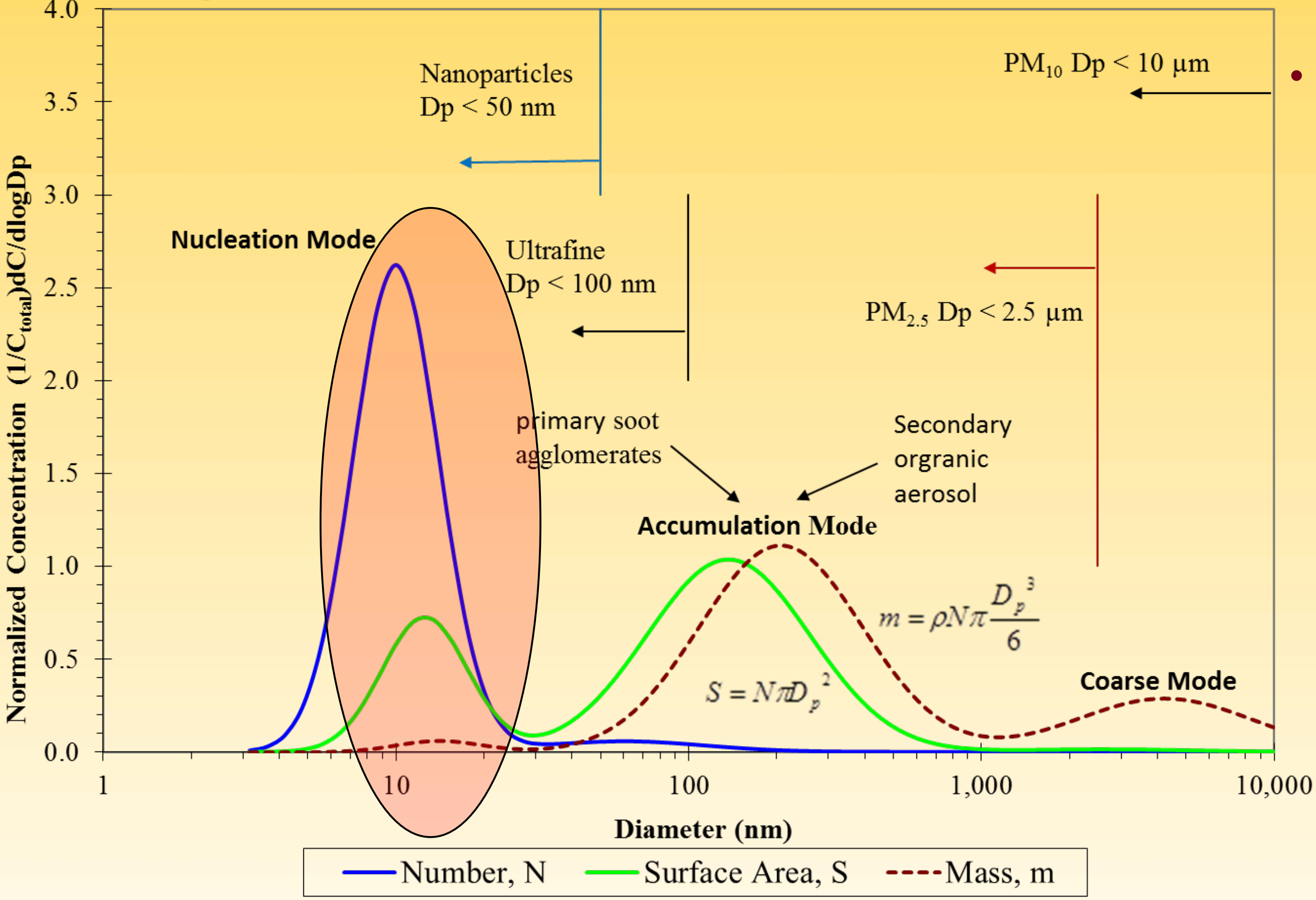
- Particles that form from mainly gaseous emissions by photochemical reactions
  - Oxides of nitrogen and volatile organic carbon primary precursors
  - Secondary organic aerosol, sulfates, nitrates, haze, $PM_{2.5}$, O_3
  - Time scale: hours to days

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



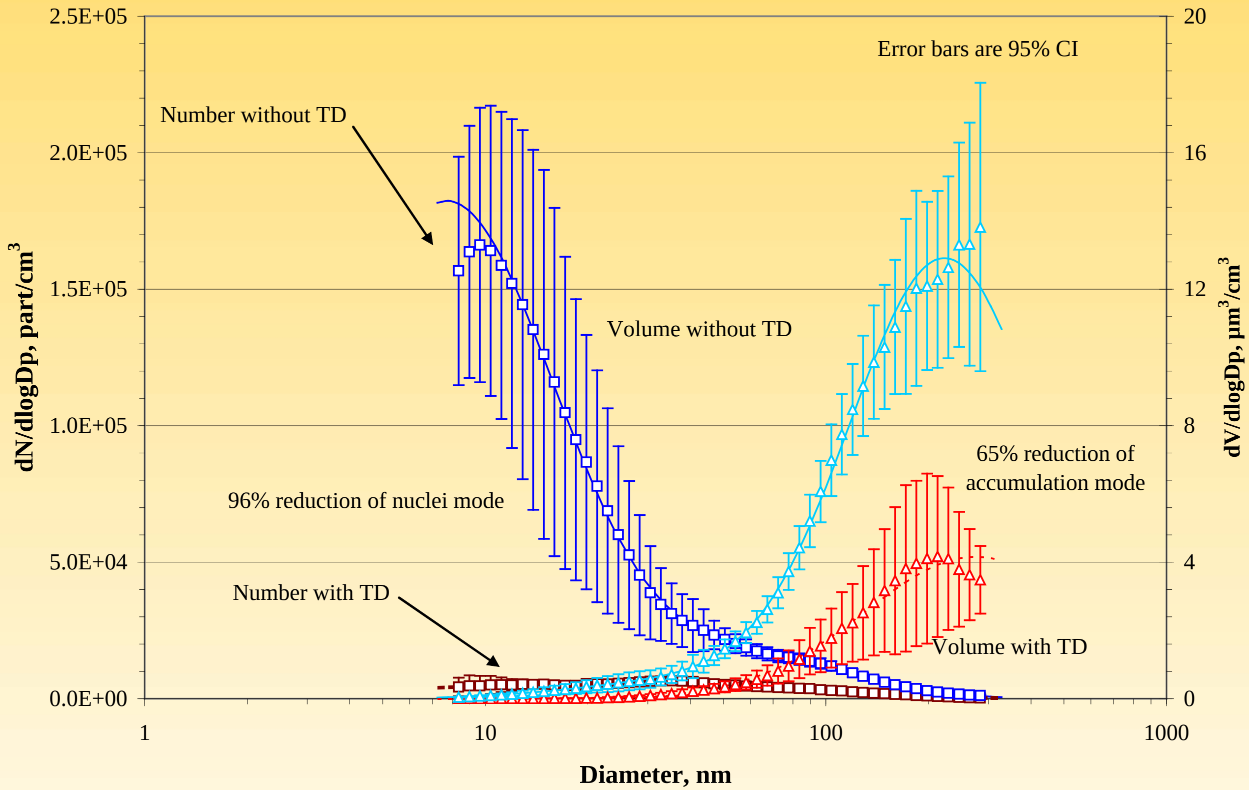
Kittelson, D. B., W. F. Watts, and J. P. Johnson 2006. "On-road and Laboratory Evaluation of Combustion Aerosols Part 1: Summary of Diesel Engine Results," Journal of Aerosol Science 37, 913–930.

Under ambient conditions most of the particle number in the nucleation mode



- Nucleation mode
  - Typically 3 – 30 nm
  - Mainly particles that form as exhaust dilutes and cools
    - Mainly semi-volatile hydrocarbons and sulfates
    - traces of ash, elemental carbon
  - Usually contains most of particle number but little mass
  - Most of material from DPF diesels here
  - Particles are short lived
    - Removed by coagulation, diffusion
    - Lifetime minutes

Much of the on road aerosol is volatile, especially in the nuclei mode region



- Overall average 60 hours of on-road sampling in cross country Diesel traffic (pre DPF)
- 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 – this is also seen in 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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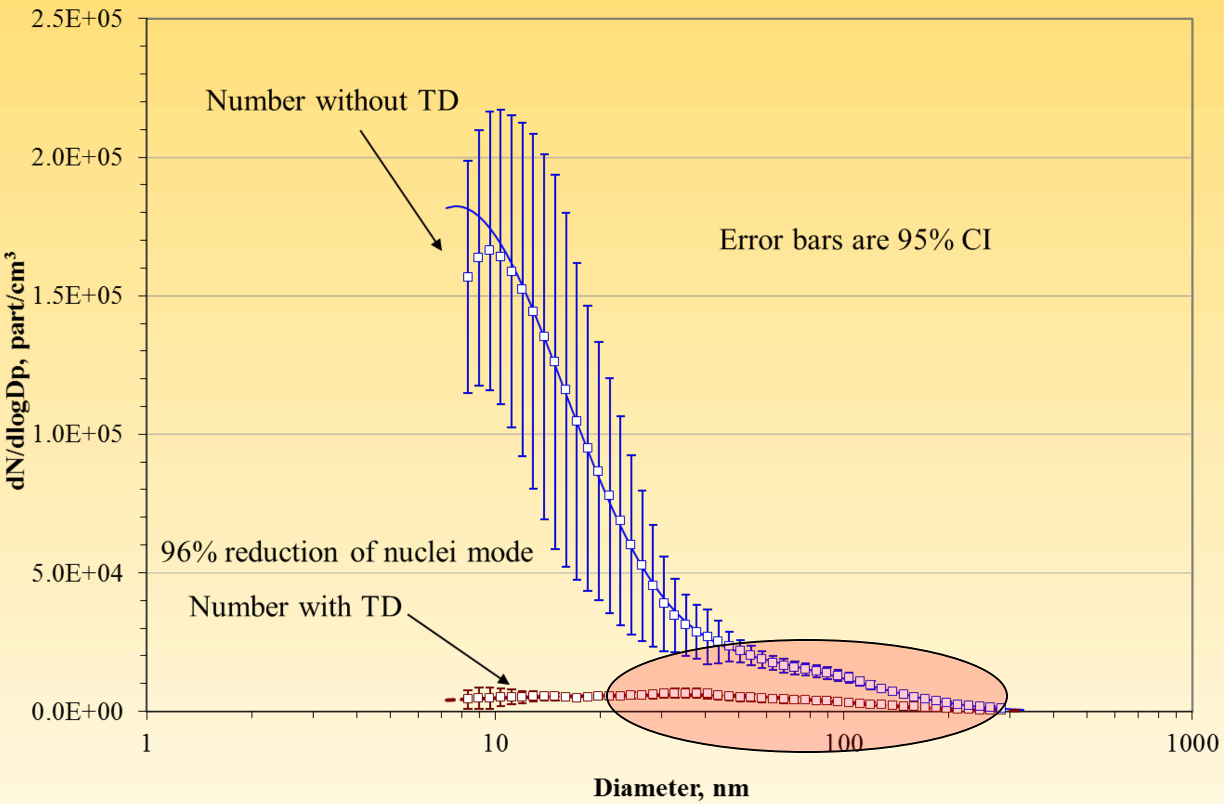
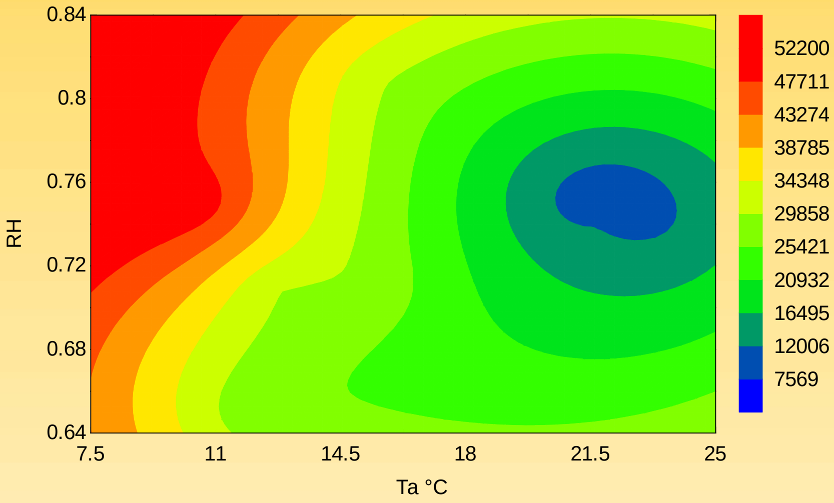
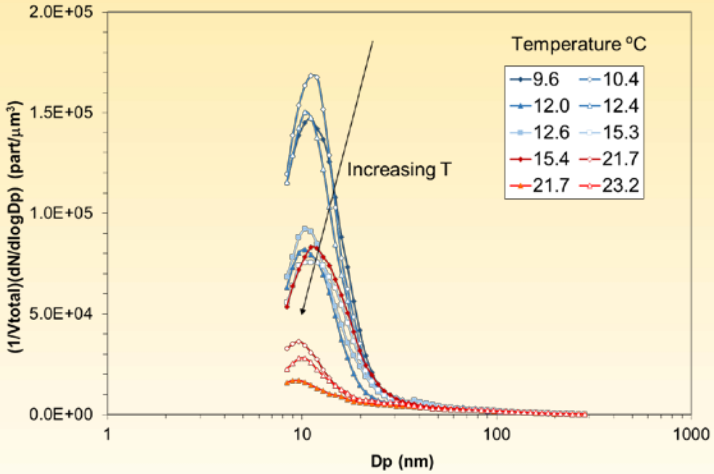


- Overall average 60 hours of on-road sampling in cross country Diesel traffic
- Thermal denuder (TD) used to remove volatile particles
- 96% reduction in nuclei mode region
- The shaded region is what would be measured by the EU number method – Mainly accumulation mode number

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

Influence of ambient temperature on the relative size of the nuclei mode – on-road data



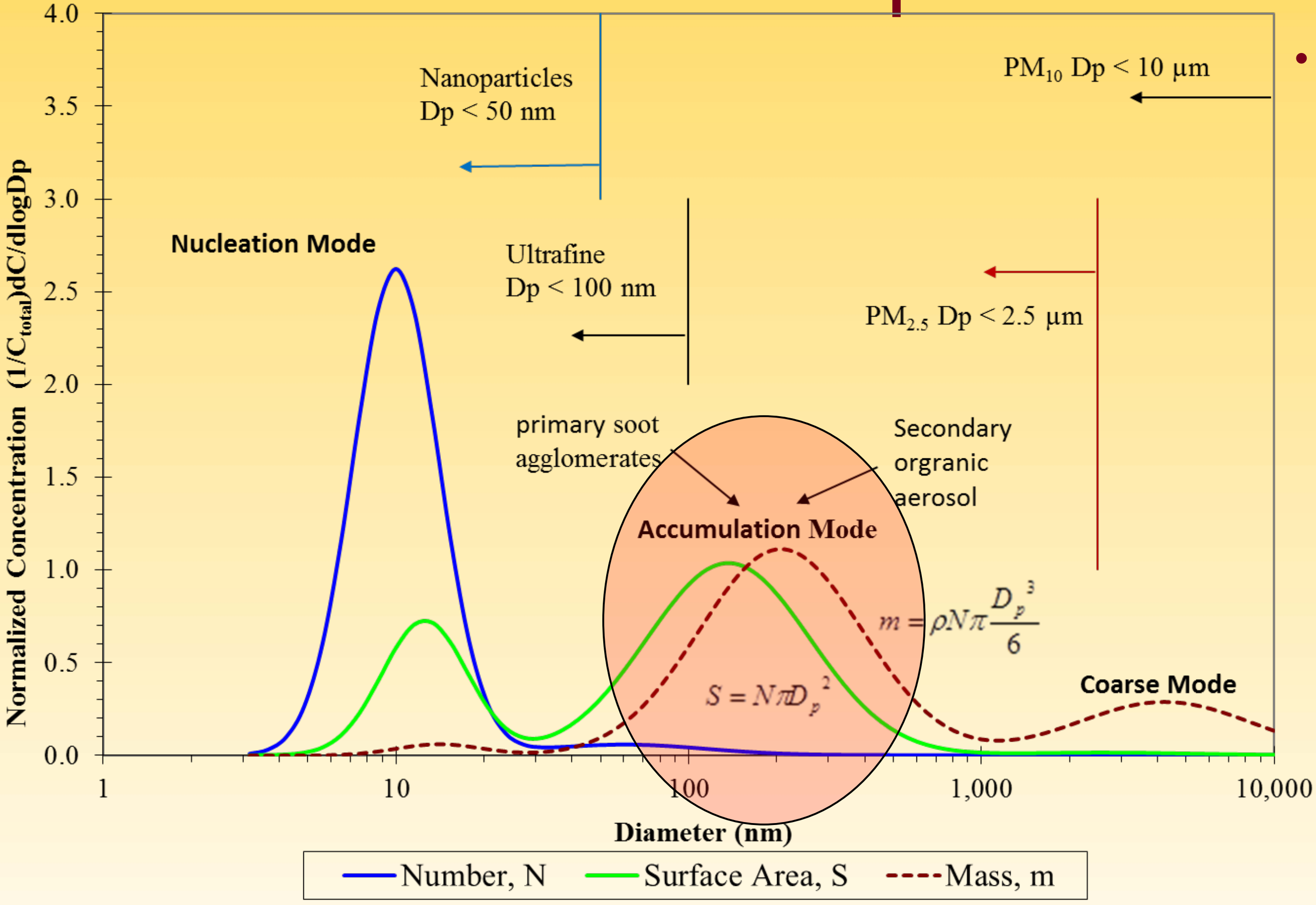


- The top plot shows the N/V ratio [particles/µm3] is influenced by ambient conditions
- The lower plot shows changes in the shape of the size distribution
  - The relative size of the semi-volatile nuclei mode is increased by an order of magnitude by decreasing ambient temperature from 23 to 10 ºC
  - Solid soot particles are not expected to change

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

If we are measuring number should we measure, solid, semi-volatile, or both?

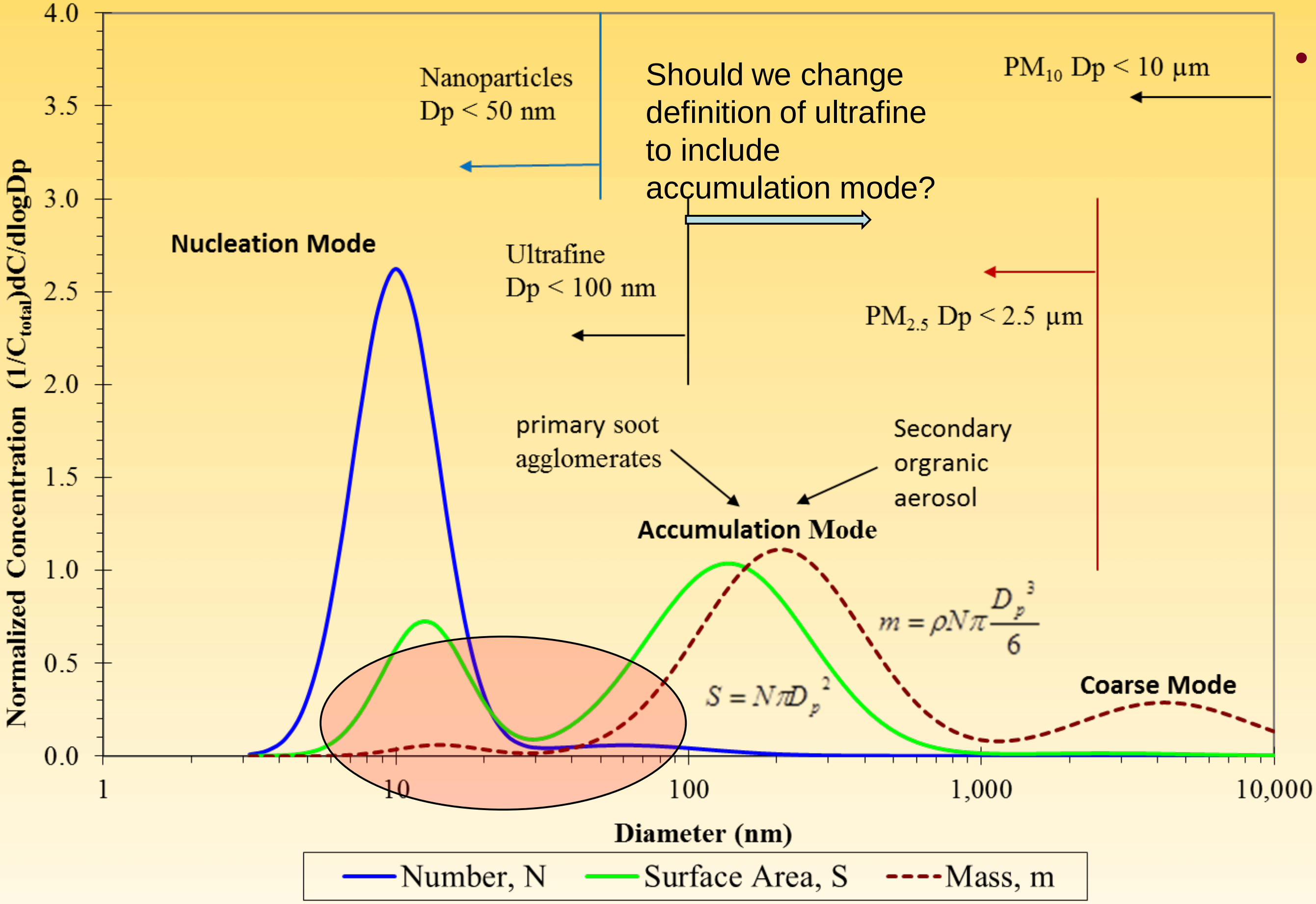
The accumulation mode contains most of the particle mass



- Accumulation mode
  - Typically 30 – 500 nm
  - Contains both primary and secondary particles
    - Primary – elemental and organic carbon, sulfates, ash
    - Secondary – secondary organic aerosol. sulfates nitrates.
  - ***Contains most of the mass, PM2.5***
  - Relatively long atmospheric residence time – days

Concentration proportional to area under curve in each size range

But ultrafine mass only captures a fraction of the accumulation mode



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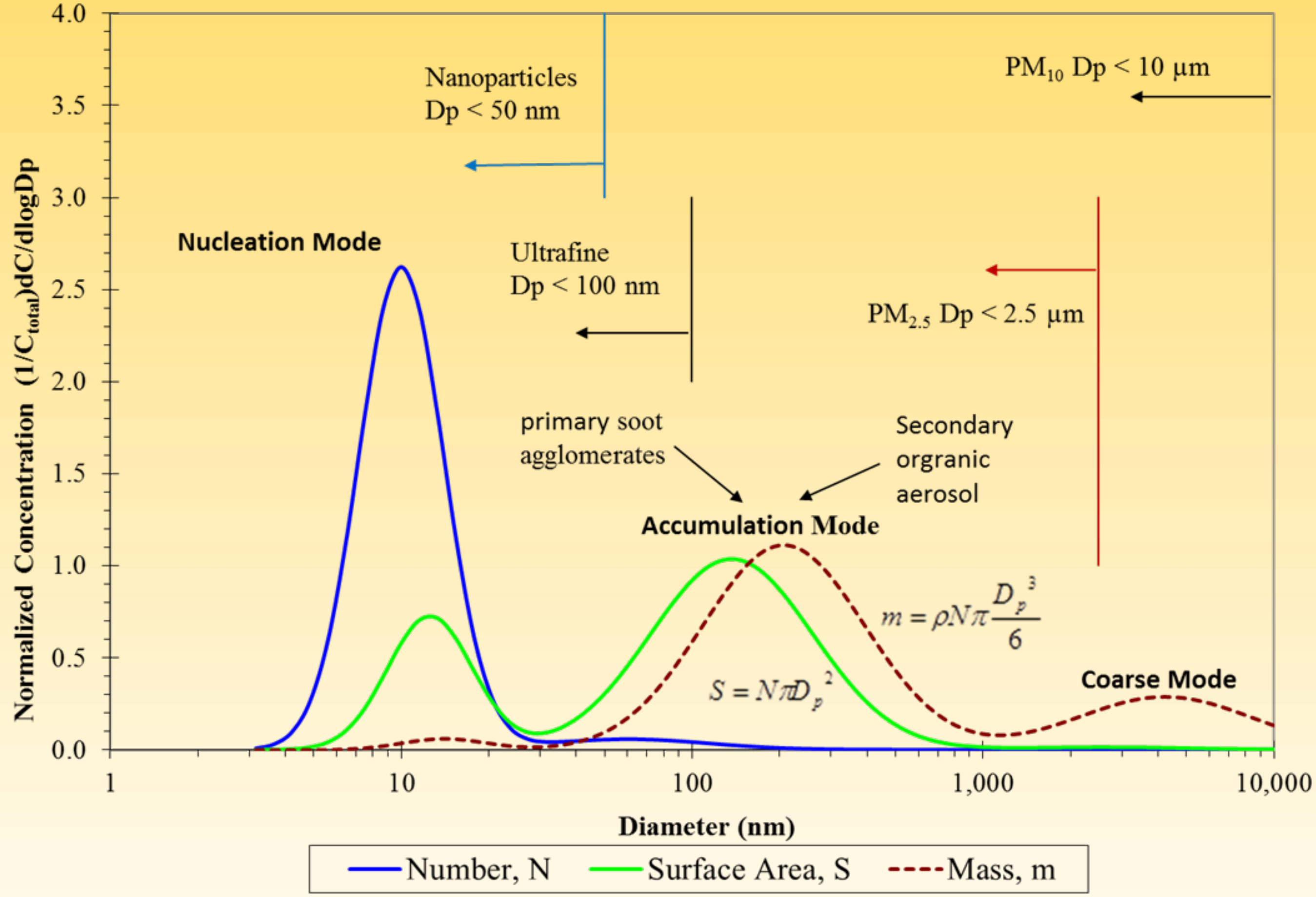
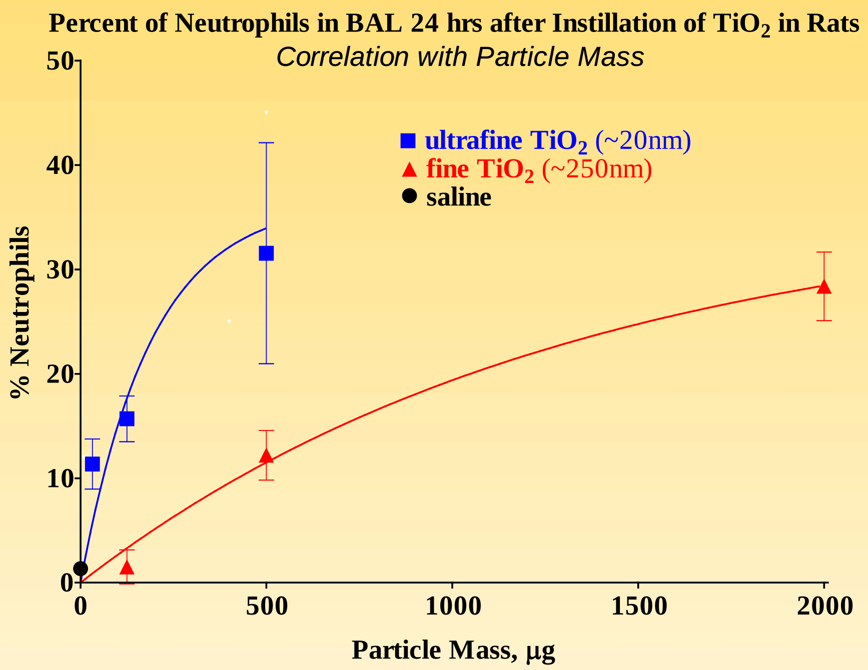
Concentration proportional to area under curve in each size range

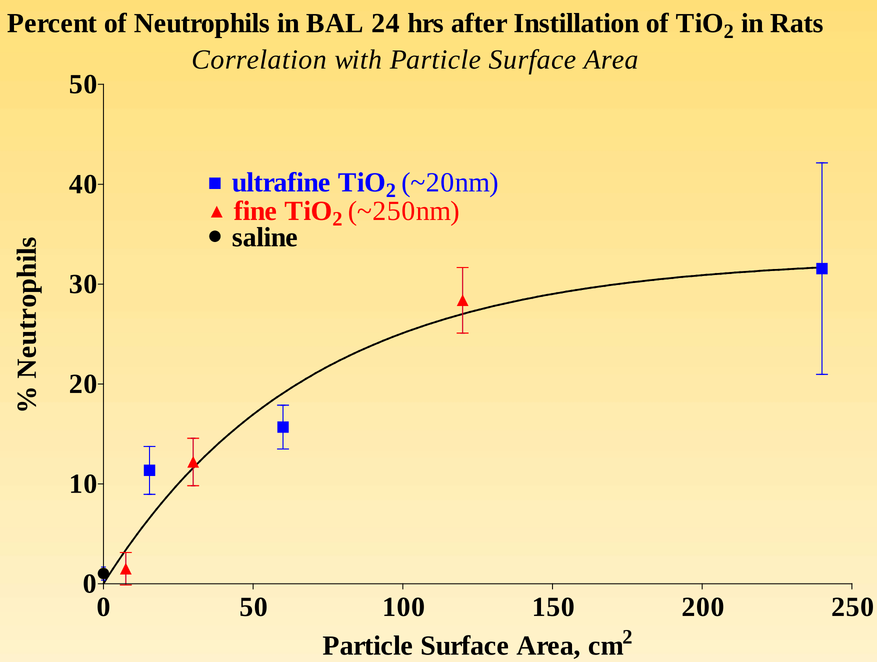
If we are measuring mass should we measure ultrafine, accumulation mode, or?

Surface area captures both the nucleation and accumulation modes



Is surface area is better measure of health effects than number, mass?

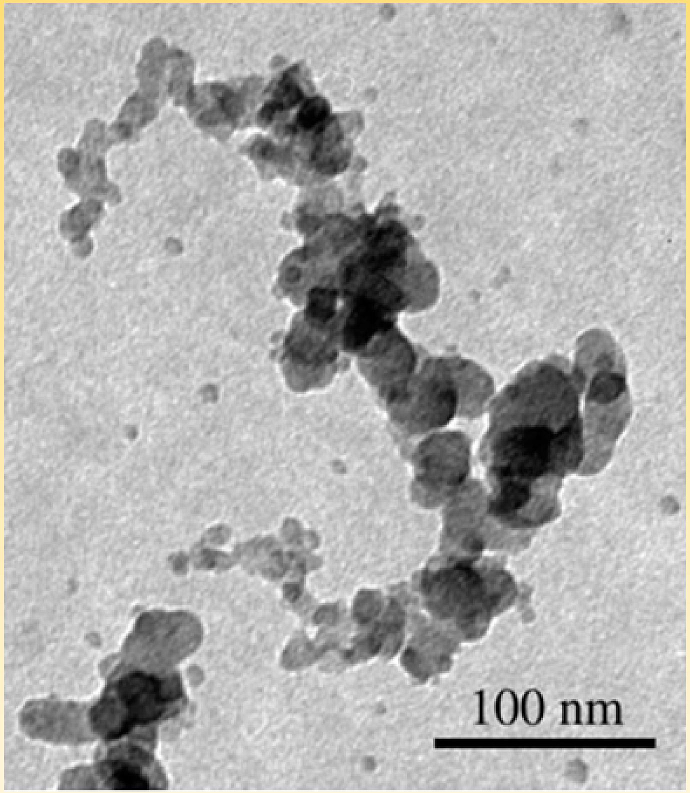




Oberdorster's work suggests best correlation of biological impact is surface area

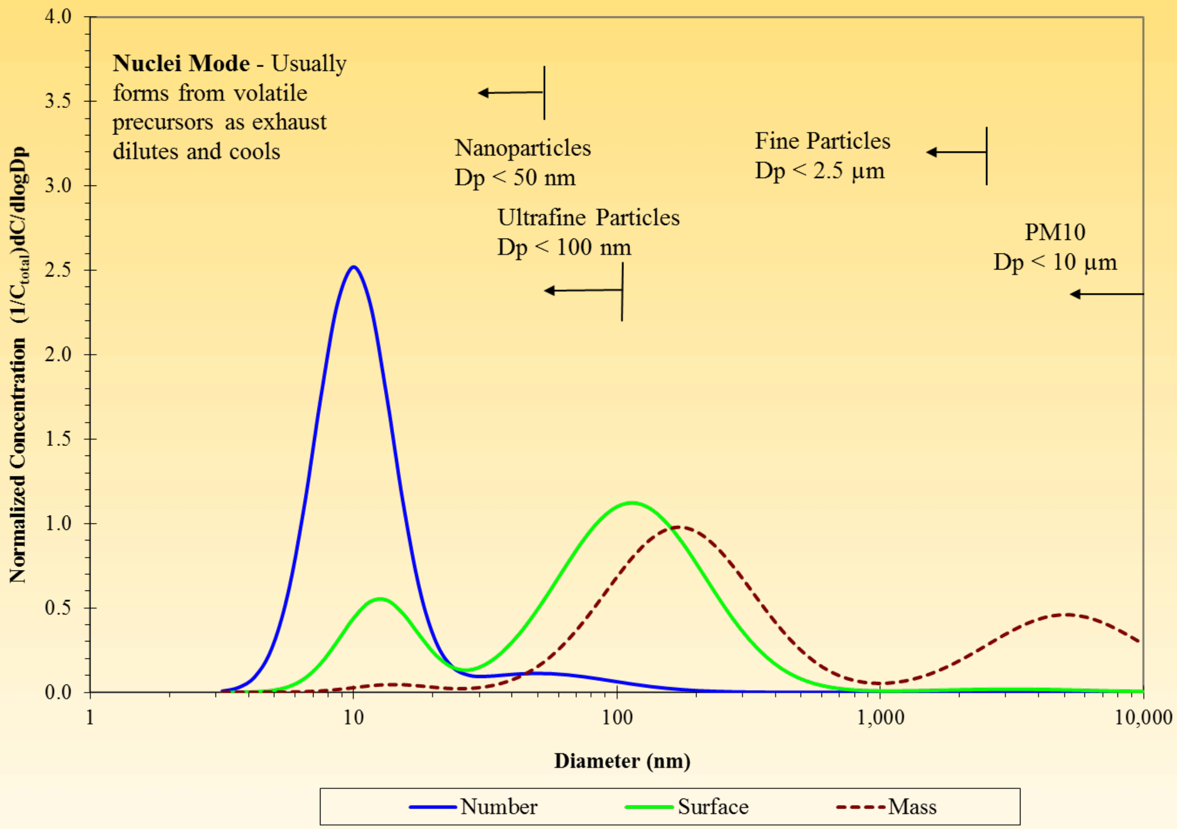
Oberdorster, G., Pulmonary effects of inhaled ultrafine particles, *Int. Arch. Occup. Environ. Health* **74**:1-8 (2001).

What is the surface area of this particle?



- The BET method determines the mass of non-reactive gas (N_2 CO_2, ..) in a monolayer on the surface of the particle. For carbonaceous particles this is usually close to the surface area of the individual roughly spherical particles comprising the aggregate
- The surface area determined by mobility sizing is the surface area of a spherical particle that has the same aerodynamic drag, it is related to external envelop area available for momentum transfer
- The active surface area is related to the amount of electrical charge transferred to a particle under controlled charging conditions. It depends on external envelop area and factors related to mass transfer and charge equilibrium

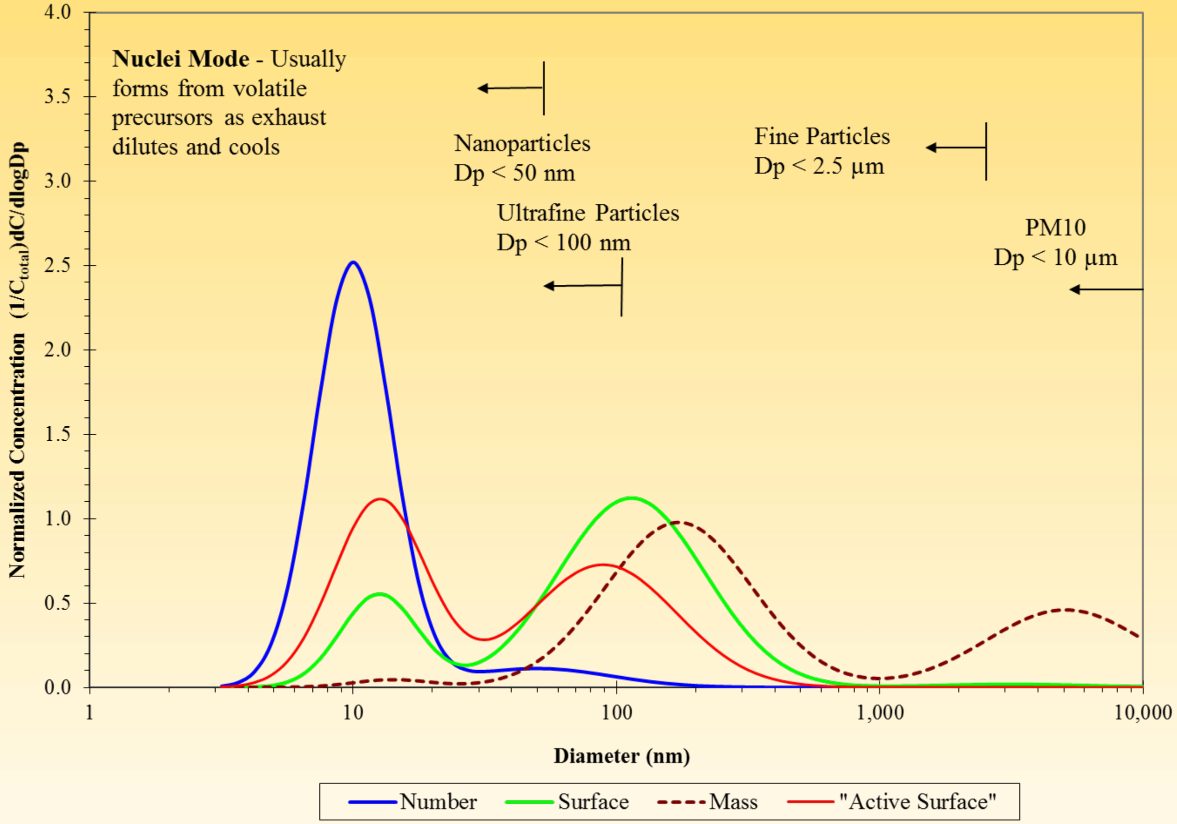
How do we measure number, ultrafine mass, accumulation mode mass, surface area?



- Condensation particle counter
  - Number
  - Expensive
- Sizing instruments (SMPS, FMPS, EEPS, DMS, ELPI)
  - Number
  - Surface
  - Mass (with effective density)
  - Expensive
  - Require skilled operators
- Cascade impactor
  - Ultrafine mass
  - Accumulation mode mass
  - Not real time
  - Time consuming

- Is there a simpler low cost metric that could be widely deployed? Maybe.

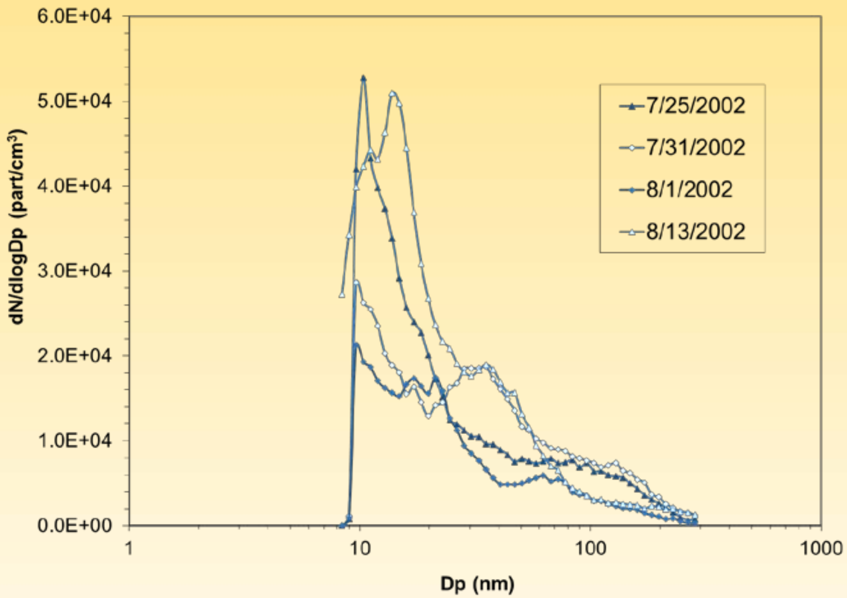
Like surface area, active surface captures both nucleation and accumulation modes



- Inexpensive instruments are available that measure so called "active surface" or "lung deposited surface area, LDSA"
- Active surface distribution shown in light orange
- Captures both nucleation and accumulation mode
- These instruments respond to $Dp^{1.1}$ to $Dp^{1.7}$ depending on details of charging and collection system

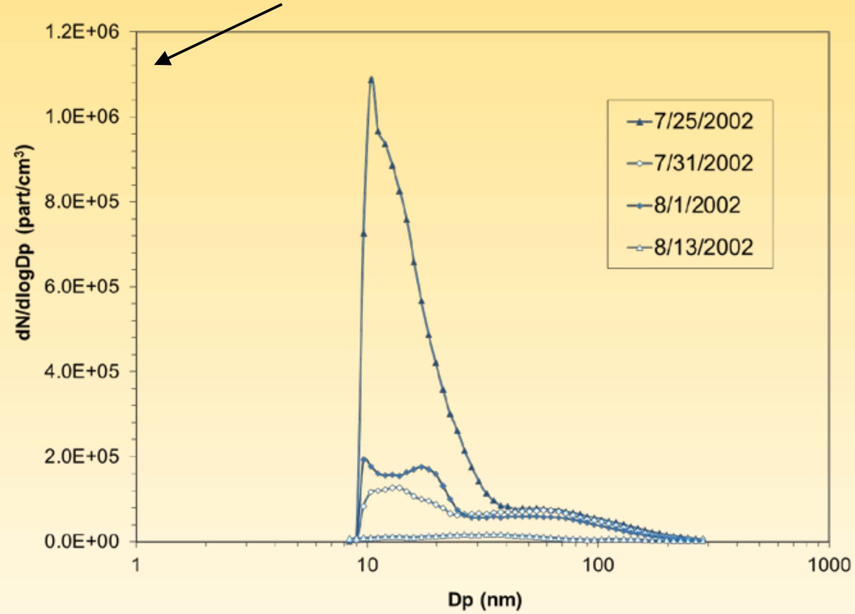
On-road data for examining relationships among, UFP, N, m accum, LDSA

Rural roadway background, each SD average of ~ 30 SMPS scans

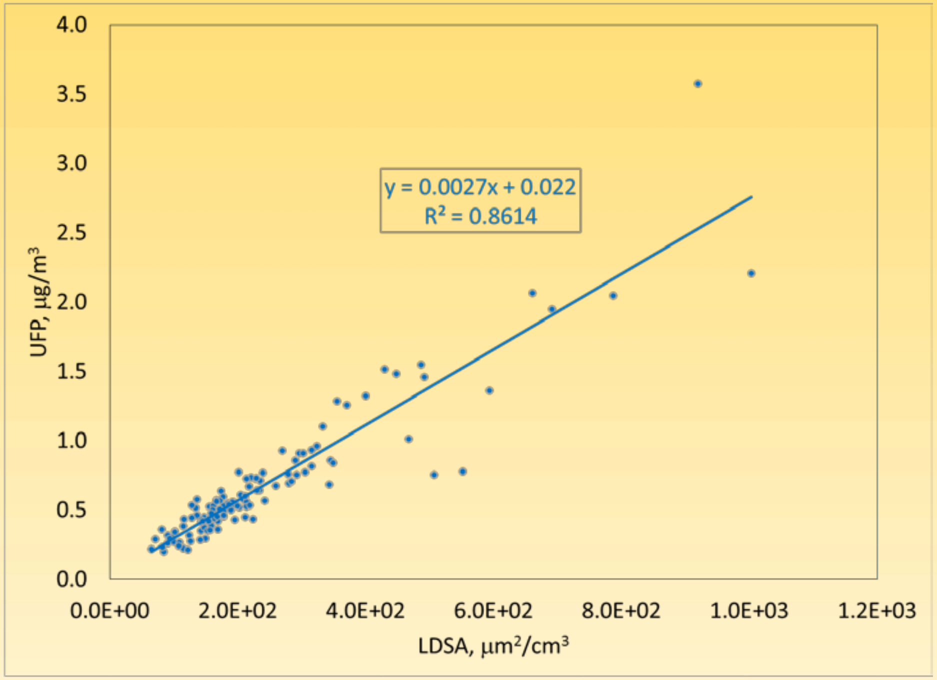


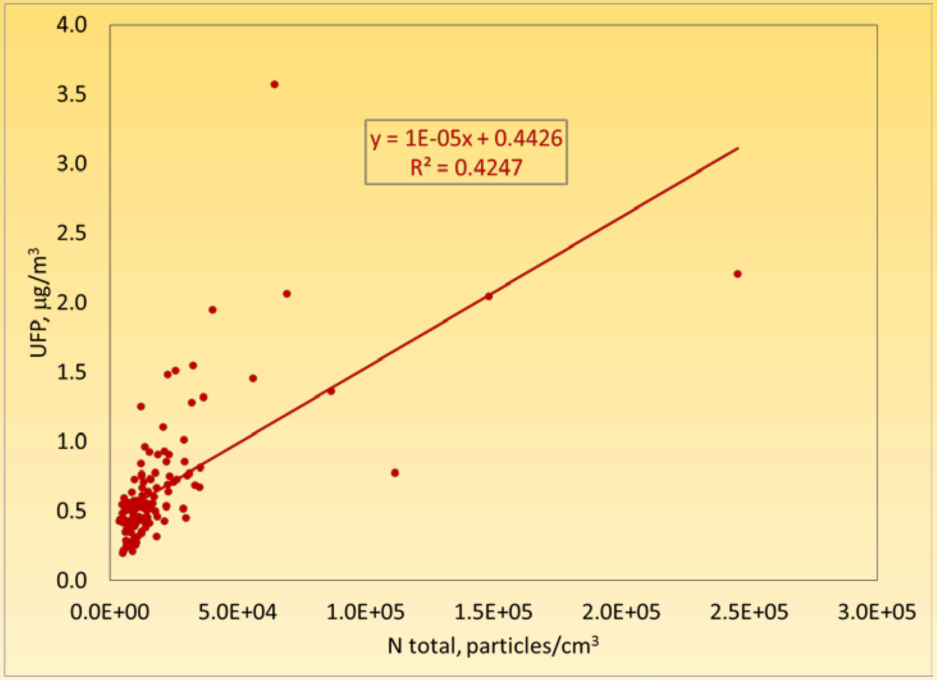
Rural roadway diesel plume sniffing, each SD average of ~ 30 SMPS scans

20 x larger scale



How well does ultrafine mass (UFP) track with N total and LDSA? Roadway background



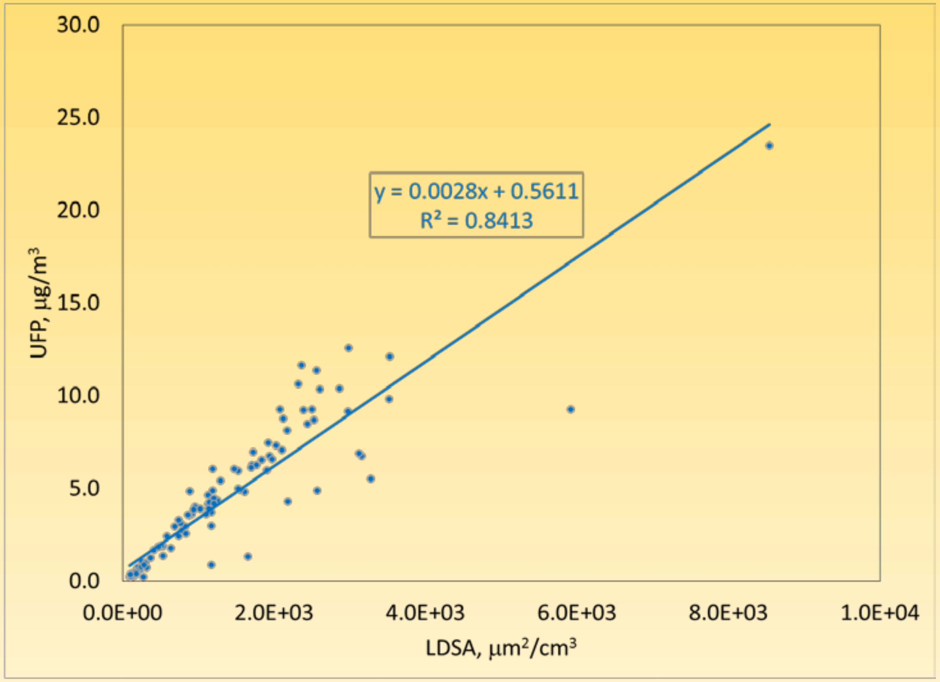


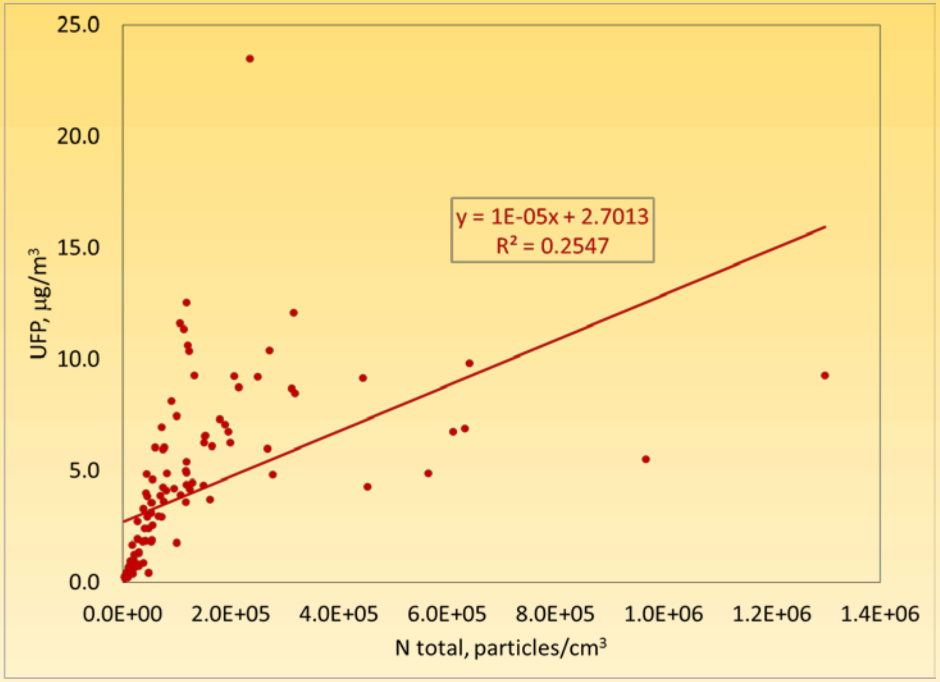
Correlation

	UFP	*m accum*	*LDSA*	*N total*
UFP	1			
m accum	0.729682	1		
LDSA	0.928117	0.821291	1	
N total	0.651714	0.430176	0.809101	1

Note that both UFP and accumulation mode mass are well correlated with LDSA

How well does ultrafine mass (UFP) track with N total and LDSA? Plume measurements





Correlation

	UFP	*m accum*	*LDSA*	*N total*
UFP	1			
m accum	0.809428	1		
LDSA	0.917229	0.824189	1	
N total	0.504682	0.266461	0.727116	1

Note that both UFP and accumulation mode mass are well correlated with LDSA

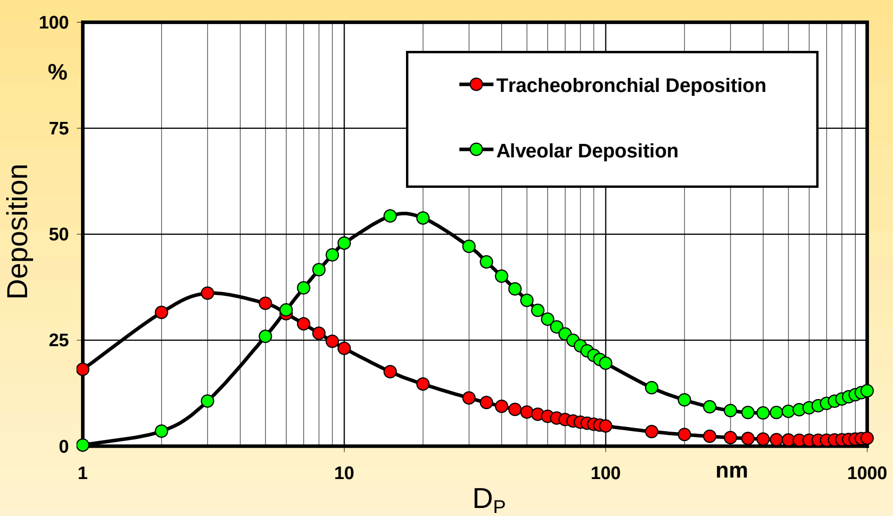
What is the best metric for ultrafine particles?

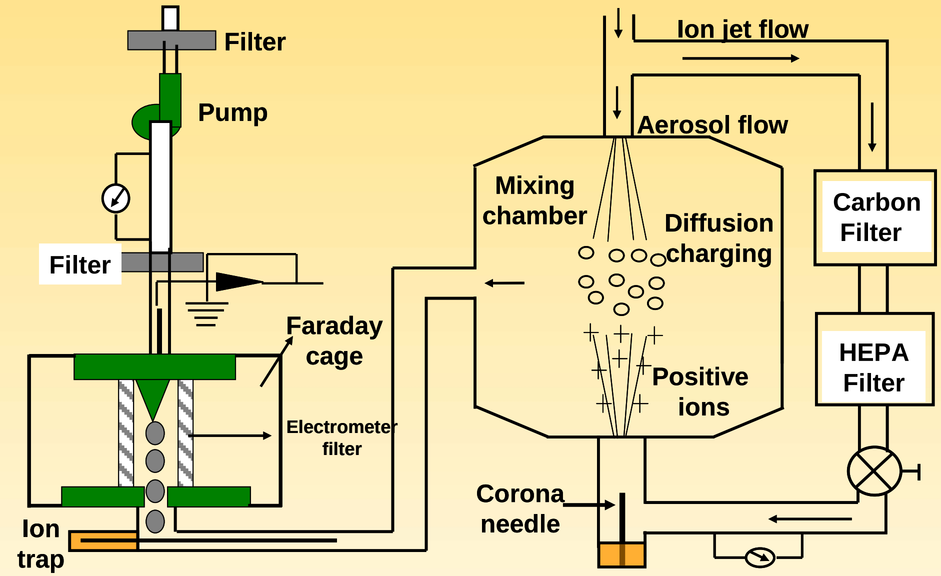
- Assume we want a low cost surrogate for UFP mass
- Instruments and supporting activity should be inexpensive to allow widespread deployment
- Both number and LDSA meet that requirement
- On-road data examined suggest LDSA more strongly correlated to UFP than number - relatively small data set
- Many of you have extensive size distribution data – see what correlations between different weightings suggest
- I have said nothing about chemistry but solid and volatile measurements give useful insights

Thank you. Questions?

Backup slides

A modified EAD has been developed that measures surface area deposited in the lung, LDSA – TSI NSAM





Courtesy TSI Inc.

The miniDISC – a variation on the electrical diffusion battery, measures both N and LDSA

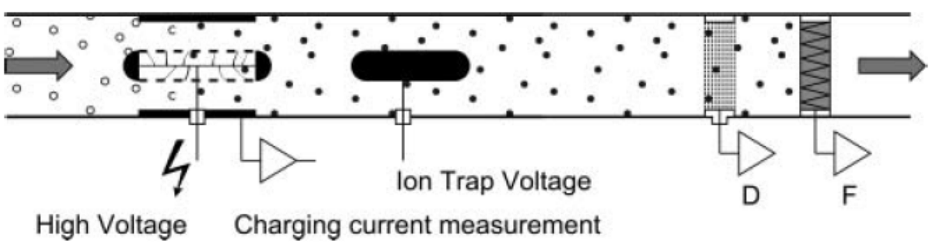
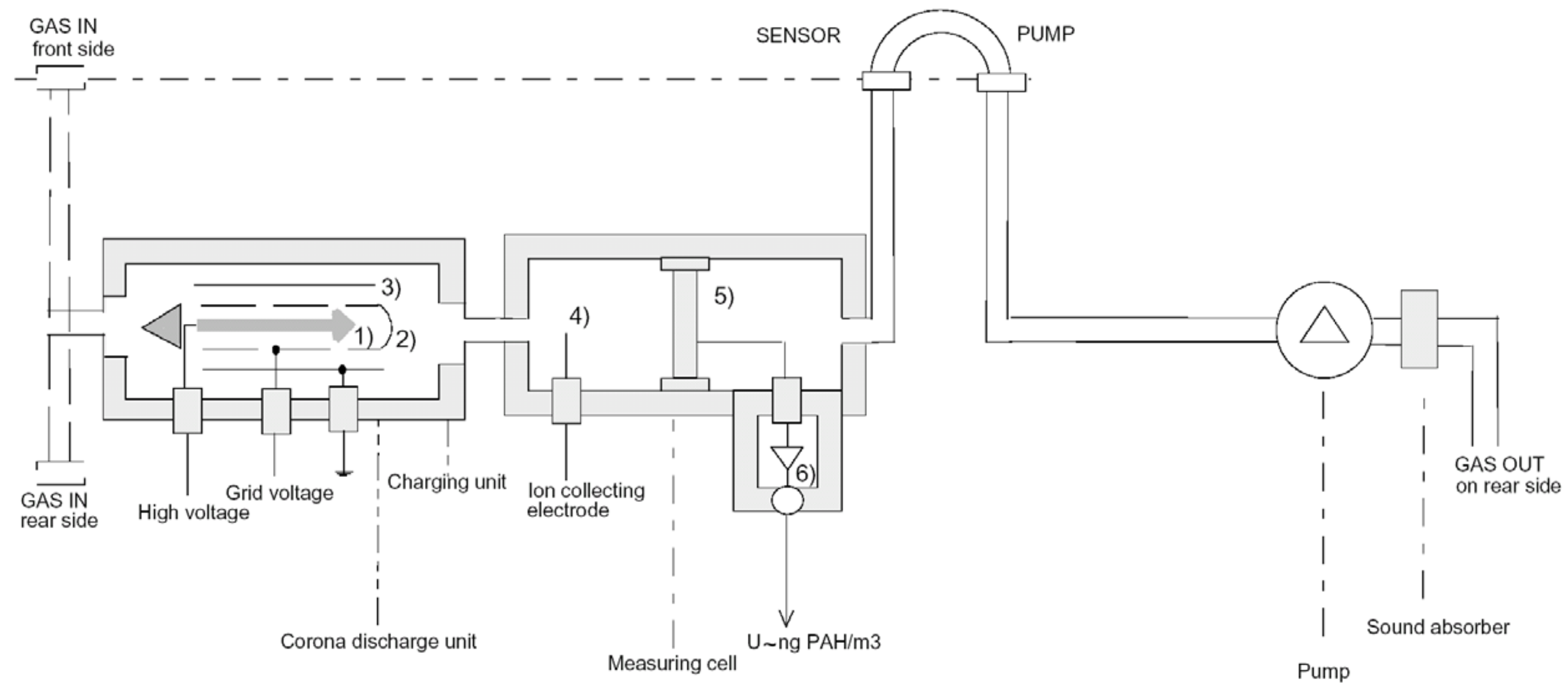


FIG. 1. Schematic overview of the miniature DiSC: Aerosol is charged in a unipolar corona charger which controls the charging current, excess ions are removed in the ion trap, and the charged aerosol is measured in two electrometer stages (D = diffusion stage, F = filter stage), allowing for particle sizing and counting.

- Low cost portable instrument
- An upstream charger puts a unipolar charge on the particles
- An ion trap removes ions carried over from the charger but not particles
- A diffusion screen preferentially collects charge from smaller particles
- A filter stage measures the current from the remaining charged particles
- **Data inversion assumes a unimodal log normal aerosol**
  - Estimates total number
  - Mean diameter
  - Lung deposited surface area

M. Fierz , C. Houle , P. Steigmeier & H. Burtscher (2011) Design, Calibration, and Field Performance of a Miniature Diffusion Size Classifier, Aerosol Science and Technology, 45:1, 1-10

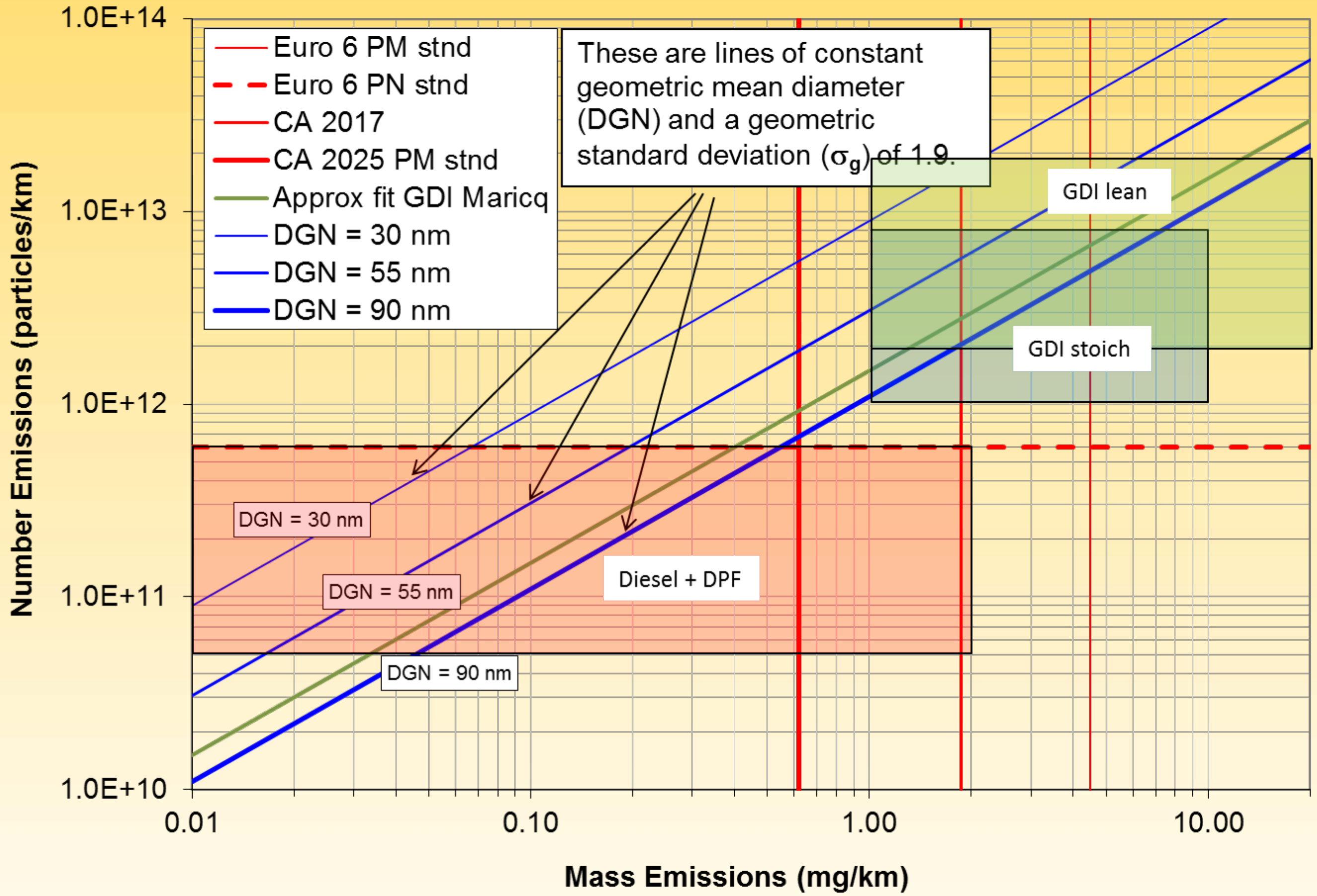
Diffusion Charger (DC)



1) Corona tip
2) Grid
3) Ground tube
4) Electron collecting electrode
5) Measuring filter
6) Charge amplifier

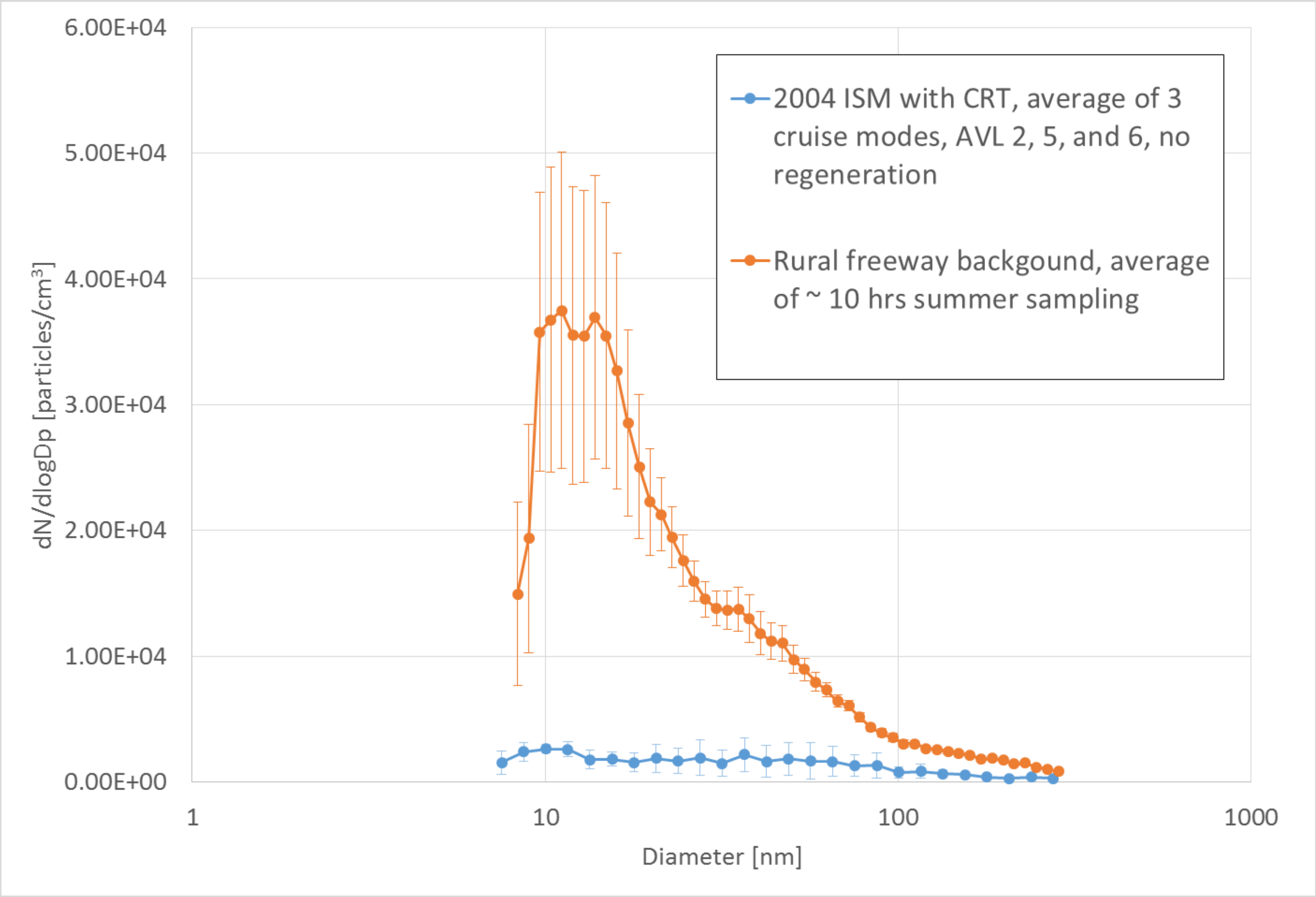
Courtesy Matter Engineering

Passenger car particle standards, mass, number, size

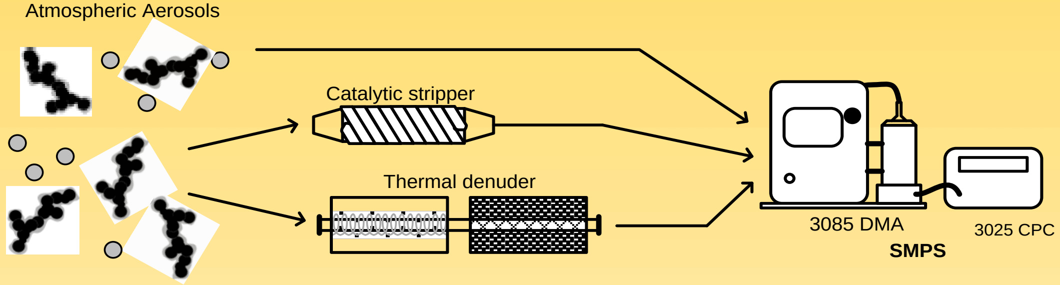


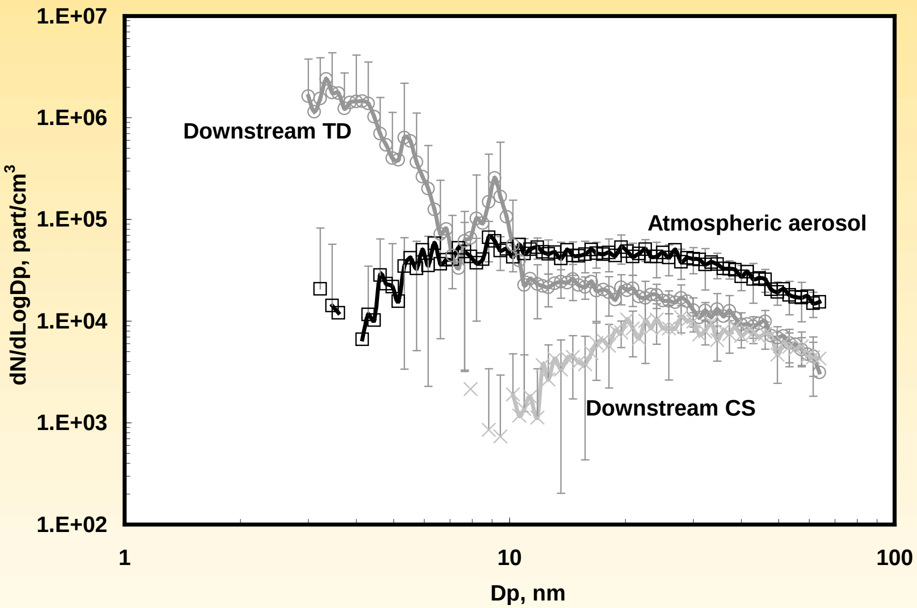
Trend line based on Maricq, 2010, shaded areas based on data from Giechaskiel, et al., 2012

Engines with particle filters often air cleaners, exhaust cleaner than rural background



Thermal denuders that evaporates volatiles without total removal may re-nucleate particles





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