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Australian Government
Department of Defence
Defence Science and Technology Group

Importance of Structural Properties in Diesel Particulate Characterisation

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Introduction

- Early 2000s
  - Weight of evidence provided causal link between adverse health effects and exposure to submicron sized diesel particulates
- Late 2000s
  - Mounting evidence of detrimental brain effects from exposure to Ultrafine particles (UFP)
- Geometrical complexity of UFP
  - Structural properties and characteristics
  - Exposure assessment in Collins class
    - Including results of DST Group measurements
  - Risk associated with exposure
    - Possible implications on RAN submariner cognition
  - Mitigation measures

Diesel Particulates (DPM)

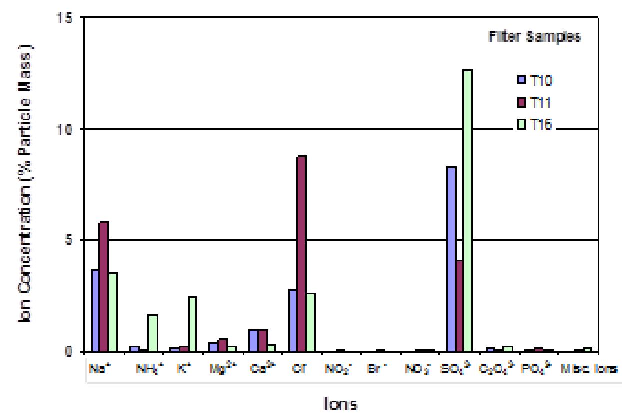
- Known Human Carcinogen (Group 1 - IARC 2012)
  - Non-metal underground mine workers (5670)
  - Av 128.2 µg/m^3 EC , 78 -216 µg/m^3 EC
  - Exposure Category 32 – 64 µg/m^3 EC, 20 y
- Much studied toxicant
  - US military vehicles, maritime sources
  - Railroad, truck drivers, German potash miners
  - Lower emissions since 1990s
  - DPM Filters in US (2007)
  - Emissions from legacy military platforms

- Collins Class (1990s) exposure assessment (SAMAP 2011)
  - 60 – 80 µg/m^3 DPM (25 – 30 µg/m^3 EC)
  - MSHA (200 µg/m^3 DPM or 125 µg/m^3 EC) and BMA (100 µg/m^3 EC)

Chemical Composition

- Organic carbon (OC)   where TC = EC + OC

- Polycyclic aromatic hydrocarbons (PAH)
  - Carcinogens
  - Size and mass distribution (Leist)
- Inorganic ions
  - Combustion products (NO_3, C_2O_4, SO_4)
  - Lubricants, fuel catalyst metals, sea salt
- Ultrafine (UFP) and Nanoparticles
  - Metals are more toxic than PAH

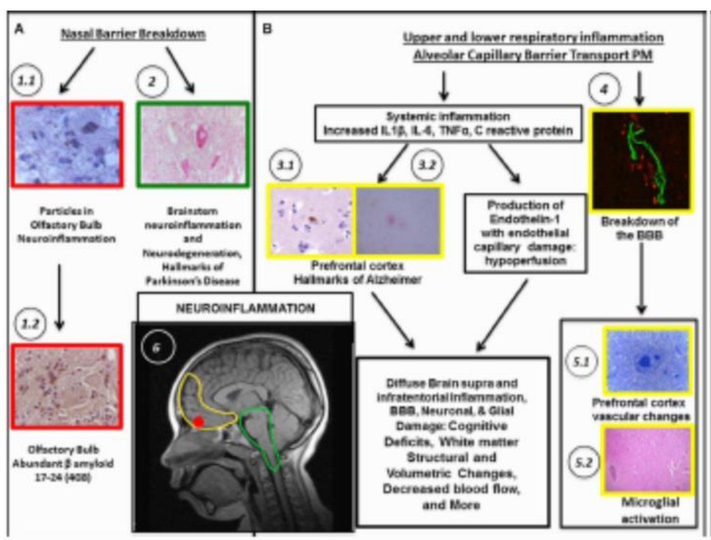


Ultrafine Exposures and Cognitive Deficits

- Mexico City PM2.5
  - Constant 25 ug/m3
  - UFP source is predominantly vehicular DPM
- Prefrontal cortex is target region
  - UFP initiates disruption of nasal and olfactory barriers
  - Breakdown of Blood-Brain Barrier (BBB) and deposition of UFP
  - Neuroinflammation, neurodegeneration (Alzheimers and Parkinsons Disease (PD) neuropathology) in autopsied children and young adults
  - CNS dysfunction (memory, executive, emotion), white matter lesions, altered brain structure in children and young adults (MRI)
- Highly exposed adults exhibited poor performance in cognition but general intelligence in normal range.

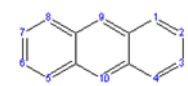
Transport Mechanism (Post Mortem)

- PM and UFP in cells of nasal barrier
- Transport of UFP Metals on PM to OB neurons
- Translocation of UFP to frontal cortex blood vessels and neurons
- Red blood cells overloaded with UFP and nanoparticles



Exposures to DPM Components

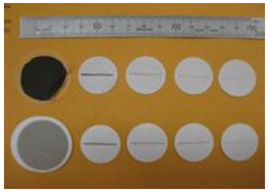
- Black Carbon (EC)
  - Cognitive deficits in children (Boston)
- Metals (Mn) used in engine manufacture
  - Parkinsons Disease-like pathology in rats
- Pre-natal exposure by PAH (Los Angeles)
  - Detrimental effects
  - Brain white matter development
  - Cognition
  - Behaviour in later childhood



Metrics for Inflammation Response by UFP

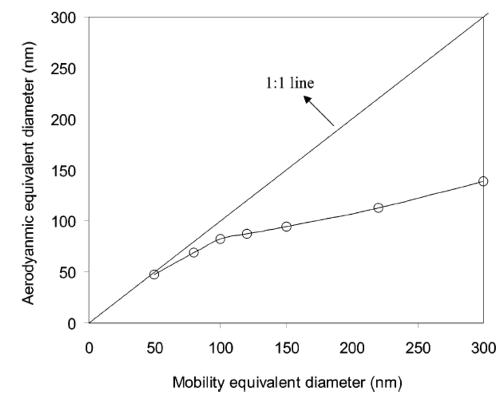
- Lung inflammation response correlated with N, particle size , not surface area (Witmack in EHP 2007)
- Active surface area instruments use collision cross section based on adsorption kinetics, not adsorption area
- Surface area related to size of nuclei of agglomerate, not particle size distribution (PSD)
  - Long analysis times (2-3 days)

- Mass and PSD measurements
  - Real time
- Geometrical complexity and multi-components of UFP
  - Size, morphology and composition

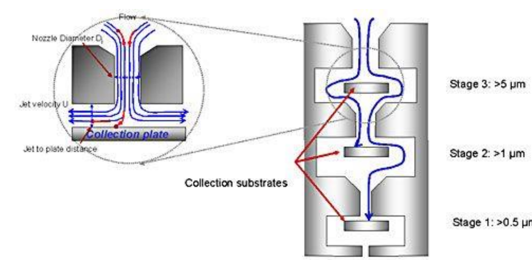


Collins Class UFP Structural Properties

- Fractal and shape dimensions, effective density
- Relationship between mobility and aerodynamic size
- Mobility
  - Charge, size, shape
- Aerodynamic
  - Drag, inertial, gravitational

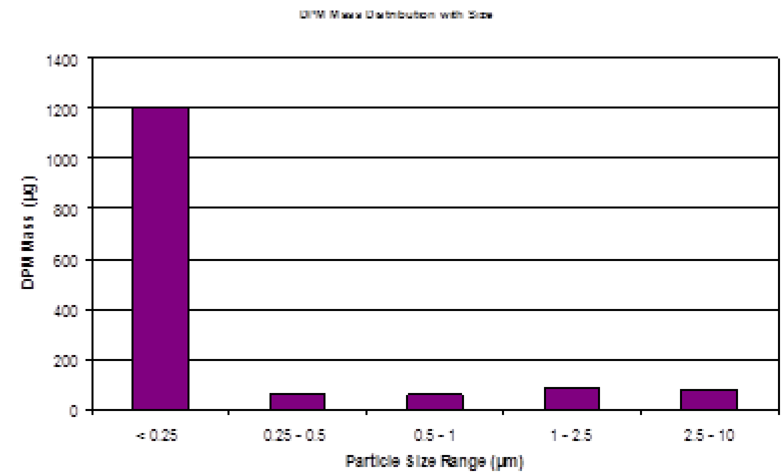


- Determined from measurements of mobility PSD using SMPS (11 nm – 1um) and size fractionated mass using impactors
  - Sioutas and MOUDI

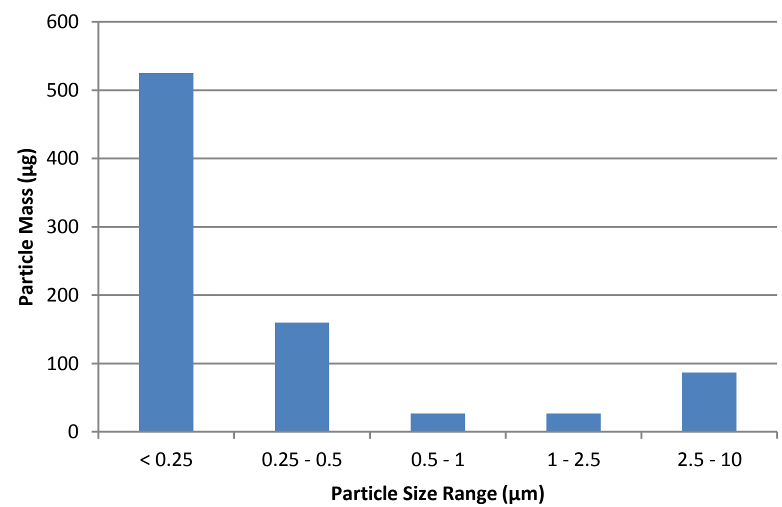


Euro 0 Engine Mass Size Distributions (MSD)

- Collins Class
  - Hedemora V18B/15UB (7.3 L)
  - Mass < 0.25 µm (250 nm)
  - Max engine load

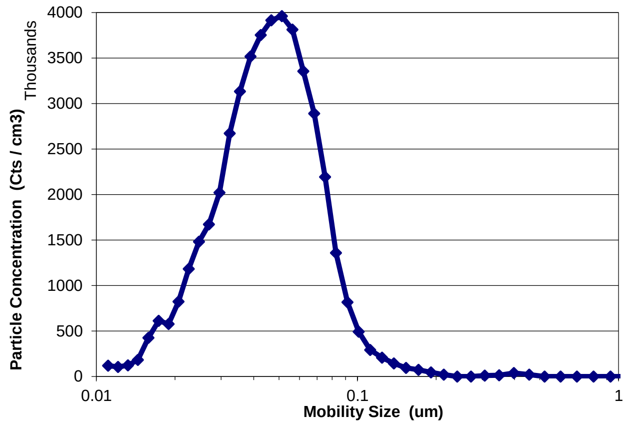


- Unimog Truck (1 L)
  - MB L6 OM353.939
  - Mass < 0.25 µm (250 nm)
  - Variable load and Idling



Typical Particle Size Distributions (PSD)

- MB OM353.939 Euro 0
  - Peak 51.3 nm
  - 4 x 10^6 cts/cm3 (Idling)
- Euro 4 (Burtscher 2005)
  - Mean diameter (Geom SD)
  - 60 nm – 100 nm
  - Peaks 70 – 80 nm
  - Insensitive to engine load
  - No effect of engine size
  - No effect of engine type



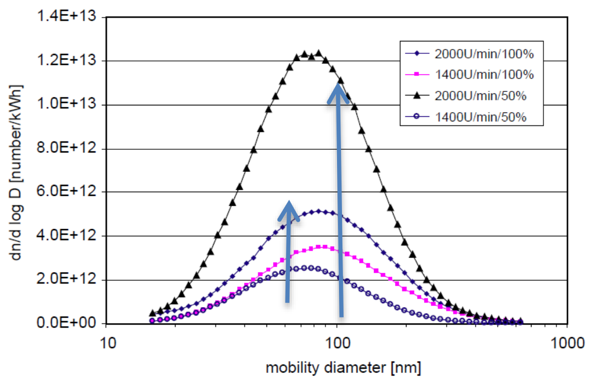
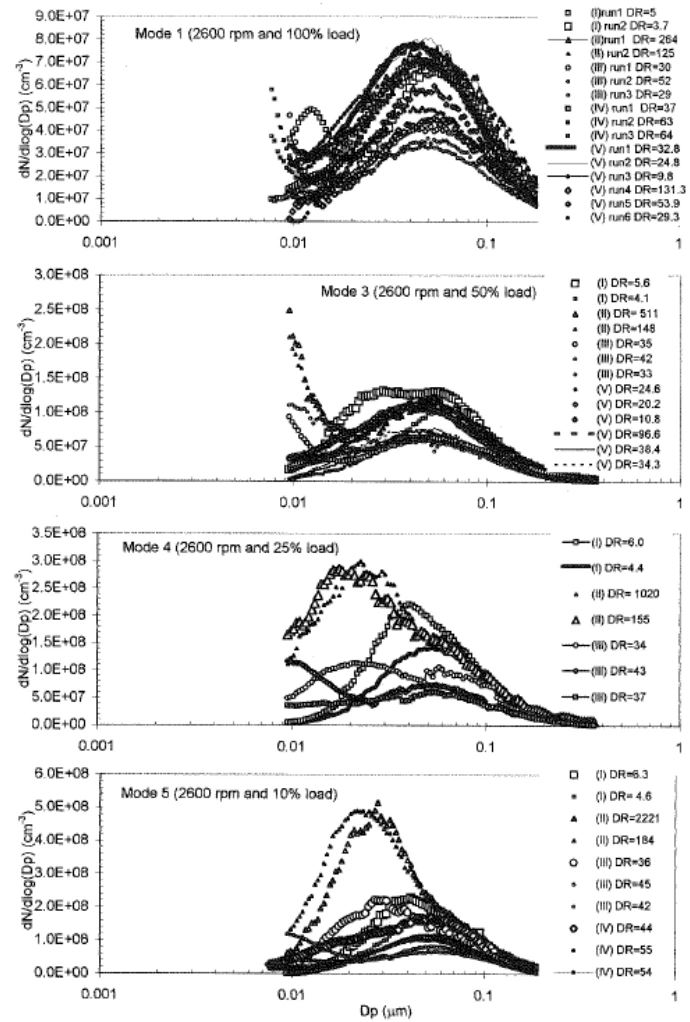


Fig. 3. Size distributions of diesel agglomerates emitted from a heavy-duty diesel engine, measured on an engine test bench equipped with a partial flow dilution system. The size distribution can well be approximated by a lognormal distribution. Mean diameter: 60–100 nm. As shown by a large number of measurements with different engines at different operating conditions, the geometric standard deviation stays fairly constant (Harris and Maricq, 2001, 2002). Depending on fuel, lubricant oil, and operating and sampling conditions, a second peak in the range 10–20 nm may occur (nucleation mode, see later).

Effect of Dilution and Load on Mobility Size

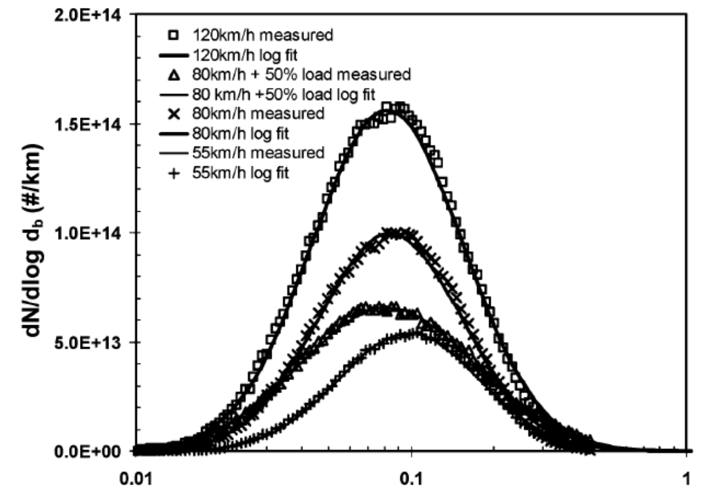
- 1995 Perkins Phaser
- Model AE 762337B
- Turbocharged
- EPA Tier 1
- Peak 40 nm – 55 nm
- 20 nm – Fuel or Sulphuric acid droplets



IGURE 2. Particle size distributions (after dilution correction) at selected modes measured with SMPS over five campaigns.

Morphological Properties, Engine Size and Load

- Audi A4 1.9 L TDI (car)
- Volvo DH 10A -285 (Bus)
- Sisudiesel 420 DSRE (Tractor)
- Various engine sizes , TDI
- 1.9 L (4), 9.6 L (6), 4.2 L (4)
- Euro II, II and I, 23 – 2000 ppm S
- Fractal decreases with increasing load
- And particle size
  - Small 2.3 – 2.9 (sphere = 3)
  - Large 2 – 2.75
- Density decreases with increasing size



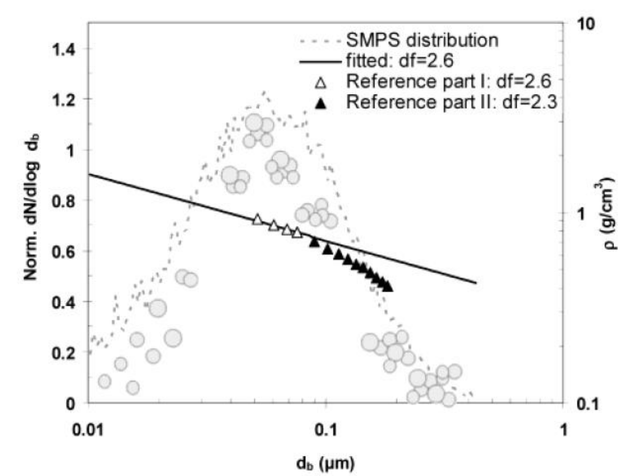
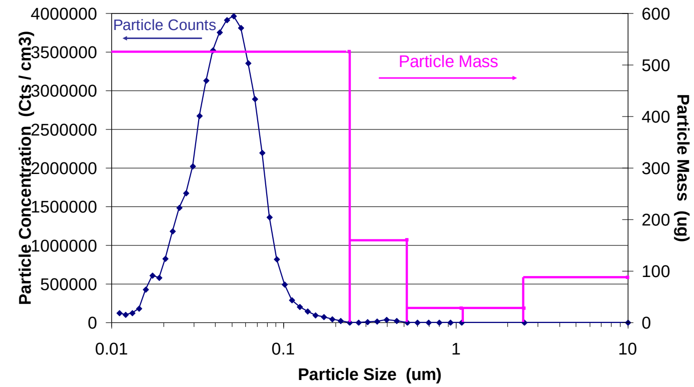
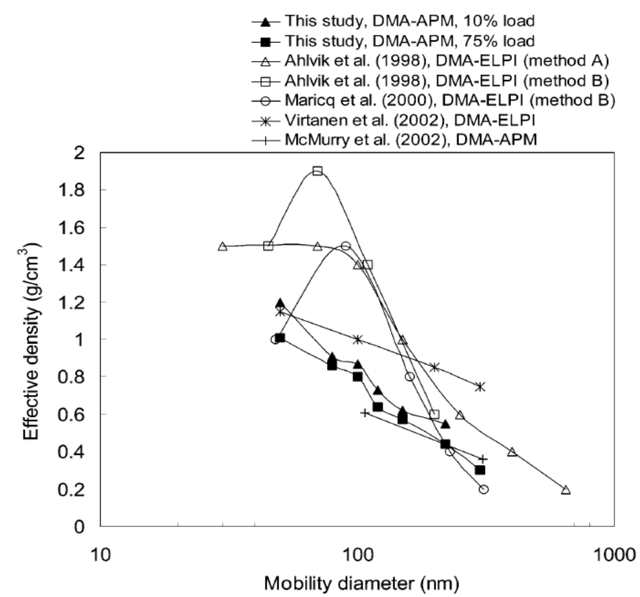


FIGURE 6. Fitted density profile compared to reference method. Suggestion for different morphologies in different size regimes sketched in the figure.

Estimated Hedemora UFP Size Distribution

- Difficulty obtaining PSD
- High performance engine
  - 10 ppm S fuel for aftertreatment
- Expect peak 50 – 80 nm
- Use surrogate engine PSD
  - MB engine PSD (0.01 – 1 µm)
  - Impactor mass distribution
    - (< 0.25 µm – > 2.5 µm)
- Effective densities
  - Several engines



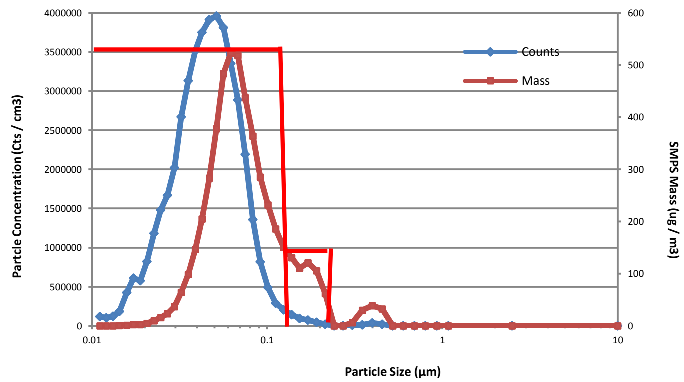


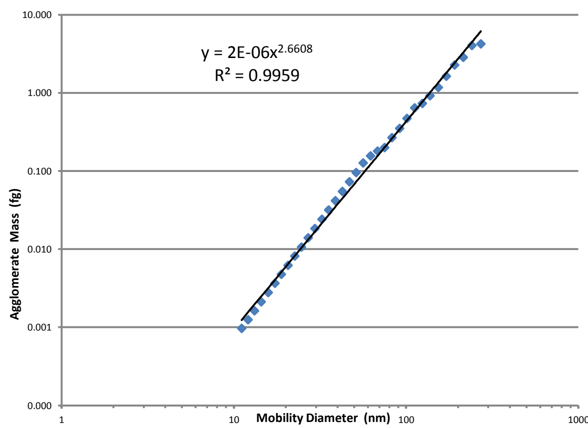
Fractal Dimension From Mass Distribution

- Since mass is constant over size range 50 – 220 nm,

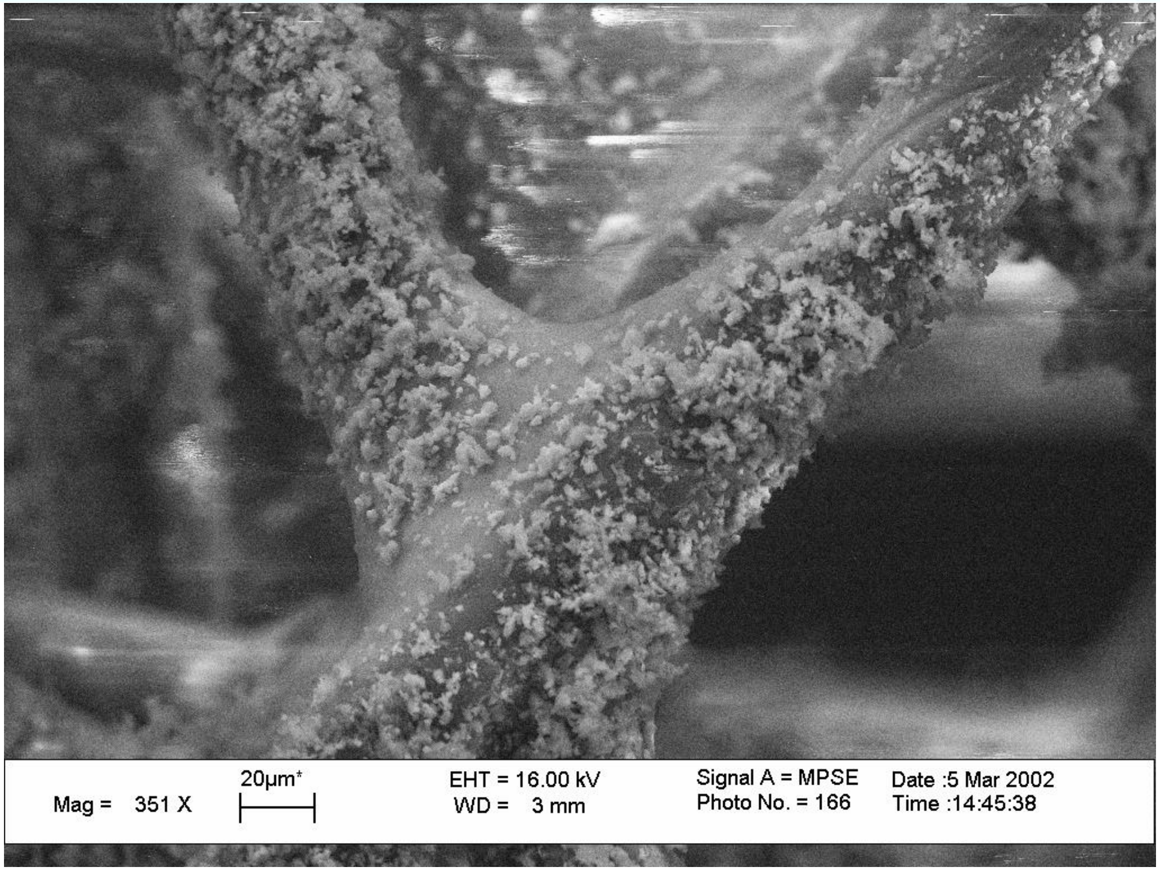
$$M = k_m \left(\frac{D_{\text{mobility}}}{d_p} \right)^{D_{\text{fm}}},$$

  - where $d_p \approx D_{mob}$ for size range
  - k_m is the prefactor
  - D_{fm} is the fractal dimension





- For assumed Hedemora PSD,
  - D_{fm} = 2.66 Kittelson = 2.35
  - K_m = 2×10^{-21} Kittelson = 7.35×10^{-21}
  - UFP are compact spherules
  - Collins Class *compact spheroids* 100 – 400 nm (Mazurek 2003)



SEM of DPM on Foam Filter in Collins Class

Discernible small particles are ~ 1µm and 100 nm and 400 nm Ultrafine particles were determined on isolated surfaces.

Dynamic Shape Factor

- Volume equivalent diameter
  - Peaks of different diameters with same masses
  - 62 - 68 nm and 138 - 191 nm

$$x = \frac{D_{\text{mobility}}/C_{\text{mobility}}}{D_{\text{volume}}/C_{\text{volume}}},$$

  - where C is the slip correction factor
- Shape factor (Sphere = 1)

χ = 1.2 for 68 nm Kittelson = 1.3 for 80 nm

χ = 1.9 for 191 nm Kittelson = 2.0 for 200 nm

- 68 nm particles - *compact* spherules
- 191 nm particles - *agglomerated*

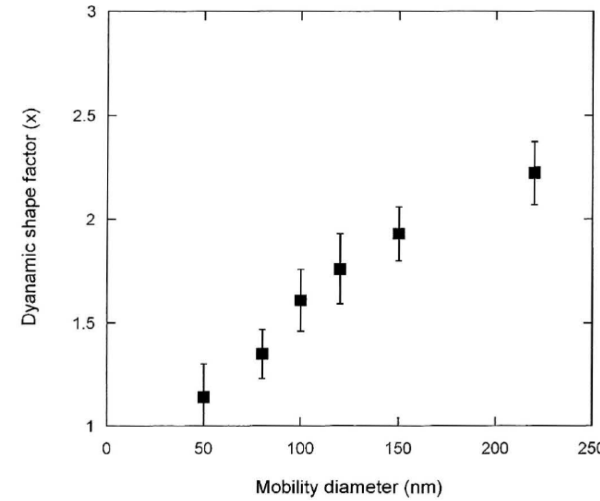
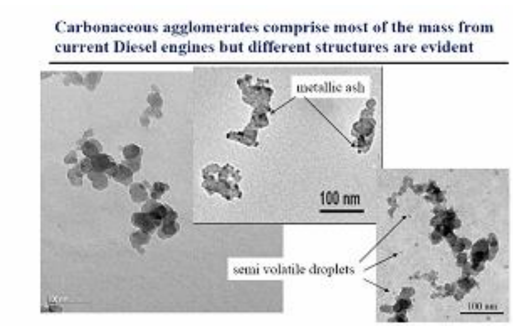
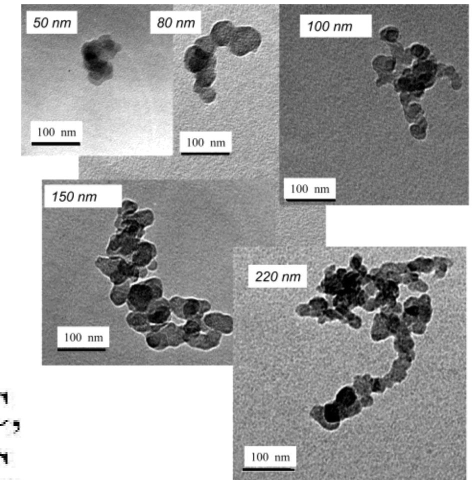


Figure 11. The dynamic shape factor as a function of mobility diameter. The error bars represent the standard deviations. John Deere engine, 50% load, 1400 rpm, EPA fuel (360 ppm S).



Inherent Density and OC Content

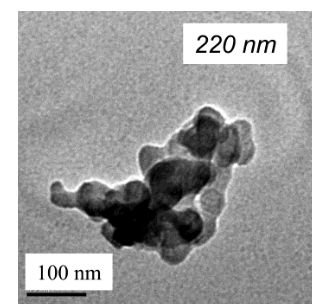


- Inherent density of EC core given by

$$\rho_{\text{inherent}} = \frac{M_{\text{OC}} + M_{\text{EC}}}{V_{\text{OC}} + V_{\text{EC}}} = \frac{M_{\text{OC}} + M_{\text{EC}}}{\frac{M_{\text{OC}}}{\rho_{\text{OC}}} + \frac{M_{\text{EC}}}{\rho_{\text{EC}}}} = \frac{x + (1 - x)}{\frac{x}{\rho_{\text{OC}}} + \frac{1-x}{\rho_{\text{EC}}}},$$

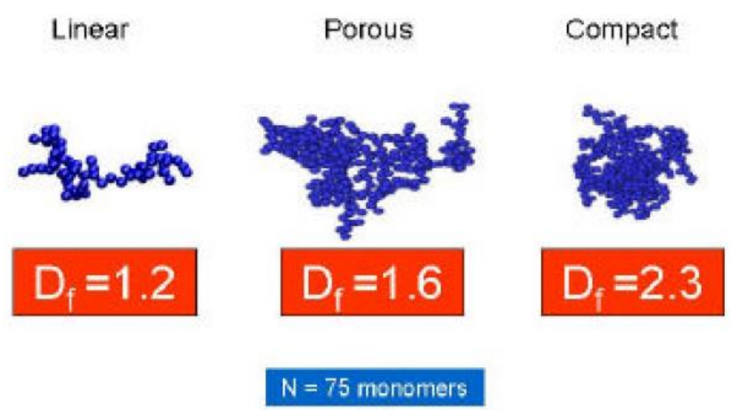
where M_{OC} is the mass of condensed OC, M_{EC} is the mass of EC, V_{OC} is the volume of condensed OC, V_{EC} is the volume of EC, and x is the mass fraction of condensed OC ($x = \frac{M_{\text{OC}}}{M_{\text{OC}}+M_{\text{EC}}}$),

- EC/OC decreases with increasing size
  - Lower density



- Hedemora EC/OC (SAMAP 2011)
  - 50 nm (51% OC), 200 nm (59% OC)
  - Composition of EC, PAH, Fuel
  - Lubricant and fuel catalyst metals of varying toxicities

Fractal Equivalents



- Same mass, higher fractal → spheroidal
- Same mass, varied fractal → varying size
- Same size, higher fractal → higher dose by mass

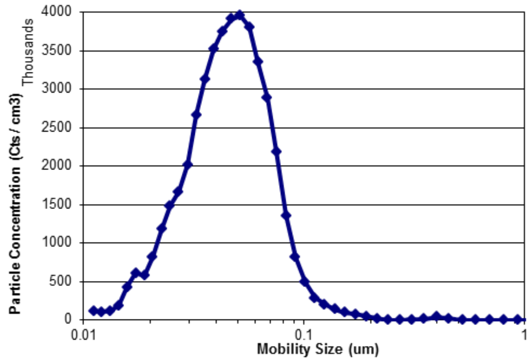
UFP Structure - Pathology Observations

- PM and UFP found in human nasal barrier in autopsies, but UFP translocated to frontal cortex blood vessels and neurons.
  - Size and shape (increased toxicity and mass dose)
- UFP in human lung capillary membrane
  - Initiated disruption of BBB is shape dependent
- Human red blood cells overloaded with UFP and nanoparticles near disrupted blood vessels in frontal cortex.
  - Compact shapes of UFP (increased toxicity and mass dose)
- Transport of metals on PM and UFP, but compact UFP metal deposition in frontal cortex of autopsied young canines.
  - Smaller size and shape

- *PM-2.5 also exert toxicity, but after initiated disruption of BBB by UFP*

UFP Exposure Assessment for Submariners

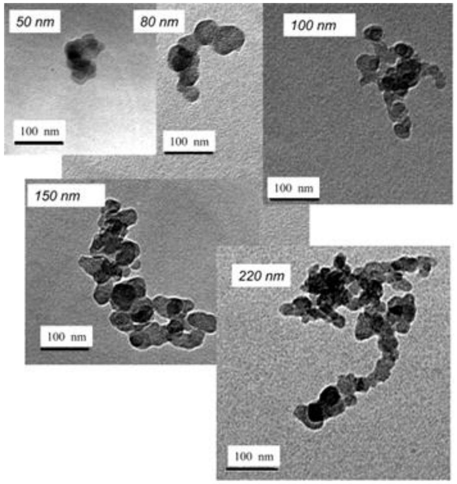
- Assumptions for Hedemora engine
  - Compact spheroidal UFP
  - High OC content (PAH, aromatic HC)
  - Lubricant and fuel catalyst metals



- Implications of Continuous Exposure
  - ≈ $5x10^6$ particles/cm^3 (DFG/MAK 8h Proposal 10^8 particles/cm^3)
  - But 33% of DPM limit by mass
    - Possible risk to cognitive performance
    - Supported by recent animal studies

- Mice exposed to PM2.5 at US NAAQS level (9 months)
  - Promotion of Alzheimers-like neuropathology (Bhatt 2015)

Conclusions



- UFP structural properties and characteristics
  - Size, morphology, chemical composition
  - Relationship between mobility and UFP mass
  - UFP of Hedemora emissions
    - Spheroidal in size range of 50 -100 nm
    - Mass localised in UFP and nanoparticles
      - More toxic than larger particles for same mass
- *Compact shapes deliver proportionally higher dose by mass*
  - *Cytotoxic (breakdown of BBB)*
  - *Neurotoxic (cognitive impairment)*
- Exposure to RAN submariners
  - Possible risk of decreased cognitive performance
  - Mitigation by less frequent exposures
    - Normal cognitive capability in less exposed children
    - Mexico control city

Questions