Particle Measurement Methodology: On-road and laboratory measurements of nanoparticles from Diesel engines

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This work is part of the CRC E-43 Project, “Diesel Aerosol Sampling Methodology”

- Prime Contractor: University of Minnesota
- Subcontractors: West Virginia University, Paul Scherrer Institute, Carnegie Mellon University, Tampere University, University of California, Riverside, Desert Research Institute, University of California, Davis

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Typical Diesel Particle Size Distributions, Both Mass and Number Weightings Are Shown

- **Fine Particles** (Dp < 2.5 µm)
- **Ultrafine Particles** (Dp < 100 nm)
- **Nanoparticles** (Dp < 50 nm)
- **PM10** (Dp < 10 µm)

Usually consists of particles formed from volatile precursors as exhaust mixes with air during dilution.

Usually consists of carbonaceous agglomerates that have survived the combustion process.

- **Nuclei Mode**
- **Accumulation Mode**
- **Coarse Mode**

*Normalized Concentration, dC/C* total */dlogDp*

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**Legend:**
- **Mass Weighting**
- **Number Weighting**
Nanoparticles are alive and well on Minnesota highways – preliminary results from a MNDOT study of transportation related nanoparticles

Measurements made at passenger car air inlet level moving with mainly light-duty vehicle traffic

$\frac{dN}{d\log D_p}$ (Particles/cm$^3$)

Mid-point diameter, nm

- 55 mph average 10 scans
- Traffic jam average 30 scans

I-94 and I-694

I-494
Particle formation history – most volatile nanoparticles form during dilution

Formation

Carbon formation/oxidation
\[ t = 2 \text{ ms}, \ p = 150 \text{ atm.}, \ T = 2500 \text{ K} \]

Ash Condensation
\[ t = 10 \text{ ms}, \ p = 20 \text{ atm.}, \ T = 1500 \text{ K} \]

Exit Tailpipe
\[ t = 0.5 \text{ s}, \ p = 1 \text{ atm.}, \ T = 600 \text{ K} \]

Sulfate/SOF
Nucleation and Growth
\[ t = 0.6 \text{ s}, \ p = 1 \text{ atm.}, \ D = 10, \ T = 330 \text{ K} \]

Atmospheric Aging
Exposure

Fresh Aerosol over Roadway–Inhalation/Aging
\[ t = 2 \text{ s}, \ p = 1 \text{ atm.}, \ D = 1000, \ T = 300 \text{ K} \]

Increasing Time

This is where most of the volatile nanoparticles emitted by engines usually form.

There is potential to form solid nanoparticles here if the ratio of ash to carbon is high.

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Current understanding of formation of nanoparticles by engines

- Most of the particles are formed from volatile precursors by nucleation and growth as the exhaust dilutes and cools in the atmosphere
  - Nanoparticles are mainly volatile and easily removed by heating
  - There is no evidence large concentrations of solid nanoparticles except in the presence of metallic fuel additives
  - Low levels of soot in the exhaust compared to volatile precursors may make nanoparticle formation more likely
  - The formation of nanoparticles is very, very dependent on dilution conditions
- Initial indications are that heavy hydrocarbons (lube oil) and sulfuric acid are primary constituents of volatile nanoparticles
  - Indicated by studies of particle nucleation and growth rates
  - Direct composition measurements by TDPBMS
  - Further work required but conventional methods may be inadequate
E-43 Questions

• Do modern Diesel engines produce nanoparticles under real world dilution conditions?
• Can we make laboratory measurements that mimic real world measurements?
• What is the composition of the nanoparticles? How long do they persist in the atmosphere?
• Do new low carbon emitters produce more nanoparticles than older designs?
E-43 Experiments - completed

- Cummins engines
  - Chase experiments
    - ISM engine CA and EPA fuels
    - L10 engine EPA fuel
  - Wind tunnel – ISM engine CA fuel
  - Chassis dyno
    - ISM engine CA and EPA fuels
    - L10 engine EPA fuel
  - Engine dyno
    - ISM engine CA and EPA fuels
    - L10 engine EPA fuel
E-43 Experiments - completed

• Caterpillar engines
  – Chase experiments
    • C15 engine CA and EPA fuels
    • 3406C engine EPA fuel
  – Chassis dyno
    • C15 engine CA and EPA fuels
    • 3406C engine EPA fuel
  – Engine dyno Caterpillar
    • 3406E (C15) in CVS cell
    • 2 additional 3406E in performance cell
E-43 Experiments - ongoing

- Validation experiments
  - Loss measurements and calculations
  - Instrument calibration and inter-comparisons
  - Dilution system refinements (Caterpillar C12)

- Chemical analysis - engine dyno tests at U of M
  - UC Riverside thermal desorption particle beam mass spectrometer (TDPBMS) – completed tests with Deere and Caterpillar (C12) engines, plans for Cummins engine tests this summer
  - Nano-MOUDI samples collected from Caterpillar engine for analysis by DRI and UC Davis
U of M Mobile Laboratory built to study formation of nanoparticles in the atmosphere for the CRC E-43 project
Principal Instruments in MEL

- SMPS to size particles in 9 to 300 nm size range
- ELPI to size particles in 30 to 2500 nm size range
- CPC to count all particles larger than 3 nm
- Diffusion Charger to measure total submicron particle surface area
- Epiphaniometer to measure total submicron particle surface area
- PAS to measure total submicron surface bound PAH equivalent
- CO$_2$, CO, and NO analyzers for gas and dilution ratio determinations
University of Minnesota, E-43, Mobile Aerosol Laboratory during a Roadway Chase Experiment
Preliminary results

- Cummins on highway cruise, wind tunnel, and CVS results, ISM engine CA fuel
- Cummins ISM engine EPA fuel on highway and CVS
- Cummins and Caterpillar as measured on highway
Average on road data Cummins engines EPA fuel – all show nuclei mode

ISM engine cruise

L10 engine Cruise

ISM engine acceleration

L10 engine acceleration
Normalized size distributions with Cummins ISM engine and California fuel – light load highway cruise
Normalized size distributions with Cummins ISM engine and EPA fuel – light load highway cruise
Average on road results for Caterpillar C15 show distinct fuel effect
E-43 Questions and preliminary indications

• Can we make laboratory measurements that mimic real world measurements? *(results are extremely sensitive to sampling system design but we can design systems that measure potential)*

• Do modern Diesel engines produce nanoparticles under real world dilution conditions? *(yes)*

• What is the physical nature of the nanoparticles? *(mainly volatile materials like heavy hydrocarbons, sulfuric acid, and … no evidence of significant solid fraction)*

• Do new low carbon emitters produce more nanoparticles than older designs? *(no substantial difference has been observed initially)*

• Gigabytes of data have been collected and are currently being analyzed with completion targeted for this fall.