Particle Measurement Methodology: E-43 Overview and Postmortem

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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, Dessert Research Institute, University of California, Davis
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Typical Diesel Particle Size Distributions, Number, Surface Area, and Mass Weightings Are Shown



- Do modern Diesel engines produce nanoparticles (more appropriately, nuclei mode particles) under real world dilution conditions?
- Can we make laboratory measurements that mimic real world measurements?
- Do new low carbon emitters produce more nanoparticles than older designs?
- What is the composition of the nanoparticles?
- How long do they persist in the atmosphere?

E-43 Experiments – current and older technology engines without aftertreatment

- 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
 - Tests of ISM engine at U of M
 - TDPBMS
 - Tandem DMA

- Caterpillar engines
 - Chase experiments
 - 3406E (C15) engine CA and EPA fuels
 - 3406C engine EPA fuel
 - Chassis dyno
 - 3406E (C15) engine CA and EPA fuels
 - 3406C engine EPA fuel
 - Engine dyno Caterpillar
 - 3406E (C15) in CVS cell
 - 2 additional 3406E in performance cell
 - Tests of C12 engine at U of M
 - Dilution system development
 - TDPBMS

University of Minnesota, E-43, Mobile Aerosol Laboratory during a Roadway Chase Experiment



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Nuclei modes were observed for most on road conditions, especially in colder weather

ISM Truck, Loaded 55 MPH Cruise, EPA Fuel



Summer 2000 tests gave consistent nuclei mode formation, less temperature influence



3406E Truck, Loaded, 60 MPH Cruise, EPA Fuel

A clear pattern showing a significant on-road nuclei mode emerged for overall averages







Recent experiments in which we sample our own plume show consistent nuclei mode formation and reveal more detail



Volvo Plume Sniffing, 55 MPH Cruise, EPA Fuel



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Comparison of lab and chase measurements – Typical composite results, EPA fuel

Composite Graphs: Cat CD, 3406E, EPA, BG1 Vs. Chase



Comparison of lab and chase measurements – CA fuel - larger nuclei mode in lab

Composite Graphs: Cat CD, 3406E, CA, BG1 Vs. Chase



Dp (nm)

Nuclei mode formation is very sensitive to dilution conditions for most, but nor all engine conditions. At idle and light load the mode likely forms in the tailpipe.



The nuclei mode is quite unstable and may vary in size during steady engine operation

1.00E+10 May 19 2000 Time of day 1.00E+09 + 13:07:32 → 13:09:09 + 13:18:35 1.00E+08 - 13:21:37 dN/dlogDp (part./cm3) 1.00E+07 ***** 18:01:56 18:03:40 1.00E+06 18:05:29 1.00E+05 1.00E+04 Corrected for dilution ratio, not corrected for particle losses 1.00E+03 10 100 1000 1

ISM Engine, 1800 RPM, 100% Load, EPA Fuel

Diameter (nm)

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Composite on-road chase results show much less scatter. Character of size distribution from current and older technology similar.



Dp (nm)

Comparison with previous studies: Nuclei mode particles from newer engines are at lower concentrations and somewhat smaller in diameter



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The nuclei mode is nearly entirely volatile under most, but not all conditions



A thermal denuder (TD) operating at 300 C was used to remove volatile particles as indicated. EPA certification fuel, 330 ppm S, was used in all tests shown above. The ISM was a 390 HP current technology engine, the L10 a 275 HP older technology engine.

Recent U of M experiments for Caterpillar Show Systematic Influence of Thermal Denuder and Existence of a Non-Volatile Nuclei Mode at Light Load

U of M Caterpillar C12, EPA Fuel, Idle

U of M Caterpillar C12, EPA Fuel 1530 RPM, 704 N-m (Highway Cruise)



The nuclei mode is usually sensitive to fuel sulfur content, but a significant nuclei mode may form even with very low sulfur fuel and lube oil



Applying Advanced Particle Characterization Methods to Physical and Chemical Characterization of Diesel aerosols



Particle Technology Laboratory

TDPBMS Measures the Volatility and Mass Spectra of the Volatile Fraction of *All* **the Particles in Selected Size Ranges Between 15 and 300 Nm - Summary Results**

- Engines
 - Deere 4045T medium-duty
 - Caterpillar C12 heavy-duty
 - Cummins ISM
- Fuels
 - Federal pump fuel, 360 ppm S
 - California pump fuels, 50 and 96 ppm S
 - Fischer-Tropsch, < 1 ppm S
- Test conditions
 - Light and medium load

- Composition of volatile fraction
 - Organic component of total diesel particles and nanoparticles appears to be mainly unburned lubricating oil
 - Major organic compound classes are alkanes, cycloalkanes, and aromatics
 - Low-volatility oxidation products and PAHs have been found in previous GC-MS analyses, but are only a minor component of the organic mass
 - Nanoparticles formed with higher S Federal pump fuel contain small amounts of sulfuric acid but those formed with the lower S fuels show no evidence for sulfuric acid

Draft Report on Chemistry of nano-MOUDI Samples, Gives OC/EC Results Generally Consistent with TDPBMS

Data Shown Are for ISM engine, 1400 rpm, 366 N-m (medium load cruise)



Thermal desorption total ion profile – C12 engine, light load, EPA fuel, 32 nm stage



Applying advanced physical characterization methods to Diesel aerosols – types of measurements

- Volatility measurements
 - Select single particle size with DMA
 - Heat
 - Observe diameter change and relate to volatility
- Hygroscopicity measurements
 - Select single particle size with DMA
 - Humidify
 - Observe diameter change and relate to content of hygroscopic material

Volatility of Diesel nanoparticles – 30 nm size selected particles are heated size changes observed

Cummins ISM, pump fuel (350 ppm S), 1400 rpm , medium load



- •Two particle types of different volatilities present.
- •Volatile particles more abundant

•Significant shrinkage occurred when temperature was in the range of 50- 110 $^{\circ}C$



Volatility of diesel nanoparticles – plot of peak diameter shifts during heating. All but the smallest sizes consist of two particle types





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Evaporative shrinkage of n-alkanes and Diesel nanoparticles. Diesel nanoparticles behave like C28-C32 – lube oil?



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Hygroscopicity of diesel nanoparticles – ISM engine pump fuel (350 ppm S) medium load



Corresponds to ~ 5% mass H_2SO_4

•Similar water uptake was observed light engine load with pump fuel

•With CA fuel (96 ppm S), no water uptake was observed either at medium or light engine load.

E-43 Questions

- Do modern Diesel engines produce nanoparticles (more appropriately, nuclei mode particles) under real world dilution conditions?
- Can we make laboratory measurements that mimic real world measurements?
- Do new low carbon emitters produce more nanoparticles than older designs?
- What is the composition of the nanoparticles?
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Neighborhood Aerosol Measurements Downwind/Upwind Comparison



Nuclei Mode Decays Rapidly Downwind of Roadways

- Modeling (Capaldo and Pandis, 2002) indicates
 - For typical urban conditions, characteristic times and transit distances for 90 % reduction of ultrafine concentrations are on the order of a few minutes and 100-1000 m, respectively.
 - For a given wind speed, ultrafine particles are expected to survive and travel a factor of ten greater distances in a rural flat area as compared to an urban downtown location.
- Mobile particle sources will influence the aerosol particle number concentrations mainly near roadways.



E-43 Questions and answers

- Do modern Diesel engines produce nanoparticles (nuclei mode) under real world dilution conditions?
 - Yes and so do mixed on-road fleets, even in the absence of significant Diesel traffic.
 - Nuclei mode formation strongly dependent on ambient temperature and traffic conditions.
- Can we make laboratory size distribution measurements that mimic real world measurements?
 - On-road results are very dependent upon dilution conditions like ambient temperature and previous operating history what condition are we trying to mimic?
 - However, we found that although laboratory results are also extremely sensitive to sampling and dilution conditions, we could design systems that give results similar to onroad composite highway cruise and acceleration conditions measured under moderate summer conditions (20-30 C).
- Do new low carbon emitters produce more nanoparticles (nuclei mode) than older designs?
 - No substantial difference has been observed for engines tested in E-43.
 - Nuclei mode concentrations are markedly lower than reported in previous studies
 - Nuclei mode formation linked to volatile precursor (hydrocarbon and sulfuric acid) concentrations, especially under on-road conditions

E-43 Questions and answers

- What the chemical and physical characteristics of the nanoparticles?
 - TDPBMS measurements (Ziemann, et al., 2002) showed that they consist mainly volatile materials like heavy hydrocarbons, sulfuric acid, and ...
 - This is supported by tandem DMA and and DRI/UC Davis analysis (preliminary results) of nano-MOUDI samples
 - No evidence of solid fraction except at very light load
- How long do they persist in the atmosphere?
 - Modeling (Capaldo and Pandis, 2002) indicates that for typical urban conditions characteristic times and transit distances for 90% reduction of total number (mainly ultrafine) concentrations are on the order of a few minutes and 100-1000 m, respectively.
 - Thus high ultrafine and nanoparticle concentrations from engines are expected to be found mainly on and near roadways a hotspot problem.
- Issues
 - More work needed to determine appropriate on-road dilution conditions to mimic, speed, congestions, temperature, etc.
 - Optimization of dilution systems
 - Currently there is no calibration standard for particle number
 - Condensation particle counter measurements show that there are significant number concentrations below the SMPS sizing range
 - Are nuclei mode particles of environmental significance?

• Instruments

- SMPS Generally worked well. Flow balancing tedious and adds uncertainty, should have new TSI platform with flow recirculation. Poor match between long column SMPS and 3025A CPC, better pairing long SMPS/3010, nano-SMPS/3025A
- CPC Generally worked well. Need to check flows and periodically remove water from sampling lines
- ELPI Many problems. Consistently gave bigger particles in accumulation mode. Interference by large nuclei mode. Needed frequently cleaned greased substrates
- EPI Very slow response but worked well in first part of program. Proved to be too sensitive and overloaded. Might hold promise for surface area measurements with very clean future engines
- DC Intermittent, especially during first part of program. When working gave fast response to particle surface. Sensitivity marginal with very clean engines or highly diluted samples
- PAS Reliable and fairly sensitive but response depends upon both composition and size
- Bag sampler Worked well, less than 10% losses
- CPC dilutor, filter bypass and leaky filter, gave inconsistent results leading to uncertainty in sub 10 nm range

- Experiments
 - On-road chase
 - Fall 1999 Cummins Chase
 - First attempts at chase experiments developing procedures
 - Difficulties finding plume with bobtail tractor
 - Variable fall temperatures peculiar results with CA fuel and ISM engine
 - Deceleration plume very hard to find
 - Summer 2000 Caterpillar Chase
 - Lots of good data
 - Higher productivity due to experience
 - Moderate summer conditions did not seem to influence results
 - General
 - Difficult to catch high plume
 - A well sheltered test track would have led to much higher productivity
 - Should have paid more attention to vehicle conditioning
 - Should have taken more background scans
 - Problems with time synchronization, need GPS on all vehicles

- Experiments
 - Wind Tunnel
 - Recirculating tunnel led to very high background, probably suppressing nuclei mode formation
 - CA fuel had low tendency to form nuclei mode under tunnel conditions EPA fuel might have been better for these tests
 - Possible tunnel stratification made background corrections difficult
 - Should have made regular CO2 and NOx background measurements
 - Provided stable Diesel aerosol for instrument comparison and bag sampler tests
 - General Problems with Engine and Chassis Dyno
 - Difficult to match unsteady on-road conditions
 - Storage and release, preconditioning issues
 - Not enough time for debugging
 - Cummins Chassis Dyno
 - Realistic exhaust system
 - Only backup dilution system available

• Experiments

- Cummins Engine Dyno
 - Generally Successful
 - Additional Cummins sponsored tests added value
 - » Transient tests
 - » Reduced sulfur fuel and oil tests
 - » Catalyzed filter tests
 - Dilution ratio uncertainty on MOUDI samples
 - Problems with 2-stage dilutor, could not use short transfer lines
 - Tight test schedule
- Caterpillar Engine Dyno
 - Generally Successful
 - Problems with 2-stage dilutor, could not use short transfer lines
 - BG1 dilution system worked well
 - Tight test schedule

• Experiments

- Caterpillar Chassis Dyno
 - Generally successful
 - BG1 dilutor worked well
 - Tight test schedule
- U of M / UC Riverside Experiments
 - Dilution system tests verified ambient temperature effects, transfer line losses, storage and release problems
 - TDPBMS and tandem DMA experiments gave important new information on composition
 - » These tests were limited to light and medium loads should be repeated at heavier loads
 - » These test should be done on engine with aftertreatment
 - Need additional dilution system development

Particle Losses in Typical Instruments and Sampling Lines Are Significant and May Cause the Nuclei Mode to Be Underestimated by a Factor of 2 to 3 or More

