Diesel Aerosol sampling in the atmosphere
Notes to accompany slides for

DIESEL AEROSOL SAMPLING IN THE ATMOSPHERE
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Slide 3 shows a typical Diesel exhaust size distribution in both number and mass weightings. Most of the mass is found in the so-called accumulation mode that mainly consists of carbonaceous agglomerates and adsorbed hydrocarbons and sulfates. Most of the number is found in the nuclei mode which usually consists of volatile materials like sulfuric acid and heavy hydrocarbons. The nuclei mode is not usually present in the tailpipe but forms from particle precursors as the exhaust dilutes and cools in the atmosphere. This mode often contains 90% or more of the particle number and nearly all the particles in the nanoparticle (Dp < 50 nm) range.

Slide 4 describes some of the factors that have led to our interest in nanoparticle measurement.

Slide 5 shows number weighted size distributions measured in the diluted exhaust of a medium-duty Diesel engine. A two stage dilution system that allowed the temperature, residence time and relative humidity in the primary dilution region (dilution ratio ~ 12) to be varied. Both residence time and temperature had a strong effect on the nuclei mode. The slide shows the influence of residence time at fixed temperature and humidity. Changing the residence time from 100 ms to 1 s changes the number of particles in the nuclei mode by nearly two orders of magnitude, while having no noticeable influence on the accumulation mode.

Slide 6 describes the objectives of the CRC E-43 project. Some results from the first two are discussed here, but we are only now starting detailed analysis of results. The results described here are still preliminary.

Slides 7 and 8 show the University of Minnesota mobile laboratory. In slide 7 the sampling boom over the cab may be seen. The sampling boom is designed to be at essentially the same height as typical truck exhaust stacks. Slide 8 shows the lab being used to characterize the exhaust of a truck in a highway chase experiment. The lab contains the suite of instruments listed in Slide 9.

Slides 10 and 11 show typical size distributions measured in highway chase experiments. All size distributions show a clear nuclei mode. The variation in concentration from run to run results from instantaneous differences in dilution ratio as our position in the exhaust plume varies. Typical dilution ratios in these experiments range from about 500 to several thousand. Slide 12 shows average normalized size distributions measured at two different ambient temperatures. For this engine and fuel we found a much stronger tendency to produce a nuclei mode at lower ambient temperatures. We believe that this is due to changes in the particle formation process during dilution, not from changes in the materials emitted by the engine. Slide 13 shows how dilution air temperature changes the size distributions measured in a laboratory with an engine running under constant operating and ambient conditions. These measurements were made with a smaller engine of an older design than the one used in the chase experiments. Although the results should not be directly compared, the influence of dilution air temperature on the nuclei mode is remarkably similar.
Slide 14 shows another aspect of the nuclei mode. Here the same engine as was used in the chase experiments was being tested in the laboratory. Two operating conditions are shown, with and without a thermal denuder designed to remove volatile particles. Without the thermal denuder large nuclei modes are observed. On the other hand, when the diluted exhaust sample is passed through the denuder, heated to 300 C, and then cooled back to ambient in an activated charcoal lined heat exchanger; the nuclei mode is removed. This shows that the mode consists of volatile materials. Slide 15 summarizes how we believe the nuclei mode forms and grows. It appears to generally consist of sulfuric acid and heavy hydrocarbons.

Slide 16 show how some of the other instruments in the mobile laboratory track with one another during chase experiments. Here the responses of the condensation particle counter (CPC) and the diffusion charger (DC) are shown. Slide 17 shows the response of the DC plotted against that of the CPC. The slope of the plot may be used to determine the diameter of average surface.

Slides 18, 19, and 20 show results obtained with the electrical low-pressure impactor (ELPI) during a highway drive on urban freeways in Minnesota. The lower size limit of the ELPI is 30 nm so it does not see the entire nuclei mode. These results were obtained driving in medium to heavy traffic continuously sampling whatever entered the sampling boom. In general the particle size is lower when higher concentrations are observed. This is clearly evident in slide 19, which is a plot of instantaneous size against concentration. It also is clearly apparent in slide 20, which shows size and concentration the mobile laboratory passed through a highway tunnel. Concentration increases sharply at the same time that mean diameter drops. The relationship between concentration and size suggests that freshly emitted exhaust particles grow as they age in the atmosphere. High concentrations indicate that the sample is dominated by tiny freshly emitted particle while lower concentrations are likely associated with aged background particles.

Slide 21 summarizes what we have learned so far with our ambient measurements.

REFERENCES


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This work is based in part on preliminary results from 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
- Sponsors: Coordinating Research Council and the National Renewable Energy Laboratory with co-sponsorship from the Engine Manufacturers Association, the Southcoast Air Quality Management District, the California Air Resources Board, Cummins, Caterpillar, and Volvo.

- Other information is based on work sponsored by Perkins Engine Company and Cummins Diesel
Typical Diesel Particle Size Distribution - Log Scale

Typical Engine Exhaust Size Distribution
Both Mass and Number Weightings are Shown

- **Fine Particles**: $D_p < 2.5 \, \mu m$
- **Ultrafine Particles**: $D_p < 100 \, \text{nm}$
- **Nanoparticles**: $D_p < 50 \, \text{nm}$
- **Nuclei Mode**
- **Accumulation Mode**
- **Coarse Mode**
- **PM10**: $D_p < 10 \, \mu m$

Normalized Concentration, $dC/C_{total}/d\log D_p$

Diameter (\(\mu m\))
Background

• Concerns about particle size
  – New ambient standards on fine particles
  – Special concerns about ultrafine and nanoparticles
  – Indications that reductions in mass emissions may increase number emissions

• Difficulties associated with measurement of ultrafine and nanoparticles
  – Often more than 90% of particle number are formed during exhaust dilution
  – Semivolatile nanoparticle concentrations may be changed by orders of magnitude during sampling and dilution
Influence of Residence Time on Number Weighted Size Distributions

$D_N/D\log D_p$ (Part./cm$^3$)

Residence time = 1000 ms

$T_{\text{dilution}} = 32 \, ^\circ\text{C}$,
Primary DR ~ 12

1600 rpm, 50% load

Residence time = 1000 ms – 100 ms – 230 ms
Goals and Objectives of the E-43 Program

- Measure on-road particle size distributions (number, volume, surface area) in the exhaust plume of heavy-duty diesel vehicles.
- Attempt to reproduce these results under laboratory conditions (chassis dynamometer, wind tunnel, engine dynamometer)
- Model atmospheric aging and dispersion of freshly emitted diesel aerosols
- Determine size fractionated chemical composition of diesel particulate matter collected in laboratory and in wind tunnel
In Order to Understand the Environmental Impact of Nanoparticles We Must Study Their Formation in the Atmosphere. This is the U of M E-43 Mobile Laboratory.
University of Minnesota, E-43, Mobile Aerosol Laboratory during a Roadway Chase Experiment
Principal Instruments Used in MEL for Initial Chase Experiments

- 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$_2$ and NO analyzers for dilution ratio determinations
Typical On Road Size Distributions - 55 mph

6 October Cruise CA light load ISM Truck

Diagram showing particle size distribution over time with different data points and labels.
Typical On Road Size Distributions - 40-55 mph Accelerations

1 October Accel. CA light load ISM Truck

![Graph showing typical on-road size distributions with data points and a background average line.](image-url)
Ambient Temperature Appears to Have an Influence on Nanoparticle Formation. These Data Are for the Same Vehicle and Engine Conditions but Different Temperatures

The open symbols show runs made at 11 C
The closed symbols show runs made at 21 C

Average plume minus background SMPS size distributions normalized to 1 $\mu$m$^3$/cm$^3$ volume concentration are shown here
We Also See Clear Dilution Air Temperature Effects in U of M Single Stage Dilution Tunnel, DR=1000:1

Medium Duty Diesel Engine Meeting 1995 Heavy Duty Standards
Nanoparticles Are Formed by Modern Engines but They Are Semivolatile - Formed during Dilution, not in the Engine

+ TD denotes use of thermal denuder at 300 C

1800 rpm, 100%
1800 rpm, 100% + TD
Light load cruise
Light load cruise + TD

Rated power

With thermal denuder

Federal Fuel (~330 ppm S)
Formation of Semivolatile Nanoparticles

• It appears that sulfuric acid is the trigger for nanoparticle nucleation - at least at higher loads.

• However, there is not enough sulfuric acid in a typical diluting exhaust stream to explain observed nanoparticle diameter growth rates. (Khalek, Kittelson, and Brear, 2000).

• New measurements with a particle beam mass spectrometer show that 25 nm particles from engine exhaust are mainly hydrocarbons with some sulfuric acid. (P. Ziemann, UC Riverside; P. McMurry and D. Kittelson, U of Minn.).
Continuous Instruments Usually Track Well with Each Other During Chase Experiments

Typical CPC and Diffusion Charger Response Corrected for Differences in Instrument Time Response

7 October 1999
The Relationship Between Surface Area and Number Concentrations Gives a Mean Particle Size

Comparison of CPC and Diffusion Charger Response
7 October 15:28-16:09

$y = 2E-05x + 0.4968$
$R^2 = 0.7523$

The slope of this line is related to particle size. The diameter of average surface is given by:

$D_{as} = (S/\pi N)^{0.5}$
Instantaneous Concentration and Size during Trip on Suburban/Urban Freeway (ELPI)

Lowry Tunnel

Behind Trucks

Mean Diameter — Particle Concentration
Instantaneous Concentration and Size during Trip on Suburban/Urban Freeway (ELPI)

Number Concentration (part./cm$^3$)

Diameter, DGN (µm)

Aged background particles

Freshly emitted particles
Instantaneous Concentration and Size during Trip on Suburban/Urban Freeway (ELPI)

![Graph showing instantaneous concentration and size during trip on suburban/urban freeway using ELPI.](chart.png)
Conclusions

- On-road chase experiments are a useful method for studying nanoparticle formation under real-world conditions
- Most of the nanoparticles observed behind vehicles form from particle precursors during dilution, not in the engine
  - Nanoparticle formation is sensitive to ambient temperature
  - Nanoparticles are removed by a thermal denuder
  - Heavy hydrocarbons and sulfuric acid appear to be the principal precursors
- It will be very difficult to design a sampling and dilution method that simulates atmospheric dilution