Ultrafine Particle Emission & Control Strategies

David B. Kittelson
University of Minnesota
Center for Diesel Research

South Coast Air Quality Management District
Conference on Ultrafine Particles: The Science, Technology, and Policy Issues

Wilshire Grand Hotel, Los Angeles
April 30 – May 2, 2006

Some slides have been added and modified. If you wish an updated copy contact me at kitte001@umn.edu
Outline

• Introduction
  – Emission standard
  – Typical engine and atmospheric size distributions
  – Why do we care about particle size

• Particle Formation by Diesel Engines
  – Structure and composition of ultrafine and nanoparticles
  – Particle formation during dilution

• Dilution and Sampling issues
  – Laboratory measurements
  – On-road measurement

• Diesel particle removal systems
  – Description
  – On-road evaluation

• Particles from gasoline spark ignition engines

• Future issues and conclusions
Outline

- **Introduction**
  - Emission standard
  - Typical engine and atmospheric size distributions
  - Why do we care about particle size

- **Particle Formation by Diesel Engines**
  - Structure and composition of ultrafine and nanoparticles
  - Particle formation during dilution

- **Dilution and Sampling issues**
  - Laboratory measurements
  - On-road measurement

- **Diesel particle removal systems**
  - Description
  - On-road evaluation

- **Particles from gasoline spark ignition engines**

- **Future issues and conclusions**
Emissions standards are becoming much tighter worldwide making exhaust aftertreatment essential.

- US 2010 levels correspond to about 99% reduction in PM and 98% reduction in NOx.
- 2007 prototypes are better than the PM standard by factors of 5 to 20.
Typical engine exhaust particle size distribution by mass, it consists of 3 size modes formed by different processes.
Typical engine exhaust particle size distribution by mass, it consists of 3 size modes formed by different processes:

- **Nanoparticles** (Dp < 50 nm)
- **Ultrafine Particles** (Dp < 100 nm)
- **Fine Particles** (Dp < 2.5 µm)
- **Accumulation Mode** - Usually consists of carbonaceous agglomerates and adsorbed material
- **PM10** (Dp < 10 µm)
Typical engine exhaust particle size distribution by mass, it consists of 3 size modes formed by different processes.

- **Nanoparticles** (Dp < 50 nm)
- **Ultrafine Particles** (Dp < 100 nm)
- **Fine Particles** (Dp < 2.5 µm)
- **Accumulation Mode** - Usually consists of carbonaceous agglomerates and adsorbed material
- **Coarse Mode** - Usually consists of reentrained accumulation mode particles, crankcase fumes
- **PM10** (Dp < 10 µm)
Typical engine exhaust particle size distribution by mass, it consists of 3 size modes formed by different processes

- **Nuclei Mode** - Usually forms from volatile precursors as exhaust dilutes and cools
  - Nanoparticles
    - $D_p < 50$ nm
  - Ultrafine Particles
    - $D_p < 100$ nm
  - Fine Particles
    - $D_p < 2.5$ µm

- **Accumulation Mode** - Usually consists of carbonaceous agglomerates and adsorbed material
  - PM10
    - $D_p < 10$ µm

- **Coarse Mode** - Usually consists of reentrained accumulation mode particles, crankcase fumes
  - $D_p < 10$ nm

In some cases this mode may consist of very small particles below the range of conventional instruments, $D_p < 10$ nm
Typical engine exhaust particle size distribution by mass and number, most of number in nucleation mode

**Nuclei Mode** - Usually forms from volatile precursors as exhaust dilutes and cools

- Nanoparticles
  - \( D_p < 50 \text{ nm} \)

- Ultrafine Particles
  - \( D_p < 100 \text{ nm} \)

**Accumulation Mode** - Usually consists of carbonaceous agglomerates and adsorbed material

- Fine Particles
  - \( D_p < 2.5 \mu\text{m} \)

PM10
- \( D_p < 10 \mu\text{m} \)

- In some cases this mode may consist of very small particles below the range of conventional instruments, \( D_p < 10 \text{ nm} \)

- Coarse Mode
  - Usually consists of reentrained accumulation mode particles, crankcase fumes

\[ m = N \rho D_p^3 / 6 \]

<table>
<thead>
<tr>
<th>Diameter (nm)</th>
<th>Number</th>
<th>Mass</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td></td>
<td></td>
</tr>
<tr>
<td>10</td>
<td></td>
<td></td>
</tr>
<tr>
<td>100</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1,000</td>
<td></td>
<td></td>
</tr>
<tr>
<td>10,000</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Typical engine exhaust particle size distribution by mass, number and surface area

Nuclei Mode - Usually forms from volatile precursors as exhaust dilutes and cools

Accumulation Mode - Usually consists of carbonaceous agglomerates and adsorbed material

Coarse Mode - Usually consists of reentrained accumulation mode particles, crankcase fumes

\[ S = N \pi D_p^2 \]

In some cases this mode may consist of very small particles below the range of conventional instruments, Dp < 10 nm
Atmospheric Aerosols Generally Have a Trimodal Size Distribution
Particles Sizes Span a Very Wide Range

SIZE OF SOME COMMON PARTICLES

- Gas Molecules
- Ultrafine Particles
- Viruses
- Bacteria
- Tobacco Smoke
- Atmospheric Aerosol
- Red Blood Cell (7.5 μm)
Why Are We Concerned about Particle Size?

- Health effects
- Behavior in atmospheric
  - Visibility
  - Residence time
  - Surface reactions
- Performance of aftertreatment devices
- Concerns that low (mass) emission engines may emit much smaller particles and higher number concentrations
Health

• Correlations between fine particles and excess deaths
• Increased asthma and respiratory problems in children living near roadways
• Special concerns about ultrafine and nanoparticles
  – More surface area and number per unit mass
  – Increased deep lung deposition efficiency
  – Very small particles may pass through cell membranes and along neurons
  – Effects of solid particles clear, volatile particles uncertain
Health – Ultrafine particles are deposited on the deep lung regions more efficiently than fine particles
Optical Extinction by an Aerosol is also a Strong Function of Particle Size

Size Also Determines Residence Times in the Atmospheric Boundary Layer

Source: Adapted from Jaenicke, 1993.
Note: Curve A represents the deposition of aerosol particles to the ground, while curve B also includes the effect of coagulation, which reduces the number of small particles without removing their substance from the air.

Size and Filtration (Trap Performance)

FIGURE 9.5 Single-fiber collection by interception.

FIGURE 9.6 Single-fiber collection by impaction.

FIGURE 9.7 Single-fiber collection by diffusion.

Size and Filtration (Trap Performance)

**FIGURE 9.9** Filter efficiency versus particle size for face velocities of 0.01 and 0.1 m/s [1 and 10 cm/s]; $t = 1$ mm, $a = 0.05$, and $d_f = 2$ μm.

Background - Historical Perspective

- Often cited 1996 HEI study showed dramatic increase in nanoparticle emissions
  - For a 1991 engine compared to 1988 engine, running on very low sulfur fuel
  - But 1988 engine also produced high nanoparticle emissions with 0.3% fuel
- Measurements made during 70’s and 80’s often showed high nanoparticle emissions
  - Roadway measurements nearly always associated with large nuclei (nanoparticle) mode
  - Both diesel and spark ignition sources
  - Nanoparticles mostly volatile, except with metallic additives
- **High nanoparticle emissions are not a new development!**
The new engine increased number emissions 10 to 30 fold!

The new engine sharply reduced mass emissions, by about a factor of 3.

H owever, 1979 roadway measurements made on behind a truck powered by an engine of the same family showed high nanoparticle emissions! Other roadside and on-road measurements made since the late 60's have shown high nanoparticle emissions.
Volume size distribution, measured in traffic in the 1970s, note large concentration of ultrafine particles

\[
\text{DGV} \text{ (geometric mean diameter by volume, equivalent to volume median diameter) and } \sigma_g \text{ (geometric standard deviation) are shown for each mode.}
\]

Outline

• Introduction
  – Emission standard
  – Typical engine and atmospheric size distributions
  – Why do we care about particle size

• Particle Formation by Diesel Engines
  – Structure and composition of ultrafine and nanoparticles
  – Particle formation during dilution

• Dilution and Sampling issues
  – Laboratory measurements
  – On-road measurement

• Diesel particle removal systems
  – Description
  – On-road evaluation

• Particles from gasoline spark ignition engines

• Future issues and conclusions
Combustion in Diesel Engines – burning jet, adapted from SAE 1999-01-0509

Temperatures

- 950 K
- 350 K
- 825 K
- ~1600 K
- ~2700 K

Chemistry

- Cold Fuel
- Rich Fuel/Air Mix $\phi = 4$
- Warm Air
- Products of Rich Combustion
  - CO, UHC & Particulates
- NOx
- CO2 & H2O

Entrainment of warm air and traces of oil mist and vapor
Carbonaceous Agglomerates Comprise Most of the Mass from Current Diesel Engines
**Typical composition and structure of diesel particulate matter – heavy-duty, no aftertreatment**

- Solid particles are typically carbonaceous chain agglomerates (mainly elemental carbon, EC) and ash and usually comprise most of the particle mass.
- Volatile or semi-volatile matter (sulfur compounds and organic carbon (SOF)) typically constitutes 35% (5-90%) of the particle mass, 90% (30-99%) of the particle number.
- Carbon and sulfur compounds derive mainly from fuel.
- SOF and ash derive mainly from oil.
- Most of the volatile and semi-volatile materials undergo gas-to-particle conversion as exhaust cools and dilutes.
The composition of Diesel particles is very load and size dependent – slow traffic, light load, mainly OC

Here ultrafines are mainly OC

The composition of Diesel particles is very load and size dependent – highway cruise, mainly EC

Here ultrafines are both EC and OC

Atmospheric dilution leads to nucleation, absorption, and adsorption - in excess of 90% of the particle number may form as the exhaust dilutes.

A dilution ratio of 1000 may be reached in 1 - 2 s

Exhaust solids are mainly solid carbon (EC) and ash from lube oil. Volatiles include organic carbon (OC) and sulfuric acid.
Particle formation history – 2 s in the life of an engine exhaust aerosol

Nature of particles emitted by Diesel engines – heavy duty without aftertreatment

- Engines produce a bimodal size distribution in the submicron range with a nuclei mode containing most of the particle number in the 3-30 nm diameter range and an accumulation mode containing most of the particle mass in the 30-500 nm range.
- The nuclei mode is nearly always in the ultrafine range, while the accumulation mode is partially fine, partially ultrafine. Perhaps it is better to think of modes rather than arbitrary size distinctions.
- Nuclei mode particles form mainly from volatile precursors, mainly heavy hydrocarbons and sulfuric acid.
  - Nuclei mode particles typically consist mainly of heavy hydrocarbons, however the formation of this mode is facilitated by sulfur in the fuel.
  - Their formation is very dependent on dilution conditions, especially dilution rate and dilution air temperature.
  - Their formation is favored by low carbon and high precursor concentrations.
  - Although these particles are volatile they may be relatively insoluble – this could influence their behavior in biological systems.
Nature of particles emitted by Diesel engines - heavy duty without aftertreatment

- Solid nuclei mode particles may form from metals in the lube oil under engine conditions that lead to little solid carbon formation. They also may form when metallic additives or other high metal fuels are used.
- The accumulation mode is where most “soot” or “smoke” resides
  - It consists primarily of carbonaceous agglomerates and adsorbed hydrocarbons
  - Particles in this mode are strongly light absorbing
  - The number and mobility size of accumulation mode particles are not strongly influenced by dilution conditions
  - Accumulation mode particles have been reduced sharply by better engine technology
- Solid particles may be nearly completely eliminated by filtration
- Filters cannot directly remove the gas phase precursors that lead to the formation of volatile nuclei mode particles
  - Precursors may be removed by adsorption on collected particles followed by...
  - Hydrocarbon precursors may be destroyed in catalyzed systems to the extent allowed by kinetics (mainly mass transfer) but sulfuric acid may be formed
Outline

• Introduction
  – Emission standard
  – Typical engine and atmospheric size distributions
  – Why do we care about particle size
• Particle Formation by Diesel Engines
  – Structure and composition of ultrafine and nanoparticles
  – Particle formation during dilution
• Dilution and Sampling issues
  – Laboratory measurements
  – On-road measurement
• Diesel particle removal systems
  – Description
  – On-road evaluation
• Particles from gasoline spark ignition engines
• Future issues and conclusions
Studies of Diesel Nanoparticle Formation Using a Variable Residence Time Dilution System
Nuclei mode formation is extremely sensitive to sampling conditions

- Medium-duty Diesel engine running at medium speed and load
- Increasing residence time in the primary dilution chamber from 230 ms to 1 s increases the size of the nuclei mode by two orders of magnitude
- Decreasing the temperature in the primary dilution chamber from 66 to 32 °C increases the size of the nuclei mode by about one and one half orders of magnitude
- Concerns about sampling and dilution led to continued lab work under EMA/Caterpillar sponsorship and the on-road CRC E-43 program

Sensitivity of Diesel Particle Number Emissions to Dilution Conditions - Residence Time and Temperature Effects

On-road measurements: U of M mobile laboratory built to study formation of nanoparticles in the atmosphere for the CRC E-43 project

- Instruments (primary instruments highlighted in blue)
  - 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
On-road validation: CRC E-43 - nanoparticle measurements in on-road chase and lab

Here we have a 1999 highway tractor with its plume being characterized by the University of Minnesota Mobile Emission Laboratory.
The CRC E-43 Program compared size distributions measured in the laboratory with those measured on-road.

- Results shown are composite highway cruise for a modern heavy-duty Diesel engine with full electronic engine control – no aftertreatment.
- A volatile nuclei mode is present on-road.
- The relative sizes of the two modes are more significant than the absolute levels – due to uncertainty in on-road dilution ratios.
- In general the CA fuel produced a smaller nuclei mode than EPA fuel.
- A two-stage, porous tube / ejector dilutor could simulate on-road nuclei mode formation for composite, summertime highway conditions.
- These results show that it is possible to simulate the tendency to form a nuclei mode under carefully defined on-road conditions.
- At present, it is unclear which on-road conditions should be simulated. There are many variables including:
  - Temperature
  - Previous operating history
  - Road speed
  - Exhaust system design
  - Others …
- More recent work shows that with aftertreatment lab tests may underestimate nuclei mode.
- On-road validation highly desirable!
On-road number measurements showing the role of congestion on ultrafine concentration

High speed traffic favors ultrafine formation, but congestion leads to higher total volume (~ fine PM)

Higher nuclei mode (number) concentrations are found in high speed freely flowing traffic, higher accumulation mode (mass) in congested traffic.

On-road exposure experiments
EPA/U of Rochester/U of Minnesota

- The next slide shows overall average fall 2002 on-road size distribution
  - Sampled 6 hours per day for 10 days on New York rural freeway
  - Drove in Diesel truck traffic and sample aerosol to which truckers are exposed
- Clear bimodal structure with consistent formation of nuclei mode
- A 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 – as expected from laboratory tests

On-road exposure experiments
EPA/U of Rochester/U of Minnesota

Ambient temperature (mainly) and humidity influence size of nuclei mode - U of Rochester / EPA

Daily average results for fall 2003 study - 60 hrs (10 days 6 hrs/day)

$V_{30/V}$ is the fraction of aerosol volume smaller than 30 nm and is an estimate of the volume (and mass) fraction in the nuclei mode

$V_{30/V}$ increases by an order of magnitude as ambient temperature falls from about 23 to 10 °C
Measurements of the decay of nanoparticles downwind of a major rural roadway
EEPS measurements show nuclei mode decays quickly downwind of rural roadway

These plots are the averages of 4 runs made on a road perpendicular to I94

Integrated EEPS number measurements downwind of rural freeway show rapid decay

Oct 6, 2004 EEPS measurements at various distances from I94

Avg distance traveled 300 ± 17 m for 4 tests
Avg speed 0.70 ± 0.006 m/s; Avg duration 426 s ± 20 s
1 min EEPS averaging with estimated mid-point distance traveled
Start times and speed based on GPS data
Average wind speed = 3.5 m/s

N = 20,000 + 98,000 exp(-d/92)

Conclusions – on-road measurements of nuclei mode and ultrafines

- Very large concentrations of nucleation mode particles are found under realistic on-road conditions
- The nucleation mode consists mainly of volatile particles
- Formation for the nucleation mode is favored by high speed traffic and low temperatures
- The nucleation mode decays very rapidly downwind of roadways
  - Characteristic distance 90 m
  - Characteristic time – 30 s
- Nucleation mode particles likely to be mainly an issue on and near roadways – but in CA more than 50% of PM exposure takes place while commuting
Outline

• Introduction
  – Emission standard
  – Typical engine and atmospheric size distributions
  – Why do we care about particle size
• Particle Formation by Diesel Engines
  – Structure and composition of ultrafine and nanoparticles
  – Particle formation during dilution
• Dilution and Sampling issues
  – Laboratory measurements
  – On-road measurement
• Diesel particle removal systems
  – Description
  – On-road evaluation
• Particles from gasoline spark ignition engines
• Future issues and conclusions
Possible Diesel Emission Control Pathway

OEM Emission System Strategies

DOCs only
- Minimum current diesel system: DOCs for odor control
- Vehicles are able to meet EU IV legislation through engine management.

DOCs + uncatalyzed filters (DPF)
- First system (1999); Incremental improvements in the FBC formulation and delivery and increased DPF ash storage capacity are keeping this competitive.

DOCs + catalyzed filters
- Catalyst on filter improves regeneration while DOC reduces HC, CO and NOx.
- Expands range of passive regeneration, reduces complexity.

Catalyzed filters only
- Target system for many OEMs: Further complexity reduction and cost.

PM and NOx solution
- Mixed-mode combustion synergies enable this cost saving integration

Courtesy: Tim Johnson, Corning
Diesel oxidation catalyst (DOC)

**How the DOC Functions**

- The catalyst interacts with the exhaust as it passes through the converter
- The Catalyst causes the particulate to burn at normal exhaust temperatures.
- The DOC burns the gaseous HC and CO emissions, and the lube oil, unburned fuel and carbon soot of the TPM

- Typical performance
  - ~90% CO reduction
  - ~70% gaseous hydrocarbon reduction
  - 25-30% PM reduction mainly by OC oxidation
  - Slight EC reduction
  - May increase sulfate emissions at high load

Diagram courtesy Engelhard
Diesel Particulate Filter

- Controls PM and HC, CO (Catalyzed DPF)
- Extremely high removal efficiencies
- Technology challenges
  - Regeneration strategies
    » Passive
      • Catalyzed soot filter (Engelhard)
      • CRT, CCRT (JM)
      • Fuel borne catalyst
      • NO₂ and H₂SO₄ formation are concerns
      • Exhaust temperature may be inadequate in many applications
    » Active – passive plus
      • Engine management (post injection, etc.)
      • Combustion or electric heating
  - Ash accumulation
    » Lube oil
    » Fuel additives
  - Durability, cost
  - Nuclei mode formation downstream of DPF
Wall flow particle filter, the most common exhaust filtration technology

Fig. 5: Monolithic ceramic cell filter
Fig. 6: Pore structure of a ceramic filter.
CORNING, NGK

From - A. Mayer, TTM PARTICULATE-FILTER-SYSTEMS, PARTICLE TRAPS
CRT® reduces regeneration temperature by producing NO$_2$ upstream of filter

- NO$_2$ enables low temperature soot combustion - but engine-out NO$_x$ is predominantly NO
- Oxidation catalyst converts NO into NO$_2$ with high efficiency

Courtesy Johnson-Matthey
Filter mass measurements with low emission engines - issues

- Very difficult to accurately measure filter mass at low levels
- For volatile particles, filter mass does not adequately represent suspended mass (what we breathe)
  - DPF performance measured with filters very different from that measured by instruments that measure suspended particles (VERT, SWRI, Ford,...)
  - Absolute suspended mass measurements made with aerosol centrifuge show that filters may significantly overstate the mass of volatile particles
  - Sampling and dilution may strongly influence results – consequently on-road measurements are useful
- Other measures may better predict environmental impact
  - Number, Surface area, Black carbon
- The EU is considering a solid particle number standard
  - A sampling and measurement procedure has been developed as part of the EU Particulate Measurement Program (PMP)
  - Swiss ministry suggests $10^{11}$ part/km (50 – 100 µg/km)

On-road exhaust filter evaluations the MEL

- Instruments (primary instruments in this work highlighted in blue)
  - SMPS to size particles in 9 to 300 nm size range, \( \tau = 60 \) s
  - EEPS 3090 that sizes particles in the 5.6 to 560 nm range, \( \tau < 1 \) s
  - 3025 CPC to count all particles larger than about 3 nm, \( \tau \approx 1 \) s
  - Diffusion Charger to measure total submicron particle surface area
  - PAS to measure total submicron surface bound PAH equivalent
  - \( \text{CO}_2, \text{CO}, \text{NO} \) and \( \text{NO}_2 \) analyzers for gas and dilution ratio determinations
The TSI 3090 EEPS is another fast response electrical mobility based instrument

**Preliminary Specifications**

3090 Engine Exhaust Particle Sizer™ Spectrometer

- **Particle Size Range**: 5.6 to 560 nm
- **Particle Size Resolution**: 16 channels per decade (32 total)
- **Electrometer Channels**: 22
- **Charger Mode of Operation**: Unipolar diffusion charger
- **Inlet Cyclone 50% Cutpoint**: 1 μm
- **Time Resolution**: 10 size distributions per second
- **Flow Rates**
  - Aerosol: 10 L/min
  - Sheath Air: 40 L/min
- **Inlet Aerosol Temperature**: 10 to 52°C
- **Operating Temperature**: 0 to 40°C

Sizing range 5.6-560 nm
Response time ~1 s

Particle removal by exhaust filters – On road evaluations of CRT® and CCRT®

- Most PM filtration systems being considered for 2007 are the wall flow type shown on the left. Without regeneration to oxidize soot these devices quickly plug.
- Catalyzed filtration systems like the J-M CRT® shown on the right reduce regeneration temperature by producing NO₂ from exhaust NO in an oxidizing catalyst upstream of filter.
- The J-M CCRT® has a catalyzed washcoat on the filter as well to further reduce regeneration temperature.
- NO₂ in the exhaust is an issue.
- In most applications active regeneration is also required.

Figures courtesy Corning and Johnson-Matthey
On-road evaluations of exhaust particle filters – plume sniffing of MEL with CRT, CCRT

Test conditions for on-road filter evaluations

- Tests run with J-M CRT and CCRT
  - CRT consist of oxidizing catalyst plus wall flow filter
  - CCRT consist of oxidizing catalyst plus catalyzed wall flow filter
- BP15 fuel (2007 compliant)
- Castrol low S lube oil (~1500 ppm)
- 65 mph cruise on Minnesota rural freeway
- Load and exhaust temperature varied with grade, headwind, tailwind

<table>
<thead>
<tr>
<th>Date</th>
<th>Source</th>
<th>N</th>
<th>CO₂, ppm</th>
<th>Exhaust CO₂, %</th>
<th>Exhaust temp, C</th>
<th>Ambient temp, C</th>
<th>Speed, km/hr</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>Avg</td>
<td>Std</td>
<td>Avg</td>
<td>Std</td>
<td>Avg</td>
</tr>
<tr>
<td>7/27/2004</td>
<td>Background</td>
<td>5730</td>
<td>371</td>
<td>9</td>
<td>6.4</td>
<td>1.1</td>
<td>317</td>
</tr>
<tr>
<td>7/27/2004</td>
<td>Plume</td>
<td>5182</td>
<td>527</td>
<td>88</td>
<td>6.4</td>
<td>1.1</td>
<td>318</td>
</tr>
<tr>
<td>7/29/2004</td>
<td>Background</td>
<td>5580</td>
<td>386</td>
<td>13</td>
<td>6.4</td>
<td>1.1</td>
<td>312</td>
</tr>
<tr>
<td>7/29/2004</td>
<td>Plume</td>
<td>4963</td>
<td>494</td>
<td>100</td>
<td>6.4</td>
<td>1.1</td>
<td>312</td>
</tr>
<tr>
<td>8/5/2004</td>
<td>Background</td>
<td>5924</td>
<td>395</td>
<td>12</td>
<td>6.3</td>
<td>1.1</td>
<td>312</td>
</tr>
<tr>
<td>8/5/2004</td>
<td>Plume</td>
<td>5272</td>
<td>625</td>
<td>99</td>
<td>6.3</td>
<td>1.1</td>
<td>311</td>
</tr>
<tr>
<td>8/11/2004</td>
<td>Background</td>
<td>3980</td>
<td>380</td>
<td>11</td>
<td>6.5</td>
<td>1.0</td>
<td>313</td>
</tr>
<tr>
<td>8/11/2004</td>
<td>Plume</td>
<td>3290</td>
<td>520</td>
<td>102</td>
<td>6.3</td>
<td>1.2</td>
<td>312</td>
</tr>
<tr>
<td>8/12/2004</td>
<td>Background</td>
<td>6134</td>
<td>386</td>
<td>9</td>
<td>6.3</td>
<td>0.9</td>
<td>317</td>
</tr>
<tr>
<td>8/12/2004</td>
<td>Plume</td>
<td>5274</td>
<td>588</td>
<td>95</td>
<td>6.3</td>
<td>0.9</td>
<td>317</td>
</tr>
</tbody>
</table>

a 7/27 and 7/29 a CRT was used; 8/5, 8/11,8/12 a CCRT was used

b N is the number of measurements recorded by the data logger at approximately 1 second intervals
Sampling pattern – background, plume, background


Concentration, part/cm³

CPC*LF DR
EEPS N Total
SMPS N Total

Not corrected for dilution ratio
EEPS 1 s N total

Plume sampling period
Background sampling period
Plume – background size distributions corrected for dilution ratio - BP15 fuel and LSO

- Greater than 99% removal efficiency for accumulation mode particles where most mass is found.

- Increase in nuclei mode by CRT but not by CCRT.

- Measurement below hatched line indistinguishable from background.
The CRT showed strongly temperature dependent number emissions but the CCRT showed no detectable emissions.

The kinetics of this process are consistent with conversion of SO$_2$ to SO$_3$ in the CRT catalyst – leading to sulfate formation during dilution.
Nearly all particles downstream of CRT were in nucleation mode and strongly temperature dependent.
Here the results are put into a fuel specific form so that they may be compared with other studies.

BP15 ULSD, Castrol reduced S lube

On-road measurement below hatched line indistinguishable from background
Here we compare with the on road fleet tested in the E43 program – engine out \(~350\) ppm S fuel
What if we test the CRT in the lab – same BP15 fuel and operating condition

![Graph showing particle size distribution](image)

- E43 On road average
- On road engine out
- On road CRT
- Engine lab CRT

Much smaller nucleation mode

Small but detectable accumulation mode – with clean dilution air.

> 99.9% removal efficiency
CRT accumulation mode well below the US 2007 standard (mass converted to equivalent number)
Here the an estimate of the proposed Swiss and EU number standard is added
Here the lab measurement has been treated in the manner of the PMP program removing nuclei mode.
Conclusions - On-road CRT and CCRT measurements - 1

- CRTs and CCRTs tested on-road under relatively light load conditions
- In the accumulation mode size range where most of the mass is found:
  - Neither the CRT nor the CCRT emitted concentrations significantly above background ambient air.
  - This corresponds to > 99% removal efficiency
- Significant number emissions were observed with the CRT
  - The particles are extremely small nucleation mode particles
  - These particles represent nearly no mass
  - Number emissions are extremely exhaust temperature dependent
  - The particles are believed to be mainly sulfuric acid
- CCRT number emissions could not be distinguished from ambient air
  - This effect is not fully understood
  - Apparently particle precursors are stored in catalyzed filter section
Conclusions - On-road CRT and CCRT measurements - 2

• Both systems meet all current and proposed particle emission standards, however..
  – Operating conditions where different from those of certification tests
    » Continuous high speed operation
    » No cold start
    » Passive regeneration
  – US 2007 mass standards have been converted to equivalent number
    » Proposed EU PMP standard 1 to 2 orders of magnitude more stringent than US 2007
    » It is unlikely that any filter mass based measurement system would be able to make meaningful measurements at the PMP level
• However, it should be noted that even under more difficult transient conditions of the EPA certification test 2007 engines are typically more than 5 times below the EPA standard
• Long term durability is still an issue
Outline

- Introduction
  - Emission standard
  - Typical engine and atmospheric size distributions
  - Why do we care about particle size
- Particle Formation by Diesel Engines
  - Structure and composition of ultrafine and nanoparticles
  - Particle formation during dilution
- Dilution and Sampling issues
  - Laboratory measurements
  - On-road measurement
- Diesel particle removal systems
  - Description
  - On-road evaluation
- Particles from gasoline spark ignition engines
- Future issues and conclusions
Summary - Particle Emissions from Gasoline Spark Ignition Engines (SI) (not including GDI)

- SI engine exhaust particles consist of similar materials and have similar morphology to Diesel particles
- However there are important differences
  - They usually smaller
  - They are composed primarily of volatile materials
  - Formation is generally more dependent on operating conditions than for Diesel engine
  - Perfectly premixed chemically correct combustion should not produce particles
    » Formation likely to be associated by local inhomogeneous conditions - big droplets, crevices
    » Lube oil may play an important role - especially with worn engines
Typical Composition and Structure of Gasoline Exhaust Particulate Matter

- Composition data courtesy Ricardo
  - Much more OC (UCM) than Diesel
  - UCM might be described as little tarry balls
- TEM photo from report by Blom and Nolan, Oak Ridge National Laboratory
  - Particles from gasoline SI engine have similar morphology to Diesel
  - Particles from high emitters – oil burners – show more liquid like structures
Dilution System Used for SI Engine Exhaust Particle Measurements

Adapted from:
SI Engine Particle Emissions - Influence of Load and Additives

Figure 2. Brake Specific Particle Number Emissions as a Function of Power with 95% Confidence Intervals

Adapted from:
Port Fuel Injected SI Engine - Influence of Additives on Size Distributions

Figure 3. Representative Baseline Size Distributions for the OX13391 and OX13003 Additives [2500 RPM, 90 kPa]

Adapted from:
Particle Number Penetration through the Catalytic Converter (Quad-4)

The total flow through the catalyst is proportional to the power output. At high power, high flow, the removal of high molecular weight hydrocarbons, likely particle precursors, becomes mass transfer limited.

Adapted from:
On-road and lab experiments – comparison of Diesel and gasoline SI emission

- SI emissions are much more load dependent than Diesel
- During highway cruise SI emissions are significantly lower than Diesel
- However, during hard accelerations, size distributions for gasoline light-duty vehicles were surprisingly similar to modern heavy-duty Diesel vehicles
- Diesel with CRT or CCRT has lowest emissions

Simulation of a gasoline high emitter – “Smoker”

- Most PM emissions from spark ignition engines do not come from well maintained engines running under cruise conditions
  - Cold start and hard acceleration account for most of the emissions from well maintained engines
  - Worn gasoline engines may be a major source of on-road PM
- The objective of this experiment was to simulate the behavior of a worn SI engine with high oil consumption under controlled conditions and measure its emissions
- A worn engine was simulated by the introduction of used lube oil onto the intake valve stems under controlled laboratory conditions. Leaky valve seals are a common cause for high oil consumption
- Properties and characteristics of the exhaust aerosol that were characterized included particle number and length concentrations, and the aerosol number and mass size distributions.
Tests of simulated gasoline high emitter – high oil consumption due to leaky valve seals

Corrected for dilution ratio, not corrected for particle losses
Outline

- Introduction
  - Emission standard
  - Typical engine and atmospheric size distributions
  - Why do we care about particle size
- Particle Formation by Diesel Engines
  - Structure and composition of ultrafine and nanoparticles
  - Particle formation during dilution
- Dilution and Sampling issues
  - Laboratory measurements
  - On-road measurement
- Diesel particle removal systems
  - Description
  - On-road evaluation
- Particles from gasoline spark ignition engines
- Future issues and conclusions
Particles from future engines

- Diesel engines with exhaust filters
  - Solid particles in both the nuclei and accumulation modes may be nearly completely eliminated by exhaust filtration
    » Carbonaceous particles removed from filter by regeneration
    » Ash particles from lube oil eventually plugs filters
  - If exhaust filters remove nearly all of the solid particles the only thing left will be volatile particles in the nuclei mode
    » Exhaust filters cannot directly remove the gas phase precursors that lead to the formation of nuclei mode particles
    » Hydrocarbon precursors may be destroyed in catalyzed systems to the extent allowed by kinetics (mass transfer) but sulfuric acid may form
    » Some catalyzed systems appear to trap sulfates (CCRT)
    » Filters must be regenerated, actively or passively. Care must be taken to avoid particle release and possible hotspots
Particles from future engines

- Diesel and other engines without exhaust filters or with low efficiency filters
  - With very clean Diesel combustion systems, particles from lube oil will become more important
  - Other engine cycles and fuels may also have difficulties with particles from lube oil
    - Gaseous fueled engines
    - DME
    - Low exhaust T associated with lean burn or high EGR in new low temperature combustion engines (HCCI) will make aftertreatment to control volatile lube oil related particles difficult
  - Off cycle operation of 3-way catalyst SI engines may lead to high particle emissions
  - Perhaps the most important characteristic of future engines will be how they perform as they wear out
Acknowledgements

• I have had help from many collaborators
  – In the Center for Diesel Research
    » Feng Cao, Marcus Drayton, Jason Johnson, Hee Jung Jung, Duane Paulsen, Winthrop Watts, Robert Waytulonis, Qiang Wei, Darrick Zarling, Tom Jones, Jake Savstrom
  – In the Particle Technology Lab
    » Peter McMurry, Kihong Park, Hiromu Sakurai
  – At UC Riverside
    » Herbert Tobias, Paul Ziemann
  – At Paul Scherrer Institute
    » Nick Bukowiecki, Urs Baltensperger
  – At U Rochester
    » Gunter Oberdörster
  – And many sponsors

Some slides have been added and modified. If you wish an updated copy contact me at kitte001@umn.edu