Concentrations and Size Distributions of Particulate Matter Emissions from Catalyzed Trap-Equipped Heavy-duty Diesel Vehicles Operating on Ultra-low Sulfur EC-D Fuel

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Background

• Year-long industry-government collaborative program
  – Two rounds of vehicle tests to characterize exhaust emissions
  – Evaluation of ultra-low sulfur diesel formulations (ECD and ECD-1)
  – Several fuels and filters tested in Southern California fleets

• Results from the First Phase showed significant reductions in diesel PM, CO and HC emissions as compared to CARB diesel

• Second Phase tests were designed to:
  – Evaluate durability of the control devices
  – Conduct an extensive chemical characterization for a sub-set of vehicles
Test Program

- Six program vehicles selected for characterization
  - a school bus, two grocery trucks (tractor), and three transit buses.

- Vehicles tested with
  - original exhaust system
  - subsequently fitted with DPFs provided by Engelhard (DPX™) and Johnson-Matthey (CRT™).

- Test fuels used
  - market average CARB diesel
  - ECD, ECD-1, Fischer-Tropsch (F-T) diesel, and CNG
# Test Matrix

<table>
<thead>
<tr>
<th>Vehicle</th>
<th>Fuel</th>
<th>DPF Type</th>
</tr>
</thead>
<tbody>
<tr>
<td>San Diego School Bus</td>
<td>CARB, ECD,</td>
<td>NONE</td>
</tr>
<tr>
<td></td>
<td>ECD-1, FT</td>
<td>DPX</td>
</tr>
<tr>
<td>LA MTA</td>
<td>ECD-1, CARB</td>
<td>NONE</td>
</tr>
<tr>
<td></td>
<td>ECD, ECD-1</td>
<td>CRT</td>
</tr>
<tr>
<td>CNG (2 Vehicles: MY2000 and MY2001)</td>
<td></td>
<td>NONE</td>
</tr>
<tr>
<td>Ralphs Grocery</td>
<td>CARB, ECD-1</td>
<td>NONE</td>
</tr>
<tr>
<td></td>
<td>ECD, ECD-1</td>
<td>CRT</td>
</tr>
</tbody>
</table>
## Fuel Analysis

<table>
<thead>
<tr>
<th>Property</th>
<th>CARB</th>
<th>ECD</th>
<th>ECD-1</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cetane Number</td>
<td>54.1</td>
<td>64.7</td>
<td>51.3</td>
</tr>
<tr>
<td>Sulfur, ppm</td>
<td>121</td>
<td>7.4</td>
<td>13.1</td>
</tr>
<tr>
<td>SFC Aromatics</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Total, vol%</td>
<td>22.5</td>
<td>10.9</td>
<td>23.8</td>
</tr>
<tr>
<td>PNA, wt%</td>
<td>4.1</td>
<td>0.9</td>
<td>2.8</td>
</tr>
</tbody>
</table>
Chemical Characterization

– Particulate Matter
  • TPM, PM\textsubscript{10}, PM\textsubscript{2.5}
– Volatile Organic Compounds
  • Low molecular weight alkanes and olefins (C\textsubscript{2} – C\textsubscript{5})
  • Low molecular weight aromatics (BTEX)
– Elemental & Organic Carbon
– PAHs and n-PAHs
– Elemental Compounds
– Ionic Species
– Carbonyls
– Dioxins and Furans
– Bioassays
Particle Sizing Cart
Typical Structure of Engine Exhaust Particles

- Agglomerated solid carbonaceous particle, volatile organic, sulfur compounds, ash
- Most of sulfur in the fuel
  - oxidized to SO$_2$, then
  - oxidized to SO$_3$
  - leads to sulfuric acid and sulfate aerosol
- Metal compounds in fuel and lube oil
  - lead to inorganic ash

(Seinfeld and Pandis, 1997)
Nucleation Process

- Homogeneous nucleation (Springer, 1978)
  - In the absence of condensation nuclei
  - Require large saturation ratio (S>1)
- Heterogeneous nucleation
  - Occurs on a foreign substance or surface, such as an ion or a solid particle
- Binary homogeneous nucleation
  - Two or more vapor species

(Baumgard and Johnson, 1996)
Data: BACKGROA_B
Model: LogNormal

\[ \frac{\chi^2}{\text{DoF}} = 3.6306 \times 10^{12} \]

\[ R^2 = -4654.12809 \]

\[ y_0 = 27.34666 \pm 390205.33873 \]
\[ x_c = 41.26481 \pm 3.16219 \]
\[ w = 0.55217 \pm 0.11071 \]
\[ A = 3722939.81838 \pm 528909.44602 \]
LA County MTA Transit Bus Diesel / CNG 1 / CNG 2
Steady-State 40 mph Operation

[Graph showing particle distribution (dN/dlogDp) vs. Dp (nm) with different markers for CARB, ECD1+CRT, ECD1, CNG1, CNG2, and ECD+CRT (During Warm-Up).]
San Diego School Bus
Steady-State 40 mph Operation
(Post-Engine Warmup)

$\frac{dN}{d\log D_p}$ vs. $D_p$ (nm)

- CARB-No Trap
- ECD-No Trap
- FT-DPX
- ECD-DPX
COLD START AT 40 MPH; DR=13:1
TRANSIT BUS
FUEL: ECD
EXHAUST AFTER-TREATMENT: JOHNSON-MATTHEY
AFTER WARM-UP AT 20 MPH; DR=25:1
TRANSIT BUS
FUEL: ECD
EXHAUST AFTER-TREATMENT: JOHNSON-MATTHEY
COLD START AT 40 MPH
TRANSIT BUS
FUEL: ECD 1
EXHAUST AFTER-TREATMENT: JOHNSON-MATTHEY

Data: COLD40A_B
Model: LogNormal

\[ \chi^2 = 7.806 \times 10^{15} \]
\[ R^2 = -74.7428 \]
\[ y_0 = -0.19609 \pm 1.0625593.14095 \]
\[ x_c = 13.25368 \pm 0.44287 \]
\[ w = 0.26709 \pm 0.03642 \]
\[ A = 276519565.02845 \pm 31105698.64271 \]

\( dN/d\log D_p \)

\( D_p \) (nm)
AFTERWARM-UP AT 40 MPH
TRANSIT BUS
FUEL: ECD1
EXHAUST AFTER-TREATMENT: JOHNSON-MATTHEY
IDLE: RAW PM COUNT DATA FROM CPC
(INCLUDES 90 SECONDS OF UPSCAN AND 15 SECONDS OF
DOWNSCAN; COUNTS ROUNDED OFF TO THE HIGHER INTEGER)
EC/OC

Left bar is tunnel bkgd
Right bar is sample
Bars are average of 3 replicate runs
Error bars are 1 standard deviation
Elemental Analysis: Lubricant Oil Contribution

Emissions, g/mi

<table>
<thead>
<tr>
<th>Emissions, g/mi</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0000</td>
</tr>
<tr>
<td>0.0005</td>
</tr>
<tr>
<td>0.0010</td>
</tr>
<tr>
<td>0.0015</td>
</tr>
<tr>
<td>0.0020</td>
</tr>
<tr>
<td>0.0025</td>
</tr>
<tr>
<td>0.0030</td>
</tr>
<tr>
<td>0.0035</td>
</tr>
</tbody>
</table>

Zn, P, S, Mg, Ca, Mo

CARB, ECD CRT, ECD-1, ECD-1 CRT, CNG1, CNG2

Left bar is tunnel bkgd
Right bar is sample
Bars are average of 3 replicate runs
Error bars are 1 standard deviation
Inorganic Ionic Species

Emissions, g/mi

- Cl⁻
- NO₂⁻
- NO₃⁻
- SO₄²⁻
- NH₄⁺

Left bar is tunnel bkgd
Right bar is sample
Bars are average of 3 replicate runs
Error bars are 1 standard deviation
Carbonyl Compounds
(Air Toxics)

Formaldehyde
Acetone
Propionaldehyde
Methyl ethyl Ketone (MEK)
Butanal
Glyoxal
Tolual

Acetaldehyde
Acrolein
Croton
Methylacrolein
Benzaldehyde
Valal
Hexanal
Carbonyls

Transit buses
1st bar: Tunnel bkgd
2nd bar: Tunnel bkgd uncertainty
3rd bar: Test Uncorrected
4th bar: Test Uncorrected uncertainty

CARB ECD CRT ECD-1 CRT

Formaldehyde
Acetaldehyde
Acrolein
Benzaldehyde

Emissions, g/mi

West Virginia University
Morgantown, WV 26506
BTEX

Transit Bus

Emission Level (g/mile)

Amb BckGnd
Tunnel BckGnd
Test, Non-Corr

CARB ECD+CRT ECD-1 ECD-1+CRT CNG1 CNG2
Conclusions

• Changes from CARB to ECD and ECD-1 without a DPF had minimal impact on particle size distributions and concentrations.

• DPF’s provided dramatic reductions in particle concentrations across the nanoparticle size range, and in unregulated emissions.

• Further investigations of cold-start nanoparticle emissions with the use of a DPF is recommended
  – Number count and chemical analyses
  – Particle concentrations same order as background
  – Bioassays on size-selective PM emissions
Approach

- INSULATED RAW EXHAUST TRANSFER TUBE (FROM EXHAUST STACK TO THE DILUTION TUNNEL)

- SINGLE STAGE DILUTION OF RAW EXHAUST WITH A MASS FLOW CONTROLLER-BASED DILUTION SYSTEM

- MEASURE CONCENTRATIONS AND PARTICLE SIZE DISTRIBUTIONS ON STEADY-STATE OPERATION

- COLLECT DATA DURING WARM-UP TO OBSERVE THE EFFECT OF CATALYST LIGHT-OFF ON PARTICLE SIZE DISTRIBUTIONS

- BASED UPON THE STEADY-STATE PARTICLE SIZE DISTRIBUTIONS, SELECT A FEW KEY PARTICLE SIZES FOR TRACKED DURING THE TRANSIENT OPERATION
Particle Sizing Cart

- Mini Dilution Tunnel
- Diluted Exhaust CO$_2$ Sample
- Temperature Controllers
- Refrigerated Dryer (Dilution Air)
- Heat Exchanger (Dilution Air)
- Mini Tunnel Vacuum Pump (Dilution Air)
- Dilution Air Pump
- Electrostatic Classifier
- Heater Insulation
- Dilution Air Manifold
- Raw Exhaust
- Raw Exhaust CO$_2$ Sample
- Dual CO$_2$ Analyzers (Raw & Dilute)
- CO$_2$ Sample Bypass Valves
- Thermo-Electric Chiller (CO$_2$ Sample Conditioning)
- Data Acquisition System
- CO$_2$ Analyzer Calibration Ports
- Mass Flow Controller
- Power Supply
- Condensation Nuclei Counter
- CO$_2$ Bypass Pumps
Nucleation Process (Cont’d)

• Certain number of $H_2O$ and $H_2SO_4$ molecules collide
  For critical cluster- sufficient energy to be stable
  - Greater than critical size, grow
    (less, shrink)
  - Rate of nucleation ($H_2SO_4$ hydrate (embryo) formation predicted by Reiss, 1950):

$$J = C \exp(-\Delta G^* / kT)$$

(Grow past critical size)

• Higher nucleation rate occurs at higher relative humidity, and lower temperature

C is the frequency factor, k is the Boltzmann’s constant, T is the temperature and $\Delta G$ is the free energy required to form an embryo
2-Ring PAH

Transit buses

- CARB
- ECD CRT
- ECD-1 CRT
- CNG1
- CNG2

Emissions, g/mi

WVU
Morgantown, WV 26506
3-Ring PAH

West Virginia University, Morgantown, WV 26506

Emissions, g/mi

<table>
<thead>
<tr>
<th>0.0000</th>
<th>0.0005</th>
<th>0.0010</th>
<th>0.0015</th>
<th>0.0020</th>
<th>0.0025</th>
</tr>
</thead>
<tbody>
<tr>
<td>CARB</td>
<td>ECD</td>
<td>ECD-1</td>
<td>ECD-1</td>
<td>CNG1</td>
<td>CNG2</td>
</tr>
</tbody>
</table>

- Transit buses
- RET
- 9-methylnaphthalene
- Phenanthrene
- Anthracene
- Dimethylphenanthrene
- Methyl phenanthrene
- Methylfluorene
- Flourene
- Acenaphthene
- Acenaphthylene
4-Ring PAH

Transit buses

Emissions, g/mi

CARB  ECD CRT  ECD-1  ECD-1 CRT  CNG1  CNG2

- Coronene
- Dibenz(a+h+ac)anthracene
- Benzo(ghi)perylene
- Indeno[123-cd]pyrene
- Benzo(a)pyrene
- Perylene
- Benzo(e)pyrene
- 7-methylbenzo(a)pyrene
- Benzo(b+j+k)fluoranthene
- 5+6-methylchrysene
- Chrysene
- 7-methylbenzo(a)anthracene
- Benz(a)anthracene
- Benzo(c)phenanthrene
- Methylpyrenes/methylfluoranthenes
- Pyrene
- Fluoranthene

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2-Ring n-PAH

Emissions, g/mi

Transit buses

CARB
ECD CRT
ECD-1
ECD-1 CRT
CNG1
CNG2

1,8-dinitronaphthalene
1,5-dinitronaphthalene
1,3-dinitronaphthalene
4-nitrobiphenyl
3-nitrobiphenyl
2-nitrobiphenyl
2-nitronaphthalene
1-nitronaphthalene

No Data Available
VOC’s
(Grouped by Compound Classes)

Transit Bus

- ARO (26)
- C6 + OLE (13)
- C6 + ALK (28)
- C2 - C5 OLE (17)
- C2 - C5 ALK (8)

1st Bar: Ambient Background
2nd Bar: Tunnel Background
3rd Bar: Test, Non-Corrected

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Benzene