Ionic and Organic Species in PM Emissions from Advanced Technology Heavy-Duty Diesel Vehicles

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California Air Resources Board
October 23, 2008
Acknowledgements:

CO-Investigators: CARB’s Monitoring and Laboratory Division, CARB’s Mobile Source Control Division, University of Southern California, UC Davis, U of Wisc.

Co-Sponsors:

In Kind Contributors:
### NO\textsubscript{X} and PM Retrofits Investigated

<table>
<thead>
<tr>
<th>Heavy-Duty Vehicles</th>
<th>+</th>
<th>Diesel Particle Filter</th>
<th>+</th>
<th>NO\textsubscript{X} Catalyst</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Catalyzed Filter</td>
<td></td>
<td>Vanadium SCR Oxid Cat</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Uncatalyzed Filter</td>
<td></td>
<td>Zeolite SCR Oxid Cat</td>
</tr>
</tbody>
</table>

- Baseline vehicle = no retrofit
- One vehicle tested with DPF + SCR
- DPF + SCR is of special interest as it represents most advanced technology for meeting 2010 standards
- SCRT® systems used in this project are development prototypes not commercial units

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Particle filter is game-changing technology. It achieves significant PM emission reductions from diesel engines.

PM Mass Emissions [mg/mi]

<table>
<thead>
<tr>
<th>Veh#</th>
<th>Cruise at 50mph</th>
<th>UDDS</th>
</tr>
</thead>
<tbody>
<tr>
<td>Veh#1, Baseline</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Veh#1, CRT</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Veh#1, V-SCRT</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Veh#1, Z-SCRT</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Veh#2, DPX</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Veh#3, Horizon</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Veh#4, CCRT</td>
<td></td>
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</tbody>
</table>

PM retrofits yield greater than 90% reduction in PM emissions.

Baseline Diesel Sample
Agglomerates

DPF+SCR Sample
Clean as Blank

SEM images courtesy of D. Su, Fritz-Haber Institute
Experimental Setup @ CARB’s Emissions Lab

Exhaust from Testing Vehicles → Dilution Air → CVS Tunnel (Q=2600 or 1600 cfm)

- **Filters (+ vapor traps)**
  - PM, PAHS, Nitro-PAHs, Ions, Trace elements, EC/OC, Mutagenicity

- **NanoMOUDI**
  - PM, organics and Ions

- **HiVol Sampler**
  - Organics, Ions, Redox activity

- **Cartridges**
  - Carbonyls

- **Particle Characterization**
  - EEPS, DMS, multiple CPCs, PAS, EAD

- **Thermaldenuded Sample**
  - Metals, Ions, Redox activity, CPC

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<table>
<thead>
<tr>
<th>Sample Types</th>
<th>Filter Media</th>
<th>Flow Rate Range (lpm)</th>
<th>Method</th>
<th>Instrument</th>
</tr>
</thead>
<tbody>
<tr>
<td>organic and elemental carbon</td>
<td>Quartz fiber</td>
<td>38-40</td>
<td>IMPROVE_A,</td>
<td>DRI Model 2001</td>
</tr>
<tr>
<td>Ionic species</td>
<td>PTFE filter</td>
<td>40-45</td>
<td>IC</td>
<td>Dionex</td>
</tr>
<tr>
<td>PAH</td>
<td>TX60</td>
<td>75-80</td>
<td>GC-MS</td>
<td>ASE-GC/MS</td>
</tr>
</tbody>
</table>
EC (i.e., diesel soot) is not dominant emission. More OC than EC

All retrofits yield significant reductions of EC and OC

Elevated sulfate and ammonium are observed for retrofits that also exhibit high particle nucleation
• EC/OC about equal fractions of PM emissions for baseline vehicle

• Sulfate is dominant for most retrofits during cruise operation. 40-50% of PM is sulfate for retrofits with significant nucleation events (e.g. CRT, SCRTs and DPX)

• OC dominates PM emissions from most retrofits when vehicle operates over transient cycle
### Charging Balance (Anions/Cations)

- Particles from some retrofits (e.g., CRT & Horizon) are more acidic (anions/cations > 1)
- Suspect formation of nitric acid and sulfuric acid
- Transient cycle increases acidity
- Emissions from baseline and other retrofits appear to be neutralized

#### Anion/Cation Chart

<table>
<thead>
<tr>
<th>Veh#</th>
<th>Anions/Cations</th>
</tr>
</thead>
<tbody>
<tr>
<td>Veh#1, Baseline</td>
<td>1.5 ± 0.2</td>
</tr>
<tr>
<td>Veh#1, CRT</td>
<td>3.2 ± 0.8</td>
</tr>
<tr>
<td>Veh#1, V-SCRT</td>
<td>2.1 ± 0.5</td>
</tr>
<tr>
<td>Veh#1, Z-SCRT</td>
<td>1.8 ± 0.3</td>
</tr>
<tr>
<td>Veh#2, DpX</td>
<td>1.6 ± 0.4</td>
</tr>
<tr>
<td>Veh#3, Horizon</td>
<td>2.9 ± 0.7</td>
</tr>
<tr>
<td>Veh#4, CCRT</td>
<td>3.5 ± 0.9</td>
</tr>
</tbody>
</table>

#### Notes

- Anions: sulfate and nitrate
- Cations: ammonium, potassium and sodium
Preliminary Results - Particle Phase PAHs

Baseline divided by 1000

Air Toxics (Benzene, Toluene, Ethylbenzene and Xylene)

Cruise and UDDS Cycles

- Greater than 70% reduction of BTEX by all retrofits
- For some emissions are below background

Idling

- Greater than 70% reduction of BTEX by most aftertreatment devices
- But, increased levels of Benzene observed from DPF+SCR retrofits

a. No measurements for CRT and CCRT during idle operation
b. Values not displayed are below the levels of filtered ambient air
Final Remarks

- Well-functioning retrofits are performing as designed. They reduce emissions significantly (EC/OC, PAHs, BTEX).

- No surprises. Just a few remaining questions.

- Some retrofits are prototypes. So there is room for optimization in production-ready systems.

- Chemical composition of PM emissions is altered by retrofits.

- Elevated sulfate and ammonium correspond to retrofits that also exhibit high particle nucleation.

- Study presents significant challenges for analytical analysis due to very low mass emissions from retrofit-equipped vehicles.

- Future work:
  - Complete analysis/publication of results for heavy-duty vehicles.
  - Study passenger cars fueled by diesel, E85, CNG, gasoline, biodiesel.
THANK YOU

Questions?

More about vehicle emissions research program by CARB:

http://www.arb.ca.gov/research/veh-emissions/veh-emissions.htm

See Also at AAAR08:

- **8D.5 Wednesday 4:15pm:** Novel Approaches for Speciation of Platinum and Vanadium in Mobile Source Emissions.

- **9A.1 Thursday 9:20 am:** Chemical Speciation of PM Emissions from Heavy-Duty Diesel Vehicles Equipped with DPF and SCR Retrofits.

- **9A.26 Thursday 9:20 am:** Elements Emitted from Advanced Technology Heavy Duty Diesel Vehicles.

- **10A.3 Thursday 11:15am:** Toxicity of Particulate Matter from Heavy-Duty Vehicles Retrofitted with Emission Control Technologies.