CARB’s Phase II Study: 
*Project Overview and NO\textsubscript{X}, PM, and Nanoparticle Emissions*

Jorn D. Herner\textsuperscript{1}, William H. Robertson\textsuperscript{1}, Shaohua Hu\textsuperscript{1}, Subhasis Biswas\textsuperscript{2}, Vishal Verma\textsuperscript{2}, M.-C. Oliver Chang\textsuperscript{1}, Christine Maddox\textsuperscript{1}, Paul Rieger\textsuperscript{1}, Tao Huai\textsuperscript{1}, Mark Fuentes\textsuperscript{1}, Constantinos Sioutas\textsuperscript{2}, Jean Ospital\textsuperscript{3}, and ALBERTO AYALA\textsuperscript{1,4,5}

\textsuperscript{1} California Air Resources Board, Sacramento, CA
\textsuperscript{2} Civil and Environmental Engineering, University of Southern California, Los Angeles, CA
\textsuperscript{3} South Coast Air Quality Management District
\textsuperscript{4} Civil Engineering, University of the Pacific, Stockton, CA
\textsuperscript{5} Mechanical and Aerospace Engineering, West Virginia University, Morgantown, WV

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

Co-Sponsors:

In Kind Contributors:
Background and Motivation

- CARB’s longstanding scientific need/interest in policy-relevant assessment of HDV emissions

- In 2000, Dr. Alan Lloyd asked staff the question: is diesel with a filter as “clean” as CNG?
  - Phase I: Study of emissions from CNG and clean diesel transit buses
  - Successful 2001-2003 multi-division, multi-agency investigation
  - Half a dozen publications and a dozen invited presentations (many at CRC meetings)
  - Answer = YES, both were pretty clean, but can/have been made cleaner

- Phase II builds on the triumphs and defeats of Phase I:
  - Position CARB to advance proactively on emerging motor vehicle emissions issues:
    - Ultralow emissions from emerging technology and advanced aftertreatment
    - Measurement instrumentation and protocols
    - Relative toxicity of PM components (volatile vs. non-volatile fraction)
    - ACES
  - CARB needs data for 2010-like vehicles
  - The retrofit systems of today are a glimpse into the production-ready OEM systems of the future
  - Assessing emission reduction and toxicity relevant to the older system
Retrofit Device Test Matrix
4 vehicles, 8 configurations, 3 driving cycles

Vehicle

Veh#1

Veh #1

1998 Cummins Diesel
11L, 360,000 miles

Veh #1

Settlement Abbreviation

- DOC Uncatalyzed Filter
- Vanadium SCR
- Zeolite SCR
- Oxid Cat

• SCRT® systems used in this project are development prototypes not commercial units.
## Test Matrix (cont’d)

4 vehicles, 8 configurations, 3 driving cycles

<table>
<thead>
<tr>
<th>Vehicle</th>
<th>Aftertreatment</th>
<th>Abbreviation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Veh#2, 1999 International Diesel</td>
<td>Catalyzed Filter</td>
<td>Veh#2 DPX</td>
</tr>
<tr>
<td>7.6L, 40,000 miles</td>
<td>30,000 ml</td>
<td></td>
</tr>
<tr>
<td>Veh#3 2003 Cummins Diesel</td>
<td>Uncatalyzed Filter</td>
<td>Veh#3 Horizon</td>
</tr>
<tr>
<td>5.9L, 50,000 miles</td>
<td>5,000 ml</td>
<td></td>
</tr>
<tr>
<td>Veh#4 2006 Cummins Diesel w/ Allison Hybrid drive</td>
<td>Catalyzed Filter</td>
<td>Veh#4 CCRT®</td>
</tr>
<tr>
<td>5.9L, 1,000 miles</td>
<td>1,000 ml</td>
<td></td>
</tr>
</tbody>
</table>

Vehicle: 4 different types, each with specific characteristics and performance metrics.
Experimental Setup @ CARB’s HDV Emissions Laboratory

Exhaust from Testing Vehicles

Dilution Air

CVS Tunnel

Q=2600 or 1600 cfm

FTIR

N₂O, NH₃

Bags

Gases, VOCs

Sioutas Impactor®

V₂O₅

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

VACES

Biosampler (Suspension) and Chemical assay for redox activity and electrophilicity

Particle Characterization

EEPS, DMS, multiple CPCs, PAS, EAD

Thermaldenuded Sample

Metals, Ions, Redox activity, CPC
NO$_x$ Emissions

**NO$_x$ Emissions [g/mi]**

- **Left Bar** - Cruise at 50 mph
- **Right Bar** - UDDS

**Approx. 1998 standard**

- **SCR reduced NO$_x$ by approximately 80% and 90% for UDDS and cruise cycles respectively**
- **Catalytic surfaces increase fraction of NO$_2$, to as much as 50% of NO$_x$ for the CCRT®**

**Note: although not shown, during idle, no SCR NO$_x$ reduction and NO$_2$:NO$_x$ ratio is low in all configurations.**

**NOTE: Preliminary results**
Realtime NOx Concentrations

a) Cruise 50mph

- SCR reduction of NOx is temperature dependent
- Good reduction during highway operation
- Poor reduction in stop-and-go activity

b) UDDS

G: good NOx reduction
P: poor NOx reduction
PM Mass Emissions

- Aftertreatment in Veh#1 reduced PM emissions by 90+%.
- Reductions were greatest for UDDS cycle.
- In newer engines (Veh#3 and Veh#4) retrofits reduced PM to near LOD of gravimetric ref. method.

Note: although not shown, DPFs reduced PM during idle >98%.

NOTE: Preliminary results
Much continued interest in ultrafine particle emissions

Cytotoxicity and Inflammatory Potential of Soot Particles of Low-Emission Diesel Engines

DANG SHENG SU,1,2 ANNA LUCIA SERAFINO,3 JENS-OLIVER MÜLLER,1 ROLF E. JENTOFT,1 ROBERT SCHLOGL,2,4 AND SILVANA FIORITO5
Fritz Haber Institute of the Max Planck Society, Faradayweg 4-6, D-14195 Berlin, Germany and Institute of Neurobiology and Molecular Medicine, National Research Council (CNR), Via Fosso del Cavaliere 100, 00133 Rome, Italy

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We evaluated, in vitro, the inflammatory and cytotoxic potential of soot particles from current low-emission (Euro IV) diesel engines toward human peripheral blood monocyte-call lines, mucosa and alveolar macrophages upon it. It is known that activated inflammatory cells can be activated to release pro-inflammatory cytokines.

12th ETH-Conference on Combustion Generated Nanoparticles

The 12th ETH-Conference on Combustion Generated Nanoparticles takes place
at ETH Zentrum, Zurich, Switzerland

Dear Colleagues,

Thank you all for your contribution to the 12th Conference on Combustion Generated Nanoparticles!

We invite you to the 13th Conference on Combustion Generated Nanoparticles, scheduled at the ETH Zurich 23 – 25 June 2008.

Evaluating the Toxicity of Airborne Particulate Matter and Nanoparticles by Measuring Oxidative Stress Potential—a Workshop Report and Consensus Statement

Jon G. Ayres
Liberty Safe Work Research Centre, Foresterhill Road, Aberdeen, AB25 2ZF, UK

Paul Born
Centre of Expertise in Life Sciences (CEL), Zuyd University, Netherlands

Flemming Cassee
Department of Industrial Toxicology, Centre for Environmental Health Assessment (CEFAS), Vlodrop
Average Size Distribution

**Accumulation mode** seen in: Veh#1 Baseline

**Nucleation mode** seen in:
- Veh#1 CRT1®
- Veh#1 V-SCRT®
- Veh#1 Z-SCRT®
- Veh#2 DPX

**NO nucleation** mode in:
- Veh#1 Baseline
- Veh#2 CRT2®
- Veh#3 Horizon
- Veh#4 CCRT®

**Nucleation appears to be neither vehicle nor device specific**

**NOTE:** Preliminary results

Ref: Herner et al., AAAR, Reno, 2007
When Does Nucleation Occur?

- Catalytic surfaces can store sulfate
- Conversion of SO$_2$ to SO$_3$ is temperature dependent

Each configuration emits nucleation mode particles once the post-aftertreatment exhaust reaches a **critical temperature**:

- $T_{crit} \text{ Veh#1, V-SCRT}^\circ = 330^\circ C$
- $T_{crit} \text{ Veh#1, CRT1}^\circ = 373^\circ C$
- $T_{crit} \text{ Veh#1, Z-SCRT}^\circ = 373^\circ C$
- $T_{crit} \text{ Veh#2, DPX}^\circ = 315^\circ C$

Ref: Herner et al., AAAR, Reno, 2007

**NOTE:** Preliminary results
Particle Mass Size Distribution

- For vehicles with significant particle numbers in ultrafine range, mass is also emitted in the same range.
- Baseline emissions mostly in coarse mode (> 100 nm range).
Number vs Mass Emission Factors

- Under certain conditions we saw reduced mass but enhanced number emissions.
- Horizon and Hybrid (CCRT) (without nucleation mode particle formation) lie in the left corner in the figure suggesting reduction of both number and mass EF.

Ref: Biswas et al., *Atmos. Env.*, 2008 (in print)
Particle Volatility – Number Based

\[ R = \frac{N_{\text{Exhaust}}}{N_{\text{TD}}} \]

Ref: Biswas et al., *Atmos. Env.*, 2008 (in print)
Summary

- In general, retrofits are accomplishing their design intent
- SCR retrofits can reduce NO\textsubscript{X} emissions better than 80%, except during cold cycles
- Remarkable reduction of PM mass emissions (>90%) by the retrofit devices tested
- Occasional formation of large number of nucleation mode particles by retrofits that contain catalytic surfaces
- Catalytic surfaces store sulfate for thousands of miles, suppressing nucleation
- Upon aging, retrofits promote nanoparticle formation when exhaust reaches a critical temperature
- For some retrofits, nucleation mode particle account for a significant fraction of mass emission in the same particle size range
- For some retrofits, total particle number emissions increased as mass emissions decreased
- The majority of the particles by number evaporated upon heating, suggesting that particles are predominantly internally mixed and semi-volatile
Thank you!

See also:

SESSION 9 – Particulate Matter
Wednesday 4/2/08
3:25 PM Presentation

Air Toxic Emissions from HD Diesel Vehicles Equipped with NOx and PM Retrofits

M.-C. Oliver Chang, Yanbo Pang, Paul Rieger, Jorn D. Herner, Tao Huai, Mark Fuentes, and Alberto Ayala