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The Effect of Diesel Particle Filters and Selective Catalytic Reduction - A Predictive Framework for Ultrafine Particle Formation, Toxicity and Chemical Composition

Jorn Dinh Herner, Shaohua Hu, William Robertson, Tao Huai, John Collins, Harry Dwyer, and Alberto Ayala

California Air Resources Board

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Experimental Setup

CARB Heavy duty Diesel Emissions Test Laboratory

- Ultra Low Sulfur Diesel (6ppm)
- CVS - Dilution Tunnel
- Real time particle measurements: EEPS, DMS500, SMPS, CPC’s, DC, PAS
- Cycles: Cruise at 50mph, UDDSx2, Idle
Test Matrix
4 vehicles, 6 configurations + Baseline

**Aftertreatment** - (red signifies catalyzed surface)

- **DPF**
  - Horizon
    - Uncatalyzed Filter
  - CRT
    - Uncatalyzed Filter
  - DPX
    - Catalyzed Filter
  - V-SCRT, Z-SCRT
    - Vanadium or Zeolite SCR
  - CCRT
    - Catalyzed Filter

- **SCR**
  - Urea
  - Oxid Cat

**Vehicles**

- **Veh#1**
  - 1998 Cummins Diesel
  - 11L, 360,000 miles

- **Veh#2**
  - 1999 International Diesel
  - 7.6L, 40,000 miles

- **Veh#3**
  - 2003 Cummins Diesel
  - 5.9L, 50,000 miles

- **Veh#4**
  - 2006 Cummins Diesel w/ Allison Hybrid drive.
  - 5.9L, 1,000 miles
Aftertreatment as Chemical Reactors
A Predictive Framework - Redox Chemistry

Oxidation of Diesel Exhaust

- Organics (OC, THC, PAHs) ↓
- CO ↓
- \( \text{NO}_2/\text{NO}_x \) ↑
- \( \text{SO}_2 \rightarrow \text{SO}_3 \rightarrow \text{nucleation} \) ↑
Aftertreatment *Significantly* Reduces PM and NO\textsubscript{x}

**PM Mass Reductions of 95%+**
(not temperature or cycle dependent)

**NO\textsubscript{x} Reductions of 75%+**
(dependent on temperature, i.e. duty cycle)

Herner et al., *ES&T* 2009, 43 (15), pp 5928–5933
Nucleation

Accumulation mode seen in:
- Veh#1 Baseline

Veh#1 CRT
- Veh#1 V-SCRT®
- Veh#1 Z-SCRT®
- Veh#2 DPX
- Veh#3 - Horizon
- Veh#4 CCRT®

No nucleation mode in
- Veh#1 Baseline

Veh#2 DPX
- Veh#3 Horizon
- Veh#4 CCRT

Average Size Distribution
Cruise at 50mph - Measured in the CVS (uncorrected for dilution)

- SO₂ → SO₃ → Nucleation (water or ammonia)
- Storage
Nucleation

Nucleation occurs when a **threshold** temperature has been reached leading to sulfation.
Chemical Composition of PM

- Baseline PM – 50% OC 50% EC
- Nucleating Aftertreatment – Majority Ions such as Sulfate and Ammonium
- Non Nucleating Aftertreatment – Still mostly OC with some EC
  -(DPF preferentially filters EC)
IN VITRO TEST FOR THE TOXICITY OF PARTICULATE MATTER

- Measurement of Oxidative Stress Potential
  - *in vitro toxicity test*
    - Acellular systems (DTT) / Cellular systems (macrophage cell, DCFH-DA)

• DTT highly correlated with water-soluble organic carbon (WSOC)*
• Uncatalyzed filters better at filtering EC than WSOC
• Catalyzed aftertreatment reduces WSOC

*Biswas et al., ES&T, 2009, 43 (10), pp 3905–3912
OXIDATIVE STRESS POTENTIAL OF TOTAL PM PER DISTANCE DRIVEN IS REDUCED BY ALL HD RETROFITS

DTT expression decrease with particle number increase
Conclusions

• The decrease of diesel PM and NO\textsubscript{x} with the advent of DPFs and SCR will greatly improve air quality in California.

• Secondary effects of diesel aftertreatment are becoming better understood:
  – Oxidation of exhaust is a function of catalytic loading and exhaust temp.
  – As NO\textsubscript{2}/NO\textsubscript{x} and particle number increase, organics (THC, PAH’s, WSOC, etc), CO and DTT expression decrease.

• Not all Ultrafine particles are the same
  – Nucleation mode particles, when present, post aftertreatment are morphologically, chemically and toxicologically different from traditional diesel exhaust particles.
Next Steps

• Effect of toxicity in other assays forthcoming

• Current study based on passive retrofit or pre-2010 technology.

• It will be important to test 2010 OEM technology, as effect may be different from what is described here.

Thank you