Chemical and Physical Properties of Sub-Micron Particle Emission from a Diesel Engine

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Complimentary Measurement Techniques

**Aerodyne AMS***

- ensemble average of particles – size and composition
- real-time, quantitative measurement of certain chemical classes
- large dynamic range (>10^3 observed at ORNL)
- sufficient time response 4 sec to study transients

**SPLAT-MS***

- Single particle analysis to 50 nm
- Classification of particle types
- Detection of refractory compounds

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* aerosol mass spectrometer
** single particle TOF mass spectrometer
Mass Concentrations from AMS Over a Range of Engine Conditions

1400 rpm 470 ft/lbs torque

Reduce Rail Pressure 1000 rpm 327 ft/lbs

Engine warm-up 800 rpm 4 ft/lbs

Date and Time

Vacuum Aerodynamic Diameter

Organics

dM/dlogDva (µg m⁻³)
SPLAT
Soot Particles are Most Prevalent

The most prevalent particles are composed of almost pure soot as evident by the carbon progression
SPLAT
PAHs Volatilize from Particles using Laser Heating

PAH dominated particles are most common under high RPM and low load conditions

See Poster 6PB7 – Yong Cai for more details on SPLAT
Mass Spectrum of AMS organic from heavy duty off road exhaust

Diesel Vehicle Exhaust

NYC, Canagaratna et al, in press

Heavy duty off road MS is virtually identical to that observed in ambient data.
This mass spectrum is very similar to that of lubricating oil (see next slide)
Nitrate Equivalent Mass Concentration (µg m⁻³)

Species

Others 169 ± 0.4
Water -1.22 ± 0.1
Ammonium 0.456 ± 0.02
Nitrate 0.175 ± 0.01
Sulphate 1.03 ± 0.05
Organics 78.1 ± 0.1
Oil 78.7 ± 0.2
SPLAT - At Rated Speed, Oil Components and Engine Wear and Tear Appear Products Appear in Particles

Ca, Al, and Zn indicate lube oil consumption and engine wear and tear.
Particle Composition (µg/m³):
-0.8% Water -1.2196
0.3% NH₄ 0.45646
0.1% NO₃ 0.17462
0.7% SO₄ 1.0274
49.7% Org 78.072
50% Oil 78.651

\[(NH_4)\text{meas}/(NH_4)\text{expt} = \text{NaN}\]

Runs Averaged: 1081 to 1084 (4/9/2004 10:02 to 10:05)
Comparison of AMS Mass and SMPS Volume Distributions

$D_{va} < D_{mob}$

$\Rightarrow$ fractal particles

**Effective Density:** $\rho_{eff} \sim \frac{D_{va}}{D_{mob}} \sim 0.5 \text{ g/cc}$

This comparison of AMS (mass) and SMPS (volume) distributions is very similar to what we have observed in ambient urban data, particularly during morning rush hour when primary combustion particles tend to dominate total sub-micron aerosol loading.
FIRST ATTEMPT at MASS BALANCE:

AMS (organic) vs SMPS (total)

DMA volume (1400 nm3/cm3) x ρeff (0.5g/cc) ~ 700 ug/m3 (total)
   -- AMS Mass (80 ug/m3)) x 1.35 /.9 ~ 120ug/m3 (organic matter)

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Black Carbon ~ 580 ug/m3

“BC/OC” ratio ~ 5

cf. ambient (literature) measurements,

typical BC/OC ~ 1-3

Conclusion:

On a mass weighted basis, ~3x less oil from off road engine is ~3x “cleaner” for lube oil emissions compared to typical diesel engines.
ESTIMATE of OC Emission Index for off road engine

~120 ug/m³ / ~7000 ppm ~ 0.017 ug/m³/ppm ~ 0.030 g NRPM / fg Fuel

This engine
Particle Density: DMA in front of AMS

<table>
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<tr>
<th>Vacuum Aerodynamic Diameter (nm)</th>
<th>10</th>
<th>20</th>
<th>30</th>
<th>40</th>
<th>50</th>
<th>60</th>
<th>70</th>
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</table>

**Legend:**
- Polydisperse r1080–1085 (DMA bypass)
- 60 nm r1140–1150
- 100 1115–1134
- 200 1096–1115
Coated soot fractal dimension ~ 3

"John Deere" soot fractal dimension ~ 2.5 ??

Flame soot fractal dimension ~ 1.8

Total Mass per Particle - 2.5D Fractal Particles
mass\_per\_p = C \(D_{mob}\)^{2.5}
per model of Jay Slowik and Peter Decarlo
Davidovits (BC) and Jimenez (CU)

OC Mass per Particle for OC/BC ratio ~ 6

Measured OC Mass per Particle
= AMS Mass / CPC Number Conc

Particle Density: DMA in front of AMS

Same Engine Different Day

Related Talk by Jian Wang 12A3 on Friday
Diesel soot density and fractal dimension from SPLAT

Density = \( \frac{D_{\text{aero}}}{D_m} \)

Density = \( C D_m^{D_f - 3} \)

\( D_f = 1.87 \)

\( D_f = 1.96 \)

These values are consistent with fractal dimension predicted for diffusion-limited cluster-cluster agglomeration

The simultaneous measurements of particle size density and composition makes it possible to derive the fractal dimension of the freshly emitted soot
AMS Beam Width Probe Data

AvgWirePositions(161, 3, "org",7)
1400 RPM 352 ft/lbs torque - high load

Wire Position

Organic

4/16/2004
AMS Organics Signal form On-Road Engine Running in Regen

- Regen - throttle body and injector - 4 sec every 30 sec
- Regen - throttle body and injector - 8 sec every 60 sec
- Regen - injector only - 4 sec every 30 sec
AMS Organic Signal and Laser Induced Incandescence

Graph showing LII (red) and Org (green) signals over time from 4:15 PM to 4:45 PM on 4/28/2004. The X-axis represents time in PM intervals, and the Y-axis represents the LII signal in arbitrary units.

Regen Mode:
- Throttle Body and Injector: 4 sec every 30 sec
- Throttle Body and Injector: 8 sec every 60 sec

AMS organic signal ug/M³
AMS PAH and Nitrate follow Organics
(Negligible Sulfate and Ammonia)
Aerodynamic Size Distribution from AMS
Organics Dominant Species, Small Sulfate, Nitrate

Vacuum Aerodynamic Diameter (nm)

\[
dM/d\log D_{va} \text{ (µg m}^{-3}\text{)}
\]

- Ammonium
- Nitrate
- Sulphate
- Chloride
- Organics
- PAH
AMS Size Distribution and Intensity of Organics vs. Time
Conclusions

• AMS and SPLAT provide complimentary view of Diesel exhaust

• New generations of diesel engines much cleaner

• AMS signal from engine due to fractal carbon particles with adsorbed lube oil

• AMS aerodynamic organic mass vs size distribution is bimodal – larger mode dependent on engine conditions

• Regeneration operation of engine has large effect on organic species
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