Understanding the Volatility of Primary Organic Aerosol Emitted from Light-Duty Vehicles

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- UC Davis
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Publications


Motivation - is POA Semi-Volatile?

- POA appears semi-volatile under controlled laboratory conditions (POA $>> 30 \, \mu g/m^3$)
- Understanding POA emissions and gas-particle partitioning under real-world conditions is critical to proper design of emissions control programs
Large Fraction of LDV Organic Carbon Speciated as Carbonyls

General Speciation of Carbonyls

A) Gasoline LEV by FTP
Gas-phase: 4.9 mg/L
Particle-phase: 0.3 mg/L

B) Gasoline TWC by FTP
Gas-phase: 6.7 mg/L
Particle-phase: 1.6 mg/L

C) Diesel 1999 HHDDT
Gas-phase: 38 mg/L
Particle-phase: 6.4 mg/L

D) Diesel 1999 Idle-creep
Gas-phase: 98 mg/L
Particle-phase: 13 mg/L

Al. A. = Aliphatic Aldehydes
Ar. A. = Aromatic Aldehydes
Al. K. = Aliphatic Ketones
Ar. K. = Aromatic Ketones
U. Al. = Unsaturated Aliphatics
Di = Dicarbonyls

30% of Light Duty Vehicle POA Diluted to Realistic Concentrations Doesn’t Obey Absorption Theory

Problem

• Behavior of the partitioning mechanism under atmospherically relevant conditions (<30 μg/m$^3$ OC) is difficult to study
  – Detection limit challenges
  – Representative vehicle fleet and driving cycle

• What mechanism controls the partitioning?
• What are the right conditions to vary to test different theories about dominant mechanisms?
Approach

- Sample representative on-road vehicle fleet emissions after adjustments: dilution, RH, background EC, and temperature

<table>
<thead>
<tr>
<th>Test Condition Matrix</th>
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<tr>
<td><strong>Base Condition</strong></td>
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<tr>
<td>RH = 55%</td>
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<tr>
<td>Background EC = 0 μg/m3</td>
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<tr>
<td><strong>Adjusted EC</strong></td>
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<tr>
<td>RH = 55%</td>
</tr>
<tr>
<td>Background EC = 20 μg/m3</td>
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</tbody>
</table>
Methodology

Primary Dilution System Adjustment to Exhaust

• Primary Dilution Ratio = 12.72

Secondary Dilution System Adjustments to Air Stream

• Secondary Dilution Ratio = 4.8
• RH adjustment = 55-85%
• EC adjustment = 0-20 μg/m³
## Vehicle Fleet Comparison

<table>
<thead>
<tr>
<th>Category</th>
<th>Year</th>
<th>Make</th>
<th>Model</th>
<th>Mileage</th>
<th>Engine Information</th>
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<tr>
<td>LEV PC</td>
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<th>Mileage</th>
<th>Engine Information</th>
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Analytical Methods

- OC/EC Aerosol Analyzer
  - NIOSH temperature protocol
- GC-MS
  - DFP train (Annular denuders coated in XAD, Quartz filter, and PUF) extracted in separate methanol and hexane DCM solutions
  - Samples derivatized using O-(2,3,4,5,6-pentafluorobenzyl) hydroxylamine (PFBHA) (Jakober et al. 2008)
  - Sample recovery determined using 2-F-benzaldehyde for C<7 and 8-F-1-benzosuberone for C>7 (with backup recovery standards 4-F-benzophenone and 5-F-1-Indanone) (Jakober et al. 2008)
- HR-AMS
- CRD-PAS – EC
- ToF-CIMS
MOUDI Size Distributions After Dilution to $< 5 \, \mu g \, m^{-3}$

Note: MOUDI daily size distribution under variable experimental conditions in comparison to past source sampling study. Ratio of present to past OM and EC masses ($D_A<100nm$), 1.65 and 3.25 (25% and 15% mass uncertainties), respectively.
EC Emissions by Vehicle

EC Emissions Over Drive Cycle

AMS O:C Measurements

AMS OC is Lower than Traditional OC from Car Exhaust

QA/QC Checks For OC Measurements

(a) Offline
- MOUDI-POA
- MOUDI-EC
- CVS-EC

(b) Real-Time
- AMS-POA
- PAS-EC

OC Thermograms

Significant OC evolves at T>600°C at atmospheric pressure.

How much of this material is “refractory” in the AMS at very low pressure?

Mass Fraction Remaining of POA Averaged over UC Driving Cycle

(a) OC, HR-TOF-AMS

(b) Total OC, OCEC Analyzer

(c) Carbonyl OC, GC-MS

MFR as a Function of Time

VBS Representation of Emissions

MFR Model Based on VBS

(a) UCD TD Model + AMS

(b) CMU TD Model + AMS

Residual Error in Mass Fraction Remaining Model

\[ y = 0.754x + 0.206 \]
\[ R^2 = 0.939 \]

\[ y = 0.235x + 0.568 \]
\[ R^2 = 0.515 \]

Individual Vehicle MFR Fits

Motor Oil vs. Fuel POA Emissions (Present Study)

Motor Oil vs. Fuel POA Emissions (CMU Study)

Motor Oil vs. Fuel Emissions – Fleet Characterization

Carbonyl Measurement QA/QC

OM Speciation

Light Aldehydes Account for 13-40% of POA

Gasoline Composition Trends vs. Carbonyl Trends

## Carbonyl Species Concentrations

### Emissions Rate (μg L⁻¹) for Measured Gas and Particle Phase Carbonyls

<table>
<thead>
<tr>
<th>Compounds</th>
<th>Aliphatic Aldehydes</th>
<th>Aliphatic Ketones</th>
<th>Unsaturated Aliphatics</th>
<th>Cyclic Aliphatics</th>
<th>Aromatic Aldehydes</th>
<th>Aromatic Dicarbonyls</th>
<th>Aliphatic Dicarbonyls</th>
<th>Base Case T = 25°C</th>
<th>RH</th>
<th>EC</th>
<th>RH+EC</th>
<th>Base Case T = 50°C</th>
<th>RH</th>
<th>EC</th>
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<th>RH</th>
<th>EC</th>
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<td>250 545 261 148</td>
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<td>23 37 22 24</td>
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### Base Case T = 100°C

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<th>Compounds</th>
<th>RH</th>
<th>EC</th>
<th>RH+EC</th>
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<tr>
<td>m-tolualdehyde</td>
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<td>7.5</td>
<td>1.5</td>
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<tr>
<td>p-tolualdehyde</td>
<td>2.2</td>
<td>7.5</td>
<td>2.2</td>
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<tr>
<td>2-Et-benzaldehyde</td>
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<td>31</td>
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<tr>
<td>3-Et-benzaldehyde</td>
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<td>4-Et-benzaldehyde</td>
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</table>

Humidity Affects the Total Carbonyls Concentration

### Humidity Affects Carbonyls in the POA

**A) Base Case**
- Total POC = 445 μg/L
- Other POC: 72%
- Carbonyls: 28%
- Al. A.: 92 μg/L

**B) High RH Case**
- Total POC = 379 μg/L
- Other POC: 60%
- Carbonyls: 40%
- Al. A.: 104 μg/L

**C) High EC Case**
- Total POC = 442 μg/L
- Other POC: 63%
- Carbonyls: 27%
- Al. A.: 75 μg/L

**D) High EC+RH Case**
- Total POC = 547 μg/L
- Other POC: 87%
- Carbonyls: 13%
- Al. A.: 48 μg/L

Al. A. = Aliphatic Aldehydes  
Al. K. = Aliphatic Ketones  
U. Al. = Unsaturated Aliphatics  
C. Al. = Cyclic Aliphatics  
Ar. A. = Aromatic Aldehydes  
Al. D. = Aliphatic Dicarbonyls  
Ar. K. = Aromatic Ketones

A) Base Case
Gas Phase: 2.1 mg/L
Particle Phase: 0.7 mg/L

B) High RH Case
Gas Phase: 2.2 mg/L
Particle Phase: 1.0 mg/L

C) High EC Case
Gas Phase: 1.4 mg/L
Particle Phase: 0.5 mg/L

D) High EC+RH Case
Gas Phase: 2.0 mg/L
Particle Phase: 0.3 mg/L

Emissions of Gas-Phase Organic Acids
Organic Acid (OA) Emissions
Effect of Temperature on Organic Acid Partitioning

A) [C1 acid]_{T=25°C} / [C1 acid]_{T=25°C}

B) [C3 acid]_{T=25°C} / [C3 acid]_{T=25°C}

C) [C4 acid]_{T=25°C} / [C4 acid]_{T=25°C}

D) [C5 acid]_{T=25°C} / [C5 acid]_{T=25°C}

TD Temperature (°C)
Isocyanic Acid (HNCO) Emissions

HNCO Formation Mechanism

- \( \text{NO(g)} \leftrightarrow \text{N + O} \)
- \( \text{CO(g)} \leftrightarrow \text{CO} \)
- \( \text{N + CO} \leftrightarrow \text{NCO} \)
- \( \text{H}_2(g) \leftrightarrow 2\text{H} \)
- \( \text{NH}_3(g) \rightarrow \text{NH}_3 \leftrightarrow \text{NH}_2 + \text{H} \)
- \( \text{NH} + 2\text{H} \leftrightarrow \text{N} + 3\text{H} \)
- \( \text{H} + \text{NCO} \rightarrow \text{HNCO(g)} \)

- \( 2\text{NO} + \text{NH}_3 + 5\text{CO} \rightarrow 3\text{HNCO} + 2\text{CO}_2 \)

Dependence of HNCO production rate on catalyst temperature, CO, and NO\textsubscript{X} mixing ratios

Conclusion

1) POA from light duty vehicles can be categorized as fuel products (non-volatile with T) or motor oil (volatile with T)

2) Vehicle emissions must be measured to build up a statistical distribution. Using the “average” volatility will give the wrong result.

3) Elevated RH in the dilution air enhances the production of carbonyl species that likely act as building blocks for the fuel product POA

4) Increased adsorption surface (background EC) in the dilution air inhibits total production of carbonyl species
Implications: Regional Modeling of POA

(a) 1VD Model
\[ y = 0.235x + 0.568 \]
\[ R^2 = 0.515 \]

(b) 2VD Model
\[ y = 0.754x + 0.206 \]
\[ R^2 = 0.939 \]
Implications: SOA Formation From High Emitters

![Bar chart showing contribution to EF\textsubscript{OA} for different vehicles. The chart compares the contribution of fuel and motor oil.]
Recommendations

- Measurements of POA emissions attributable to motor oil and fuel combustion are needed for a larger and more representative fleet of light duty gasoline vehicles in California.
- Further measurements should be made to explore the mechanisms of fuel-derived POA using carbonyl building blocks.
- The ability of the AMS to measure POA from light duty gasoline vehicles should be studied further.
- A clearer understanding on this issue is needed to avoid misinterpretation of results in current and future studies.