Improving chemical transport model predictions of organic aerosol: Measurement and simulation of semi-volatile organic emissions from mobile and non-mobile sources

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- CRC A74/E96 – CMU smog chamber experiments
- NSF – graduate student fellowships

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Two hypotheses:
1. Majority of primary organic aerosols are semi-volatile.
2. Important class of secondary organic aerosol precursors (intermediate volatility organic compounds) are missing from models/inventories.
US Anthropogenic VOC Emissions

2013
17,624 short tons

http://www.epa.gov/ttnchie1/trends/
Are primary organic aerosol emissions semi-volatile?
Data from a small diesel generator (and a woodstove) suggested YES.

**POA in Diesel Exhaust**

<table>
<thead>
<tr>
<th>POA EF (g/kg-fuel)</th>
<th>3</th>
<th>2</th>
<th>1</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dilution Ratio</td>
<td>200</td>
<td>150</td>
<td>100</td>
</tr>
</tbody>
</table>

Non-Volatile

SVOC Vapor

Hildeman et al. AST 1989
Lipsky and Robinson ES&T 2006

\[ X_p = \sum_{i=1}^{n} f_i \left( 1 + \frac{C_i^*}{C_{OA}} \right)^{-1} \]

Robinson et al. Science 2007

Carnegie Mellon University
What about “real-world” sources?

- Mobile sources
  - Dynamometer testing

<table>
<thead>
<tr>
<th>Source</th>
<th>Model years</th>
<th>#</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>on-road vehicles</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Pre-lev</td>
<td>1987~1994</td>
<td>11</td>
</tr>
<tr>
<td>Lev1</td>
<td>1994~2003</td>
<td>16</td>
</tr>
<tr>
<td>Lev2</td>
<td>2004 and Later</td>
<td>20</td>
</tr>
<tr>
<td>Medium duty diesel truck</td>
<td>2001, 2005</td>
<td>2</td>
</tr>
<tr>
<td>Heavy duty diesel truck</td>
<td>2006, 2007 and 2010</td>
<td>3</td>
</tr>
<tr>
<td><strong>off-road engines</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Transport transportation unit</td>
<td>1998</td>
<td>1</td>
</tr>
<tr>
<td>2-stroke</td>
<td></td>
<td>3</td>
</tr>
<tr>
<td>4-stroke</td>
<td></td>
<td>3</td>
</tr>
</tbody>
</table>

- Highway tunnel: ~2 weeks
- Wildfires – 13 different fuels
GC MS Analysis of Filter and Sorbents

Chamber 25 – 35x more dilute than CVS

QBT ~ adsorbed vapors (artifact)
Q - QBT ~ particulate carbon

MFR = \frac{C_{TD}}{C_{bypass}}
Primary organic aerosol is semivolatile

\[ X_p = \sum_{i=1}^{n} f_i \left( 1 + \frac{C_i^*}{C_{OA}} \right)^{-1} \]

Robinson et al. Science 2007

May et al. AE 2013
Biomass and diesel POA too!

(May et al. EST 2013; May et al. JGR 2013)
Primary Organic Aerosol Composition

Gas chromatogram of quartz filter sample

(Presto et al. AST 2012)
Lots of semivolatile emissions

Presto et al. AST 2012

Decreasing volatility
Decreasing volatility

Mass Fraction ($f_i$)

Detector Response

C* ($\mu g/m^3$)

Retention time (min)

SVOC

Presto et al. AST 2012
Predictions “match” observations

Gasoline Vehicle POA Partitioning

\[ X_p = \sum_{i=1}^{n} f_i \left( 1 + \frac{C_i^*}{C_{OA}} \right)^{-1} \]

May et al. AE 2013
Predicted POA Evaporation

50-60% POA Evaporates

$C_{OA} (\mu g m^{-3})$

Evaporated POA

Non-volatile

$X_p$

Particle Fraction

Mass Fraction

Gasoline

Diesel

May et al. AE 2013; May et al. EST 2013
POA Partitioning Conclusions

• Majority of POA emissions from gasoline, diesel and biomass sources is semivolatile

• POA emission inventories biased on traditional source testing biased high (by roughly 50%)

• Gas-particle partitioning of POA emissions can be represented using one volatility distribution per source class

• Chemical transport model continue to assume POA is non-volatile biasing predictions

Gas-particle partitioning of primary organic aerosol
“Gas-particle partitioning of primary organic aerosol emissions: (1) gasoline vehicle exhaust” (A. A. May et al.) Atmospheric Environment, 77, 128-139, 2013.
How important are intermediate volatility organic compound (IVOCs) emissions?
Traditional Emissions Testing

Carbon number of n-alkane

LVOCs  SVOCs  IVOCs  VOCs

Gasoline vehicle exhaust

Quartz Filter POA – Assumed “Non-volatile”

Saturation concentration (C*, µg m⁻³)
Distributing quartz filter organics in volatility space

Carbon number of n-alkane

LVOCs  SVOCs  IVOCs  VOCs

Gasoline vehicle exhaust

Saturation concentration ($C^*$, $\mu g \text{ m}^{-3}$)

Fraction

Quartz Filter

Tedlar Bag
What about IVOCs?

**Gasoline vehicle exhaust**

**Saturation concentration (C*, µg m⁻³)**

**Fraction**

**Carbon number of n-alkane**

- LVOCs
- SVOCs
- IVOCs
- VOCs
IVOCs contribution to gasoline vehicle exhaust

Zhao et al. EST 2016
IVOCs contribute 30-60% of predicted SOA from gasoline exhaust

Zhao et al. EST 2016
Diesel IVOC emissions scale with NMHC

$R^2 = 0.98$

~ 60% NMHC

Zhao et al. EST 2015
SOA formation from diesel exhaust

80%+ of SOA from IVOCs

DPF dramatically reduces IVOC emissions and SOA formation

Zhao et al. EST 2015
Gasoline vs. diesel IVOCs: aromatics vs. aliphatics

On-road Gasoline vehicles

<table>
<thead>
<tr>
<th>MZ</th>
<th>Compounds</th>
</tr>
</thead>
<tbody>
<tr>
<td>43, 57, 71</td>
<td>n- &amp; b-alkanes</td>
</tr>
<tr>
<td>119, 134</td>
<td>C4-Benzene</td>
</tr>
<tr>
<td>134, 148</td>
<td>C5-Benzene</td>
</tr>
<tr>
<td>133, 134, 105</td>
<td>C2-Benzaldehyde</td>
</tr>
</tbody>
</table>

On-road Diesel Vehicles

<table>
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<th>MZ</th>
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<tbody>
<tr>
<td>147, 148, 119, 105</td>
<td>C5-Benzaldehyde</td>
</tr>
<tr>
<td>128</td>
<td>Naphthalene</td>
</tr>
<tr>
<td>142</td>
<td>C1-Naphthalene</td>
</tr>
<tr>
<td>141, 156</td>
<td>C2-Naphthalene</td>
</tr>
</tbody>
</table>

Zhao et al. EST 2015; Zhao et al. EST 2016
IVOC Emissions Conclusions

• IVOCs are an important class of SOA precursors in vehicle exhaust
• IVOC scale with NMHC emissions
• Most chemical transport models/inventories do not account for IVOC emissions which contributes to under prediction of SOA in urban areas.

IVOC emissions papers
Papers published by EPA STAR RD834554


